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ORIGINAL CONTRIBUTION

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Preparation of silver nanoparticles in liquid crystalline systems

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Abstract Silver nanoparticles preparation and the aggregation stability of the particles was investigated in lamellar liquid crystalline systems. A liquid crystal of HDTABr/pentanol/water was first prepared. The water content was next increased while keeping the mass ratio of HDTABr and pentanol constant. Silver nanoparticles were produced by replacing the aqueous phase by Ag sols of various concentrations (0.5–5×10^{-3} mol/l) or by an in situ preparation method, i.e., interlamellar reduction of Ag^+ ions in the liquid crystalline phase. The stability of the silver nanoparticles was monitored by UV-VIS spectroscopy and TEM. The particle size ranged from 5 to 44 nm. The kinetic of silver nanoparticle aggregation was investigated. The effect of nanoparticles on structural ordering in liquid crystals was studied by XRD measurements and it was established that the lamellar distance (d_L) was only slightly altered.

Keywords Silver nanoparticles · Liquid crystalline system · UV-VIS spectroscopy · X-ray diffraction · TEM

Introduction

Liquid crystalline systems formed by cationic surfactants have been described in numerous publications. The structural characteristics of liquid crystalline mesophases, the arrangement of the molecules, and the globular, cylindrical, or lamellar structure are revealed by the analysis of the phase diagrams of surfactant/cosurfactant/water systems [1, 2, 3]. Friberg and Venable [3] studied tetradecyl trimethylammonium bromide/pentanol/water and established that the interlamellar distance is dependent on the water/surfactant ratio and the presence of the cosurfactant also affects (reduces) the extent of the swelling of the liquid crystalline system. From cationic surfactants, hexadecylpyridinium chloride/alcohol/benzene/water quaternary systems were studied by Dékány et al. [4] using X-ray diffraction methods. It was shown that water may be incorporated into the organic (benzene, cyclohexane, alcohol) inverse liquid crystalline mesophase of lamellar structure and brings about interlamellar swelling. The interlamellar distance may be manipulated not only by adjustment of the water/surfactant ratio but also by the addition of alcohols acting as cosurfactant [4].

Lamellar liquid crystalline systems are also suitable for the preparation and stabilization of nanoparticles. Quilliet et al. doped the cyclohexane/sodium dodecyl sulfate/water/pentanol system with magnetic and nonmagnetic particles. Nanoparticles were incorporated into the bilayer membranes and thereby stabilized, as verified by SAXS measurements [5, 6]. Wang et al. [7] studied systems composed of a silver hydrosol or organosol and lamellar SDS/hexanol/dodecane/water. Depending on the hydrophilic or hydrophobic character of the Ag nanoparticles, they are incorporated into the aqueous or organic portion, respectively, of the lamellar bilayer phase, and a stable dispersion is formed. Qi et al. synthesized silver nanoparticle ribbons in lamellar lyotropic liquid crystals. Tetraethylene glycol monododecyl ether/silver nitrate/water system was produced using the surfactant itself as reductant [8].

The preparation and characterization of silver nanoparticles were discussed in a great number of publications. The reasons for this are multiple, in addition to the more favorable price of silver salts. Silver nanoparticles are widely used as basic components in photographic reactions [9], as catalysts [10, 11, 12], in surface enhanced Raman spectroscopy [13, 14, 15], as well as in chemical analysis [16]. In addition, they are easily detected by the characteristic absorption maximum in the visible range.

Several methods were used for the preparation and stabilization of silver nanoparticles. The most common methods were summarized by Heard et al. [17]: reduction by $NaBH_4$, or EDTA, preparation according to Carey Lea, or radiolysis using a ^{60}Co radiation source. The sols obtained by these methods were compared in terms of particle size, absorption spectrum, and particle shape. Wang et al. [18] prepared an oleate-stabilized hydrophobic Ag organosol of solvent exchange: a hydrosol stabilized by oleate was first produced using $NaBH_4$ as reducing agent and was next transferred into the organic phase with the help of various catalysts. The hydrophobic colloids produced in this way were stable and had a narrow range of particle size. Silver hydrosols and organosols stabilized by surfactants and sols stabilized by reverse micelles were also prepared by $NaBH_4$ reduction (Pal et al. [19]). Ag nanospheres stabilized by quaternary ammonium salts were generated by Yonezawa et al. [20]. Variations in the surfactant/Ag ratio led to the production of particles of different sizes.

Ag^+ ions are readily reducible by UV irradiation [21, 22]. Kapoor [22] stabilized photochemically reduced silver particles with PVP, gelatine, or carboxymethylcellulose (CMC). This author established that the use of PVP and gelatine leads to the appearance of particles in the 6–20 nm size range whereas in the presence of CMC larger particles (20–100 nm) are formed.

Silver particles measuring 7–10 nm were prepared electrochemically by Rodríguez-Sánchez et al. [23] and the effect of various electrochemical parameters on particle size was studied. More recently, Kéki et al. [21] also applied dendrimers to the stabilization of silver particles. This method allows the preparation of particles of a very narrow size range. The particle size may be controlled by manipulating the functional group and the size of the dendrimer.

Mafuné et al. [24, 25] applied laser irradiation of metallic silver submerged in the aqueous solution of SDS. The particle size increased with increasing SDS concentration and with decreasing irradiation intensity.

We have shown earlier that silicate lamellae of a thickness of 1 nm can be intercalated into the lamellae of a liquid crystalline phase [26]. In the present work we studied the liquid crystalline characteristics of the hexadecyltrimethylammonium bromide/pentanol/water system and the intercalation and in situ preparation of silver nanoparticles in this system. We aimed at elucidating how the presence of nanoparticles alters the structure of the lamellar system and what is the fate of stable silver nanoparticles in the liquid crystalline phase.

Materials and methods

Silver sol was prepared using $AgNO_3$ (99.9%, Reanal), $NaBH_4$ (98%, Sigma), sodium oleate (technical, BDH Chemicals Ltd).

The liquid crystalline systems were prepared using the following chemicals: hexadecyl trimethylammonium bromide (HDTABr, 98%, Reanal), *n*-pentanol (99%, Reanal), milli-Q water.

The interlamellar distances of the liquid crystalline mesophase were determined by X-ray diffraction measurements in a Philips PW-1830 diffractometer (CuKα radiation, $\lambda = 0.154$ nm) between $2\Theta = 1°$ and $10°$. During the measurement the samples were covered with Mylar foil to prevent changes in composition.

Absorption spectra of silver particles were taken with Uvikon 930 spectrophotometer between 300–600 nm.

Transmission electron micrographs were made in a Philips CM-10 transmission electron microscope with an accelerating voltage of 100 kV using copper grids covered with 0.75% collodion foil. The particle size distribution was determined by using the UTSHCSA Image Tool program.

All liquid crystalline systems were checked by polarization microscopy (LEICA Q 500 MC Image Analyser System).

Preparation of Ag sol stabilized by sodium oleate. Silver sol was prepared by reduction of Ag^+ ions with $NaBH_4$ [7] (Fig. 1). To a solution containing appropriate amounts of $NaBH_4$ (concentrations: 4×10^{-3} mol/l, 2×10^{-2} mol/l, and 4×10^{-2} mol/l) and sodium oleate (2.5×10^{-4} mol/l, 1.25×10^{-3} mol/l, and 2.5×10^{-3} mol/l, respectively), placed in an ice bath and stirred vigorously, an equivalent volume of $AgNO_3$ solution (10^{-3} mol/l, 5×10^{-3} mol/l, and 10^{-2} mol/l, respectively) was added dropwise. The sol was stirred continuously until it warmed up to room temperature. It was next heated to 60–80 °C to degrade excess $NaBH_4$ and cooled back to room temperature. With increasing concentration of $NaBH_4$ Ag sol became increasingly dark brown.

Preparation of liquid crystalline systems. Hexadecyl trimethylammonium bromide/pentanol/water (HDTABr/pentanol/water) systems were prepared in the region of the lamellar phase (Fig. 2) [27]. $W_{HDTABr}/W_{pentanol} = 1.5$ was kept constant, and the water content was increased (Table 1). For preparation of the silver-containing sample, the components were combined in a ratio to give the desired composition and the mixture was intensively stirred. Before measurements the samples were allowed to stand for five days because, according to our experience, this is the time necessary for the development of the liquid crystalline structure. The liquid crystalline structure was verified by polarization microscopy. The lamellar structure is well discernible on the micrograph (Fig. 3).

Preparation of liquid crystalline systems containing silver nanoparticles. Liquid crystalline systems containing silver nanoparticles were prepared in two different ways:

1. A silver sol prepared previously (5×10^{-4} mol/l, 2.5×10^{-3} mol/l, or 5×10^{-3} mol/l Ag sol) was added to the HDTABr/pentanol mixture in a volume equal to that of the water in the original liquid crystal without nanoparticles (Table 1).
2. Silver nanoparticles were prepared in situ in the liquid crystalline system. Then 1×10^{-2} mol/l $AgNO_3$ solution and 4×10^{-2} mol/l $NaBH_4$ solution (volume ratio 1:1) in a combined volume equal to that of the water content of the system without silver (Table 1) were added to the HDTABr/pentanol mixture. In this way the Ag contents of the systems were identical with that of the sample containing 5×10^{-3} mol/l Ag sol, as prepared above.

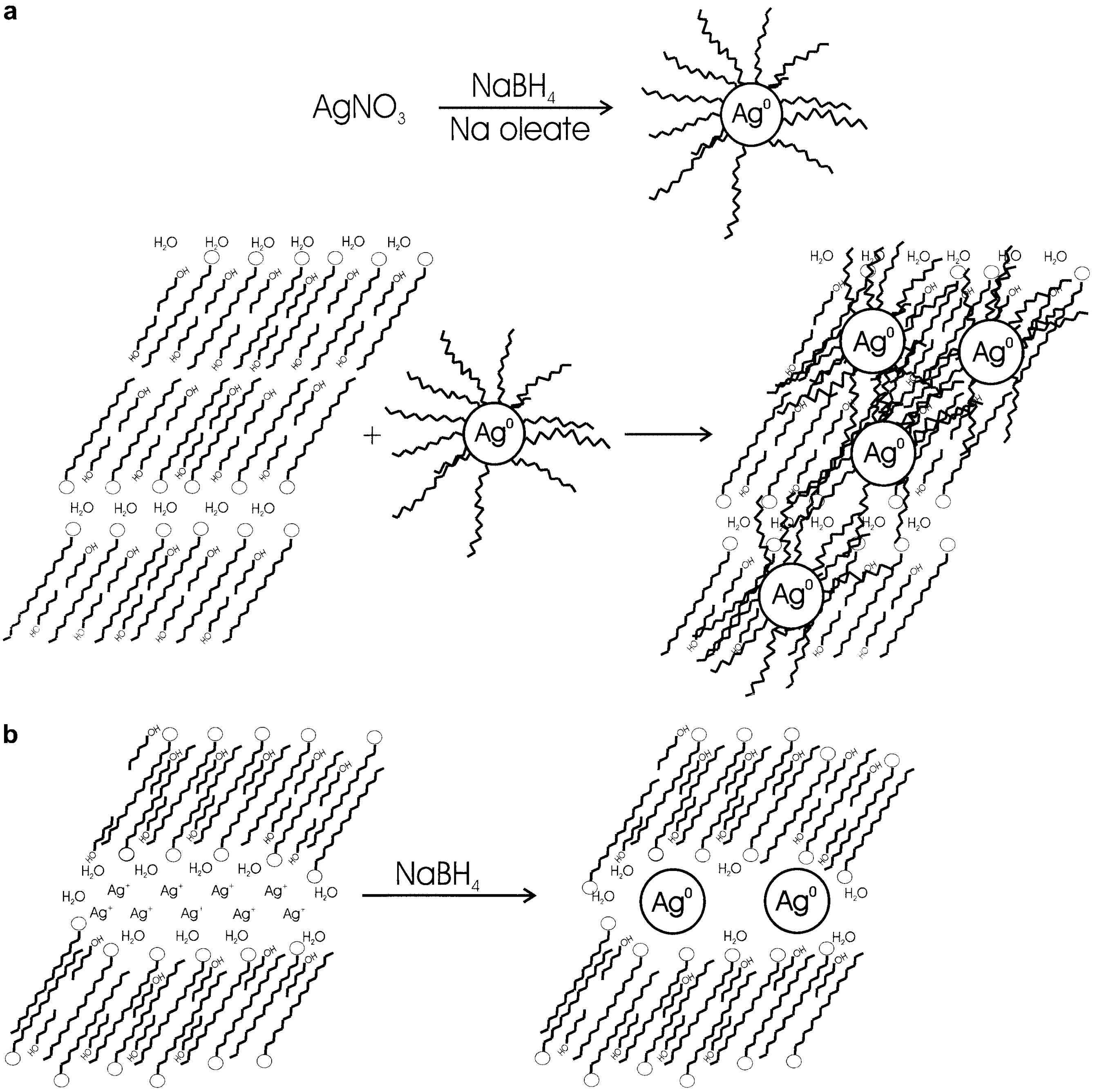


Fig. 1a, b Preparation and incorporation of Ag nanoparticles into the liquid crystalline structure

Results and discussion

UV-VIS spectroscopy

Silver nanoparticles have a characteristic absorption maximum at 380–430 nm, which makes it easy to detect them by UV-VIS spectroscopy. Direct spectrophotometry of liquid crystalline systems was hindered by several difficulties: the absorbance was too high and, due to the high viscosity of the samples, inclusion of air bubbles could not be avoided when filling the cuvettes. Prior to measurements the samples were, therefore, diluted with distilled water to give measurable absorbance values. Samples containing nanoparticles prepared in situ were diluted 20-fold whereas all the remaining samples were diluted 15-fold.

The UV-VIS absorbance spectra of the system containing 5×10^{-3} mol/l silver sol (0.33 HDTABr/0.22 pentanol/0.45 Ag sol (m/m)), diluted 15-fold at different

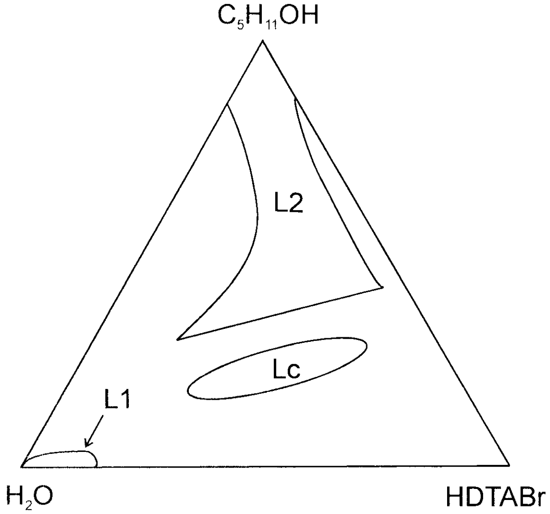


Fig. 2 Phase diagram of HDTBr/pentanol/water system

times, are shown in Fig. 4. The absorbance maximum is significantly reduced as time passes (from A = 1.567 to 0.439 in two weeks); the transmittance of the system increases correspondingly, and the number of silver particles in the liquid crystalline system is therefore lower. This means that the silver particles are not stable but tend to aggregate. This change is also observed visually: the initially vivid yellow samples gradually turn grayish. This phenomenon is more conspicuous in systems with relatively low n_{water}/n_{HDTABr} ratios. In Fig. 5 the absorbance of the series containing 5×10^{-3} mol/l silver after different time periods is plotted as a function of water content. For each composition, the value of A measured at the first day was designated as 100%. Higher water contents are associated with a smaller decrease in the absorbance. Since the lamellar distance of liquid crystals increases with increasing water content, it may be assumed that the silver nanoparticles surrounded by hydrophobic chains are stably incorporated into the lamellae of the liquid crystal (Fig. 1).

The time course of changes in transmittance also allows conclusions to be drawn regarding the kinetics of the aggregation of silver particles (Fig. 6). Aggregation is faster at lower water (Ag sol) contents (steeper curves); after the seventh day, no further changes are observed up to one month.

Table 1 Composition of liquid crystalline systems and measured lamellar distances

	W_{HDTABr}	$W_{pentanol}$	W_{water} $W_{Ag\ sol}$	d [nm]
Without Ag				
1	0.48	0.32	0.2	3.03
2	0.45	0.3	0.25	3.11
3	0.42	0.28	0.3	3.19
4	0.39	0.26	0.35	3.43
5	0.36	0.24	0.4	3.76
6	0.33	0.22	0.45	3.85
5×10^{-4} mol/l Ag sol				
1	0.48	0.32	0.2	3.02
2	0.45	0.3	0.25	3.1
3	0.42	0.28	0.3	3.16
4	0.39	0.26	0.35	3.34
5	0.36	0.24	0.4	3.6
6	0.33	0.22	0.45	3.81
2.5×10^{-3} mol/l Ag sol				
1	0.48	0.32	0.2	3.01
2	0.45	0.3	0.25	3.02
3	0.42	0.28	0.3	3.11
4	0.39	0.26	0.35	3.29
5	0.36	0.24	0.4	3.35
6	0.33	0.22	0.45	4.02
5×10^{-3} mol/l Ag sol				
1	0.48	0.32	0.2	2.92
2	0.45	0.3	0.25	2.93
3	0.42	0.28	0.3	3.19
4	0.39	0.26	0.35	3.23
5	0.36	0.24	0.4	3.7
6	0.33	0.22	0.45	3.73
In situ reduced 5×10^{-3} mol/l Ag sol				
1	0.48	0.32	0.2	3.01
2	0.45	0.3	0.25	3.07
3	0.42	0.28	0.3	3.06
4	0.39	0.26	0.35	3.24
5	0.36	0.24	0.4	3.3
6	0.33	0.22	0.45	3.92

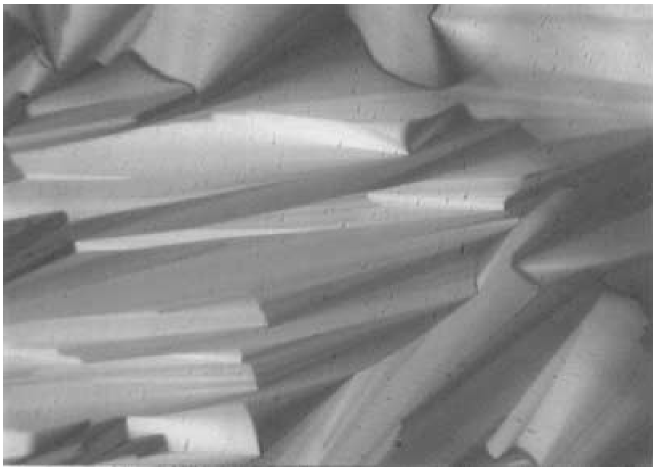


Fig. 3 Polarization microscopic picture of HDTBr/pentanol/water (0.51:0.36:0.13)

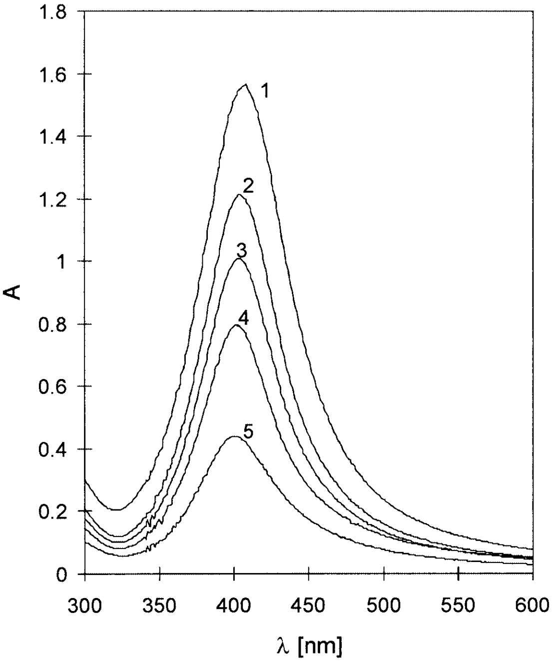


Fig. 4 The changes of the absorption spectra of HDTBr/pentanol/ 5×10^{-3} mol/l Ag sol (0.33:0.22:0.45) systems (1) after 1 day, (2) 2 days, (3) 3 days, (4) 7 days, (5) 14 days

Changes in the samples containing 5×10^{-3} mol/l Ag, prepared in situ in the liquid crystalline system were also monitored by spectrophotometry (Fig. 7, 20-fold dilution; composition: 0.33 HDTABr/0.22 pentanol/0.45 Ag sol). In this case silver is more stably incorporated: even after two weeks only a 40% decrease in absorbance is observed. The value of λ_{max} is shifted towards lower wavelengths only by 3 nm. It may be assumed that, due to steric reasons, the lamellar structure restricts the growth of silver particles, and therefore relatively

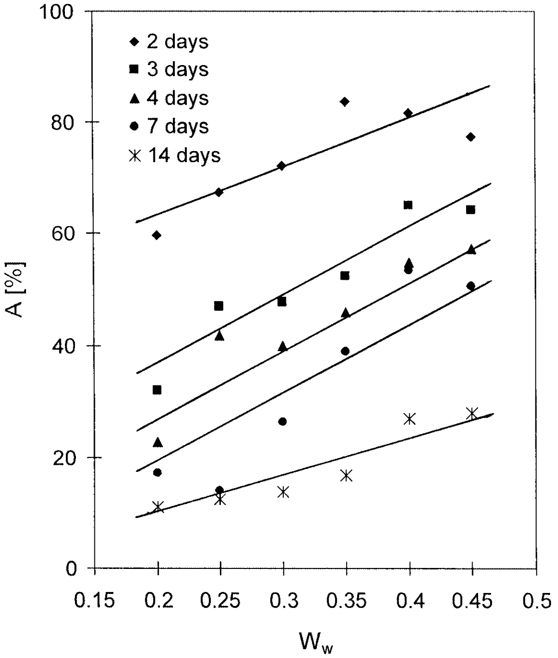


Fig. 5 The changes of the absorption ($\lambda = 404$ nm) of HDTABr/ pentanol/5×10^{-3} mol/l Ag sol systems plotted against the amount of water (notation on the figure)

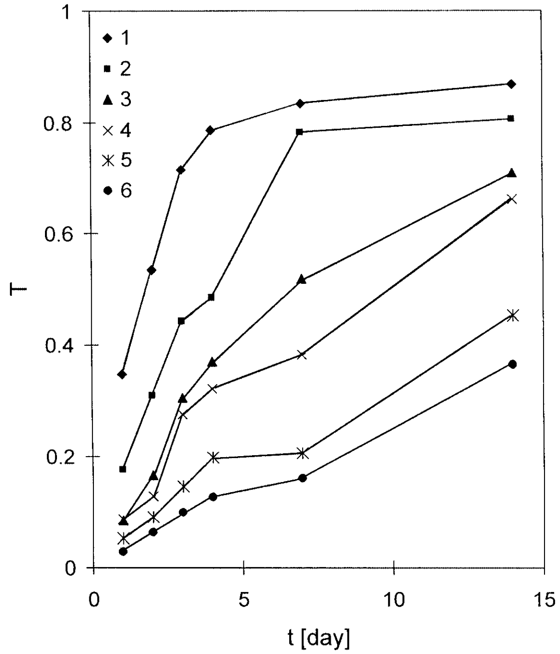


Fig. 6 The changes of the transmission ($\lambda = 404$ nm) of HDTABr/ pentanol/5×10^{-3} mol/l Ag sol systems at various water contents as a function of the time (numbers display the appropriate liquid crystalline composition of Table 1)

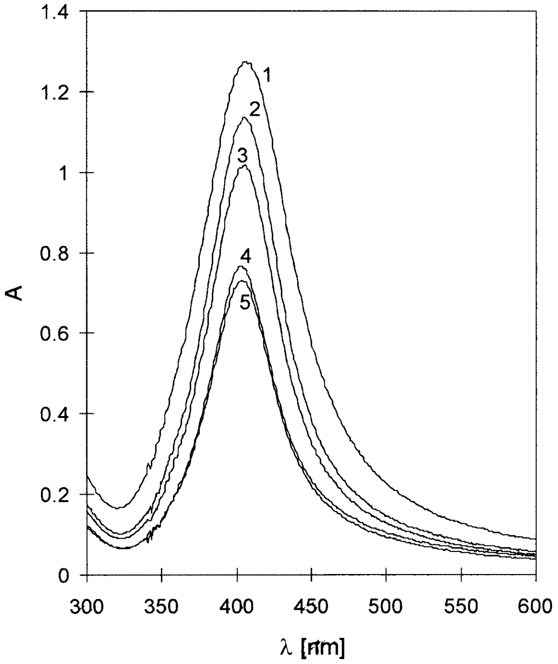


Fig. 7 The changes of the absorption spectra of HDTBr/pentanol/in situ 5×10^{-3} mol/l Ag sol (0.33:0.22:0.45) systems (1) after 1 day, (2) 2 days, (3) 3 days, (4) 7 days, (5) 14 days

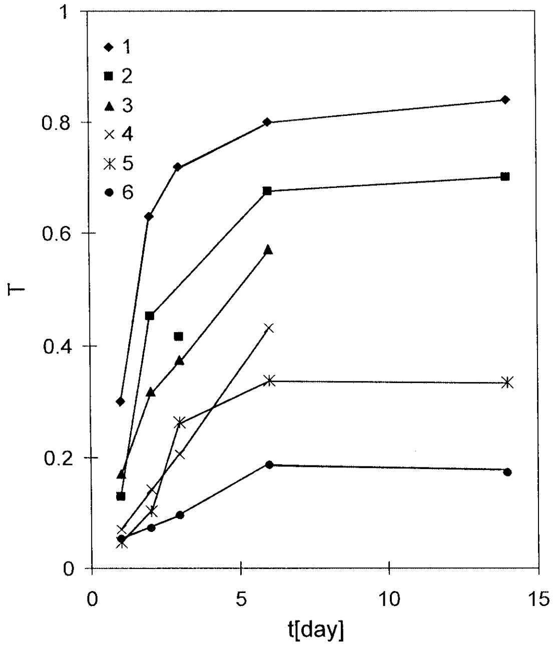


Fig. 8 The changes of the transmission ($\lambda = 404$ nm) of HDTABr/pentanol/in situ 5×10^{-3} mol/lAg sol systems at various water contents as a function of the time (numbers display the appropriate liquid crystalline composition of Table 1)

smaller (3.3-nm) particles are formed and no significant aggregation occurs. The constant in transmittance (Fig. 8) also indicates stability after six days.

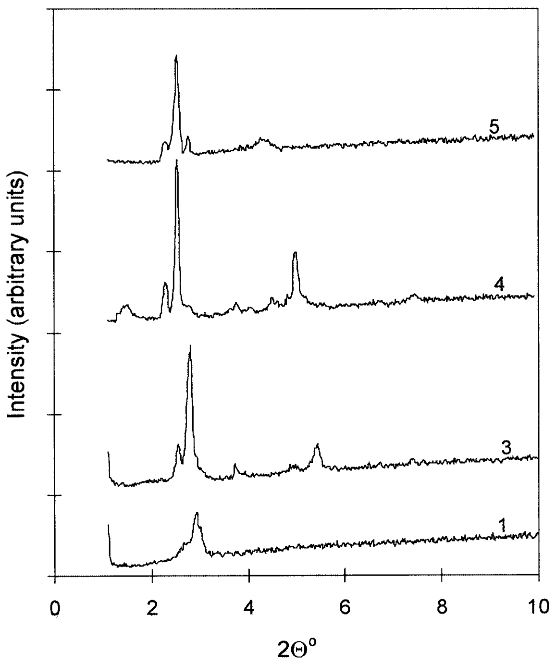


Fig. 9 XRD patterns of HDTABr/pentanol/5×10^{-3} mol/l Ag sol systems at various water contents (see notation in Table 1)

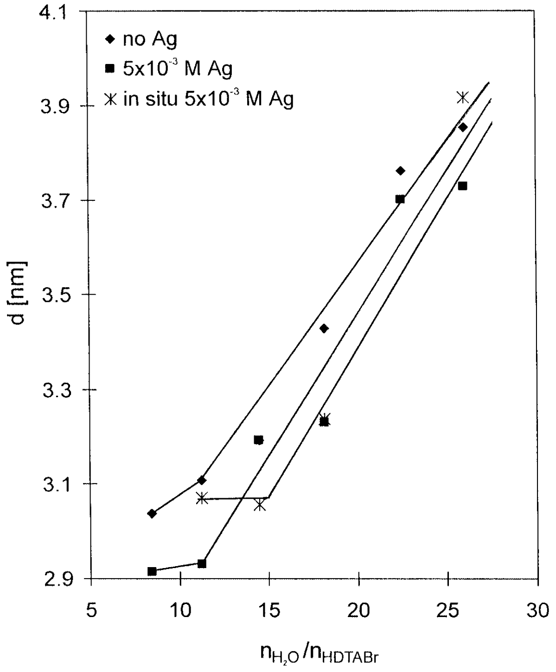


Fig. 10 The changes of the lamellar distances at different water contents of HDTABr/pentanol/water liquid crystalline system without Ag nanoparticles and at 5×10^{-3} mol/l Ag

X-ray diffraction

In our experience it takes about five days after preparation of liquid crystalline samples without nanoparticles

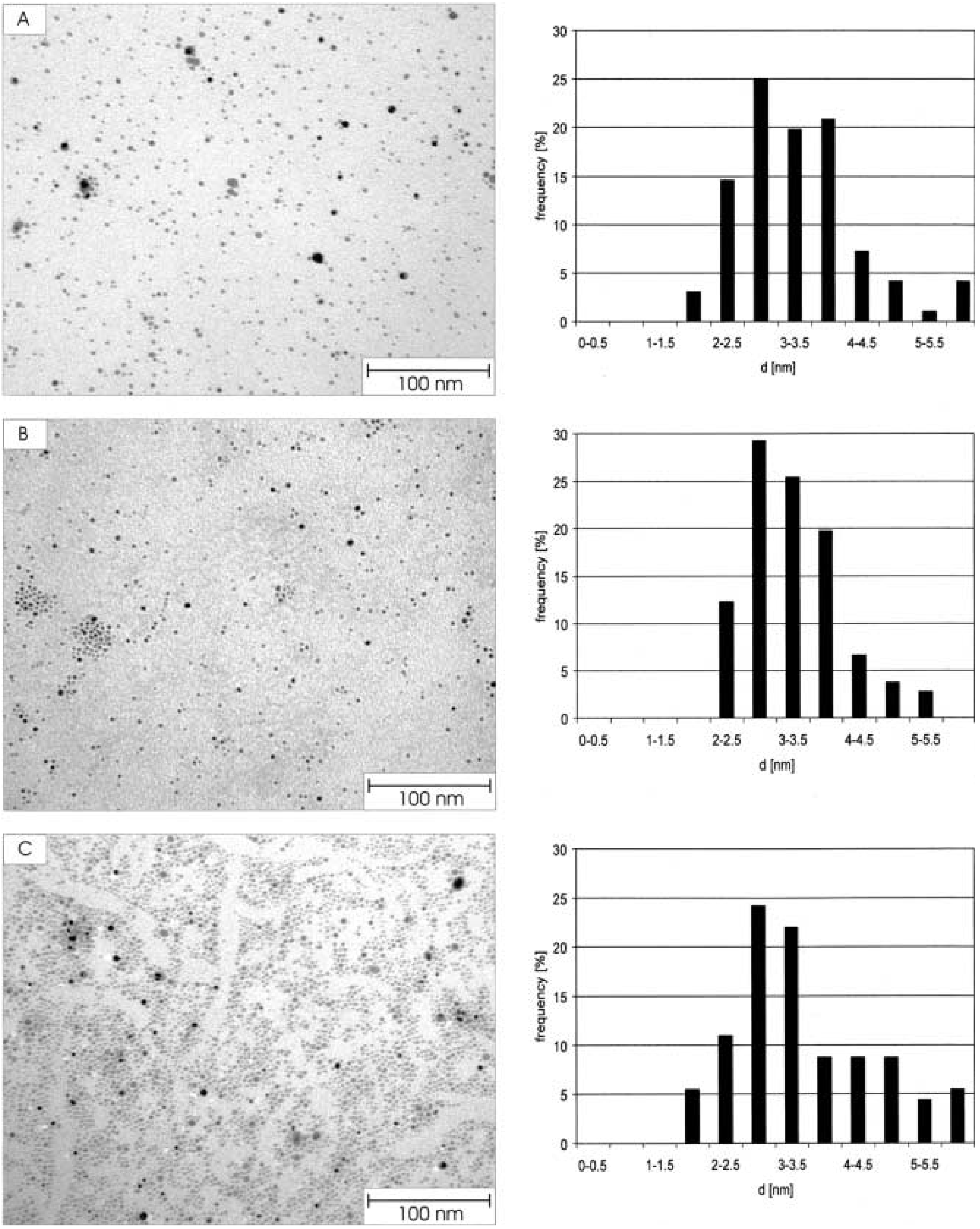


Fig. 11A–C Transmission electron micrograph and size distribution of Ag nanoparticles stabilized by Na-oleate: **A** 5×10^{-4} mol/l Ag sol; **B** 2.5×10^{-3} mol/l Ag sol; **C** 5×10^{-3} mol/l Ag sol

for the ordered structure to be established. However, the process is accelerated by the presence of nanoparticles: the ordered structure is established within a few hours and a stable lamellar distance is measured [5].

The extent of structural ordering is demonstrated by XRD diagrams (Fig. 9): sharp reflections of high intensities are obtained and even second-order reflections can be observed.

The lamellar distance of systems with various silver concentrations and systems containing nanoparticles prepared in situ is plotted as a function of $n_{\mathrm{water}}/n_{\mathrm{HDTABr}}$ in Fig. 10. The value of d_L is typically lower in the systems containing silver nanoparticles than in the original system lacking Ag. The only exceptions are the sample with 2.5×10^{-3} mol/l Ag content and the samples containing silver obtained by reduction within the liquid

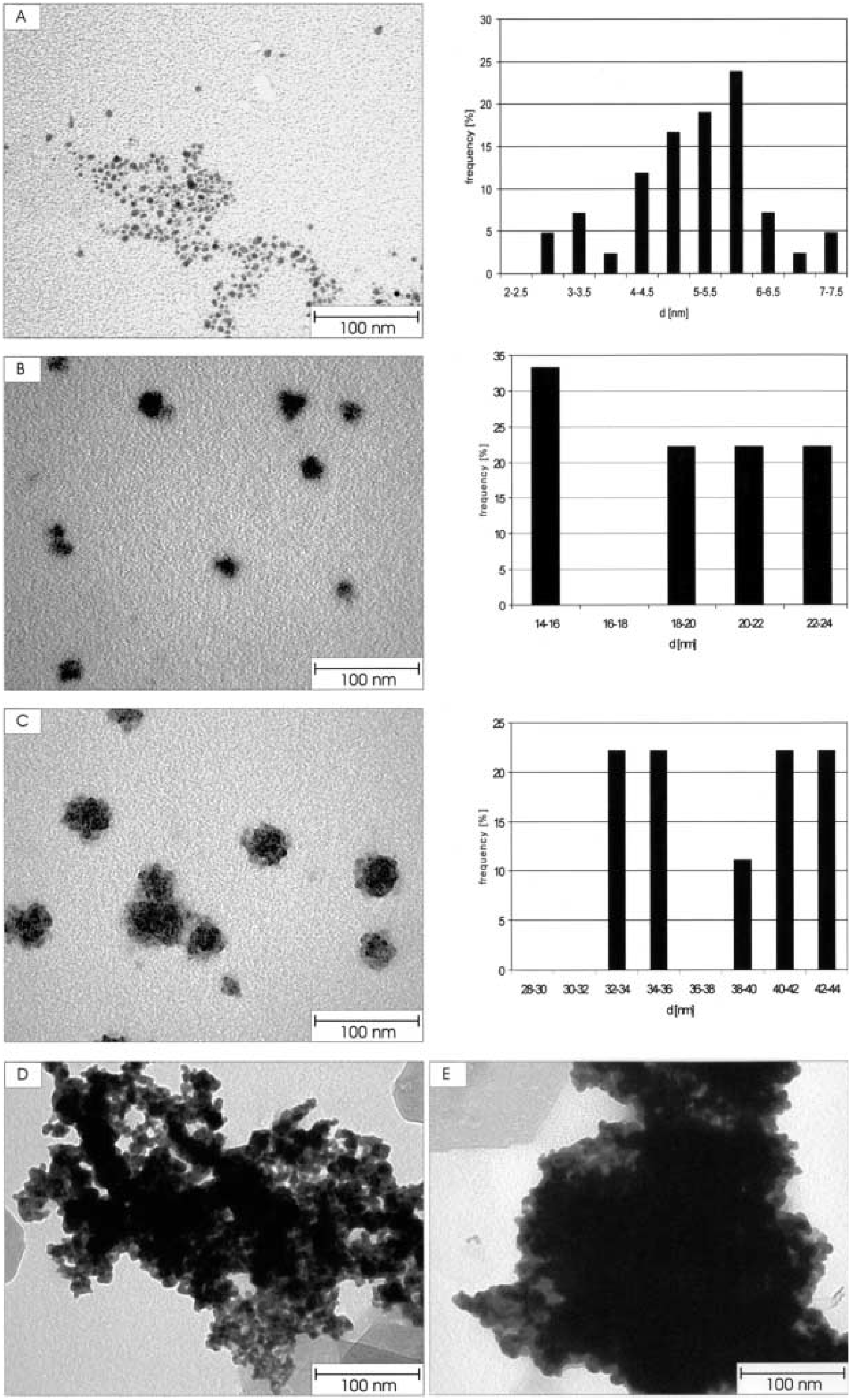


Fig. 12A–E Transmission electron micrograph and size distribution of Ag nanoparticles (5×10^{-3} mol/l) stabilized by HDTABr/pentanol/water (0.33:0.22:0.45) systems after: **A** 1 day; **B** 2 days; **C** 3 days; **D** 5 days; **E** 7 days crystal at the highest water content. The d_L values of these two series change in parallel.

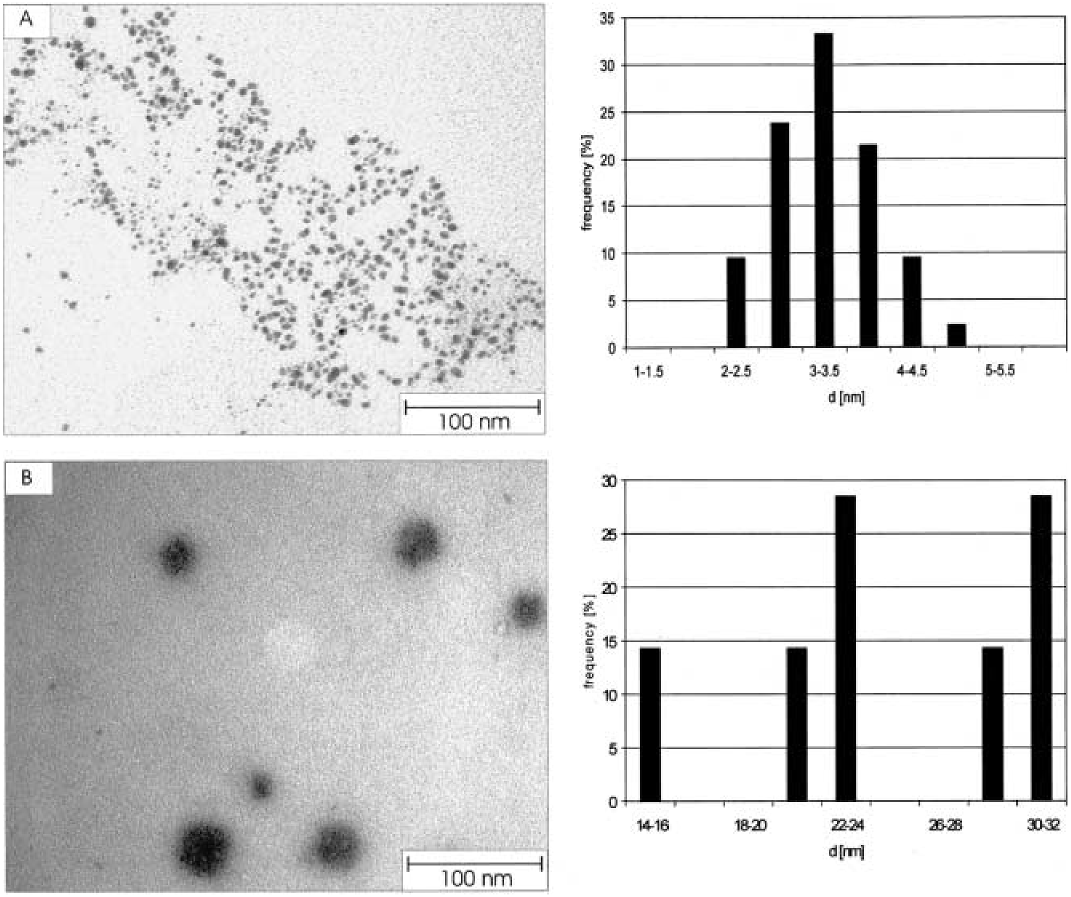
The lamellar distances do not change with time, and the aggregation of silver particles does not interfere with the structural ordering of lamellae. The reason for this is that in the course of aggregation the particles are squeezed out of the lamellae. This is also verified by the TEM pictures presented below (Fig. 12D,E).

Transmission electron microscopy

The average particle sizes in nanosols with different Ag concentrations were the following: $d=3.2\pm0.7$ nm at 5×10^{-4} mol/l, $d=3.3\pm0.9$ nm at 2.5×10^{-3} mol/l, and $d=3.4\pm1.1$ nm at 5×10^{-3} mol/l. Size distribution functions are displayed in Fig. 11. Prior to TEM measurements the original liquid crystalline systems were diluted with distilled water, because – due to the high concentration of surfactant molecules – the silver particles were undetectable. Electron micrographs of the sample containing 5×10^{-3} mol/l Ag sol, composed of 33% HDTABr/22% pentanol/45% Ag sol (m/m) are shown in Fig. 12 (magnification: 130,000). Changes in time are well demonstrated by the pictures. After one day (Fig. 12A), silver particles with an average diameter of 4.8 nm with a nearly monodisperse distribution are present. One day later (Fig. 12B), larger, aggregated particles (19.1-nm) are seen. Aggregation continues (Fig. 12C), producing even larger but as yet separate aggregates. After five days the ageing process leads to full-scale aggregation of the particles.

Similar observations were made on samples with different compositions and different silver concentrations – there was no significant difference between the samples. The data of the in situ prepared samples are shown in Fig. 13, demonstrating that at an identical Ag concentration (5×10^{-3} mol/l) the average particle size is $d=3.3$ nm and after five days it increases to $d=26.4$ nm, which indicates that aggregation is less extensive when the particles are prepared in situ.

Fig. 13A,B Transmission electron micrograph and size distribution of Ag nanoparticles in HDTABr/pentanol/water (0.33:0.22:0.45), in situ growing of the particles at 5×10^{-3} mol/l Ag^+ ion concentration after: **A** 1 day; **B** 5 days



Conclusion

The stability of silver nanoparticles in HDTABr/pentanol/water systems was studied. Sols with Ag concentrations of 5×10^{-4} mol/l, 2.5×10^{-3} mol/l, and 5×10^{-3} mol/l were prepared and used for replacing water in liquid crystals. Silver nanoparticles were also prepared in situ within the liquid crystals by adding, instead of water, appropriate amounts of 1×10^{-2} mol/l $AgNO_3$ and 4×10^{-2} mol/l $NaBH_4$ to the HDTABr/pentanol mixture. XRD showed that the lamellar distance is not altered significantly by the presence of nanoparticles and the structural order in the liquid crystal is maintained. UV-VIS spectroscopy and TEM made evident that the silver nanoparticles were less stable in systems with relatively small lamellar distances, i.e., at relatively low water contents. Stabilization of the particles required larger lamellar distances; otherwise the nanoparticles aggregated and were displaced from the lamellae. One week after preparation the stability of liquid crystalline systems containing Ag nanoparticles did not change any further.

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