APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2005; **19**: 768–773
Materials, Nanoscience and Catalysis **AOC**

Monodisperse copper- and silver-nanocolloids suitable for heat-conductive fluids

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Received 15 November 2004; Revised 6 December 2004; Accepted 12 December 2004

Copper colloid was prepared via reductive stabilization. The suspension of the trioctylaluminum-stabilized copper colloid was peptized using Korantin SH and cashew nut shell liquid (CNSL). Fluids with particle sizes <10 nm were obtained with Korantin and 7–15 nm in the case of CNSL. However, the copper colloid is air sensitive. A very straightforward one-step method leads to air-stable silver nanofluids. Thermal decomposition of silver lactate in the presence of Korantin SH and mineral oil as the medium gave a silver nanofluid. Silver particle formation and air stability were monitored using UV–VIS spectroscopy. The presence of monodispersed spherical silver nanoparticles was confirmed. Transmission electron microscopy showed a two-dimensional assembly of the silver particles with a size distribution of 9.5 ± 0.7 nm. FTIR has revealed information about the interaction between the surfactant and the silver surface. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: silver; copper; nanofluids; heat conductive media

INTRODUCTION

Heating or cooling fluids are of great importance to many industrial fields, including electronics and transportation. The thermal conductivity of these fluids plays a vital role in the development of energy-efficient heat transfer equipment. Conventional heat transfer fluids have a relatively poor thermal conductivity compared with most solids[1] with the latter have one to three orders of magnitude greater thermal conductivity than the former. The thermal conductivity of copper, for example, is 700 times that of water and 3000 times that of engine oil.[2]

Nanoparticles have unique properties that can be used to develop ultrahigh thermal conductivity fluids. Argonne National Laboratory has developed the concept of nanofluids by applying nanotechnology to thermal engineering. Nanofluids are a new class of solid–liquid composite materials consisting of solid nanoparticles (in the range of 1–100 nm) dispersed in a heat transfer fluid such as ethylene glycol, water or oil.[3]

However, nanofluid production faces some major challenges, such as agglomeration of particles in solution and the rapid settling of particles in fluids. In order to make a stable suspension, one should reduce the density difference between the particle and the fluid, increase the viscosity of the fluid, and make the particles very small or prevent them from agglomerating. Several methods exist for the preparation of metallic nanoparticles using surfactants to prevent the irreversible aggregation process. Choi and Eastman[4] developed two techniques to prepare nanofluids for thermal conductivity studies. First, a two-step process was employed to prepare nanoparticles by vaporizing a source material in a vacuum chamber followed by condensation of the vapor with an inert gas. The resulting nanoparticles are then dispersed into a fluid in a second step. However, a large degree of agglomeration was found with this two-step technique. The 'direct-evaporation' technique was then developed, which involved vaporization of a source material and condensation with a liquid. The drawbacks of this technique, however, are that the use of low-vapor-pressure liquids is essential and only limited quantities can be produced.

Bönnemann and co-workers have developed a method for the production of very small, stable nanoparticles via chemical reduction pathways, which might be suitable for application in nanofluid synthesis. Organoaluminum compounds have

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Contract/grant sponsor: National Research Foundation (SA).
Contract/grant sponsor: Deutsche Forschungsgemeinschaft; Contract/grant number: BO 1135/3-3.

been used for the 'reductive stabilization' of mono- and bi-metallic nanoparticles.[5,6] The triorganoaluminum compounds are employed as both the reducing agent and colloid stabilizer, leading to the formation of an organometallic colloidal protecting shell around the particles.[7,8] This 'modification' of the aluminum-organic protecting shell leaves the particle size untouched and allows tailoring of the dispersion characteristics of the original organosols at will. A vast spectrum of these solubilities of the colloidal methods in hydrophobic and hydrophilic media, including water, has been achieved this way.[9] Colloidal copper nanoparticles can be prepared by using the triorganoaluminum pathway; however, a large ratio of surfactant to metal is necessary in order to obtain stable suspensions. In the event of lower surfactant concentration, precipitation occurs; however, it is possible to suspend the precipitated particles again by peptization. The peptization, using different surfactants, of a copper colloid suspension prepared via the organoaluminum pathway is reported here.

Herein, we also report a novel method for the one-step preparation of silver nanoparticles dispersed in mineral oil. Colloidal silver particles have a potential in a wide variety of applications, such as biological processes,[10] as a substrate in surface-enhanced Raman scattering[11,12] and catalysis[13,14] studies. Silver nanoparticles have been of interest amongst many because they show an intense optical absorption that is assigned to the collective oscillations of free electrons, i.e. surface plasmon resonance.[15] The surface plasmon band appears around 400–420 nm and is dependent on both the cluster size and chemical surroundings.[16–18] With an even higher thermal conductivity than copper, silver has potential as a cooling fluid even at lower concentration.

By decomposing silver lactate in the presence of Korantin SH, colloidal silver nanoparticles dispersed in mineral oil were obtained. The colloidal silver nanoparticles formed were characterized by means of UV–VIS spectroscopy and transmission electron microscopy (TEM).

EXPERIMENTAL

Materials

$Cu(acac)_2$ (Sigma–Aldrich), $Al(octyl)_3$ (Crompton GmbH), Korantin SH (BASF AG), TW12 mineral oil (Wunsch) and silver lactate (Alfa Aesar, Germany) were all used as received. Cashew nut shell liquid (CNSL) was extracted in-house from cashew nut shells. Tetrahydrofuran (THF) was dried under argon.

Instrumentation

UV–VIS spectra were recorded with a 1 cm path-length quartz cell using a Varian Carey 5G UV-VIS-NIR spectrophotometer. To measure absorbencies during the reaction, known small volumes of samples were taken at different times and diluted with oil to give a final concentration of 0.5 mM. However, color changes were observed in some cases after dilution and, therefore, it was decided to collect the samples for the formation and stability studies straight from the reaction flask without dilution.

The size and morphology of the silver particles were examined by TEM. A Hitachi H7500 transmission electron microscope operating at 120 kV was used.

Samples were prepared by placing a drop of the dispersed solution on a carbon-coated copper grid. IR spectra were recorded on a Nicolet Magna 750 FTIR spectrometer. Microanalyses were performed by Kolbe Microanalysis Laboratory, Mülheim an der Ruhr, Germany.

Preparation of copper colloid $Cu(acac)_2$ and $Al(octyl)_3$.

($Al(octyl)_3$ may be replaced by other triorganoaluminum reductants, e.g. $Al(butyl)_3$, with similar results).

All experiments were done in an argon atmosphere and absolute dry THF as the solvent.

$Cu(acac)_2$ (2.6 g, 10 mmol) was dissolved in 700 ml of THF in a 1 l flask. The solution was blue–green in color. $Al(octyl)_3$ (4.4 ml, 10 mmol) in 50 ml THF was added dropwise at room temperature within 4 h.

The blue color changed to deep red and traces of shiny elemental copper were visible. A reddish precipitate settled at the bottom of the flask.

A small amount of the suspension obtained was transferred into two separate flasks for peptization with Korantin SH and CNSL.

Peptization of copper colloid with Korantin SH

To approximately 0.10 g of the copper colloid in 3 ml THF, 0.12 g of Korantin SH was added. The reddish brown suspension changed to a wine-red solution. A sample was taken for analysis with TEM.

Peptization of copper colloid with CNSL

Approximately 0.08 g mg of CNSL containing 80% of anacardic acid was added to 0.05 g of the copper colloid in 1 ml of THF. A wine red solution resulted. A sample was taken for analysis (TEM) to see if particles were still present in the solution.

Preparation of Korantin-stabilized silver colloid in mineral oil by thermal decomposition pathway

Silver colloid was prepared by thermal decomposition of silver lactate in the presence of Korantin SH. The experiment was performed under argon as well as in air. Different concentrations of Ag, viz. 0.3 vol.%, 0.011 vol.% and 0.001 vol.%, were prepared and the amount of surfactant was varied.

A typical procedure is as follows. For 0.011 vol.% silver colloid in mineral oil, silver lactate (0.32 g, 1.60 mmol), mineral oil (150 ml) and Korantin SH (1.08 g, 3.05 mmol) were stirred together at room temperature for 0.5 h. The temperature of the oil bath was increased from room temperature to 90 °C. The mixture was heated for a total of 4 h. The color of the solution varied between dark reddish brown, dark orange–brown and dark yellow–brown depending on the concentration of surfactant used.

RESULTS AND DISCUSSION

The blue color of the Cu(acac)$_2$ solution changed to a deep red upon addition of Al(octyl)$_3$, which indicated that copper is reduced from Cu^{2+} to Cu^0. The small trace of shiny elemental copper, which was visible on the flask, was a clear indication that the interaction between the copper and Al(octyl)$_3$ was not sufficient. Results from elemental analysis showed that 2.54% copper (from an expected 10%) was obtained when a 1 : 1 ratio was used, whereas the amount of copper obtained agreed well with the expected 5% when a 1 : 3 ratio was used. Thus, a ratio of 1 : 3 or above is more favorable for complete reduction. Hence, not all the copper particles were stabilized and aggregated at the bottom of the flask.

However, it was possible to solubilize the precipitate by peptization with Korantin or CNSL. From the TEM micrographs in Fig. 1 it is clear that copper nanoparticles with a uniform particle size were obtained. Particle size <10 nm was obtained in the case where Korantin (Fig. 1a) was employed. In the case where CNSL was used, some smaller particles and some larger particles are visible, with sizes between 7 and 15 nm (Fig. 1b). The influence of the protective shell is also illustrated, since the particles appeared well separated from each other. However, the copper colloid is extremely sensitive to air.

With the aim of preparing an air-stable colloidal suspension, a straightforward method was developed to prepare silver nanoparticles dispersed in mineral oil via thermal decomposition. Different concentrations of silver nanoparticles in mineral were prepared with various concentrations of surfactant.

Elemental analysis (Table 1) shows that the amount of silver lost through precipitation increases with an increase in silver concentration. This agrees well with the visual observation of a larger precipitate with an increase in concentration after reaction was complete. Nanoparticles suspended in a base liquid are constantly in random motion under the influence of several acting forces, such as Brownian and van der Waals forces. With such high-concentration suspensions and under the influence of external and internal forces, the probability for interparticle collisions is greater and, hence, may lead to aggregation. Furthermore, sedimentation may occur under gravitational forces if the clusters grow large enough.

Table 1. Elemental analysis results for various silver and surfactant concentrations

Ag (vol.%)	Ag/Korantin	Ag/(mg ml^{-1})	Ag lost (vol.%)
0.3	1	20.4	0.1
0.011	1/7	0.0975	0.0100
0.011	1/2	0.0819	0.0102
0.011	1	0.76	0.004
0.001	1/3	0.0150	0.0009

UV–VIS studies

When a large number of atoms are in close proximity to each other, the available energy levels form a nearly continuous band wherein electrons may transition. Metal nanocrystallites, such as silver nanoparticles, have close-lying bands and, therefore, the outer electrons are free and ready to move at the beckoning of an electric field.[19] When the conduction-band electrons interact with an electromagnetic field, the electrons start to oscillate coherently. This phenomenon is called surface plasmon resonance.

A typical UV–VIS absorption spectrum of Korantin-SH-stabilized silver colloid in mineral oil is shown in Fig. 2. The surface plasmon absorption maximum occurs at 420 nm with a full width at half maximum (FWHM) of 80 nm, which is characteristic of spherical silver nanoparticles and in good

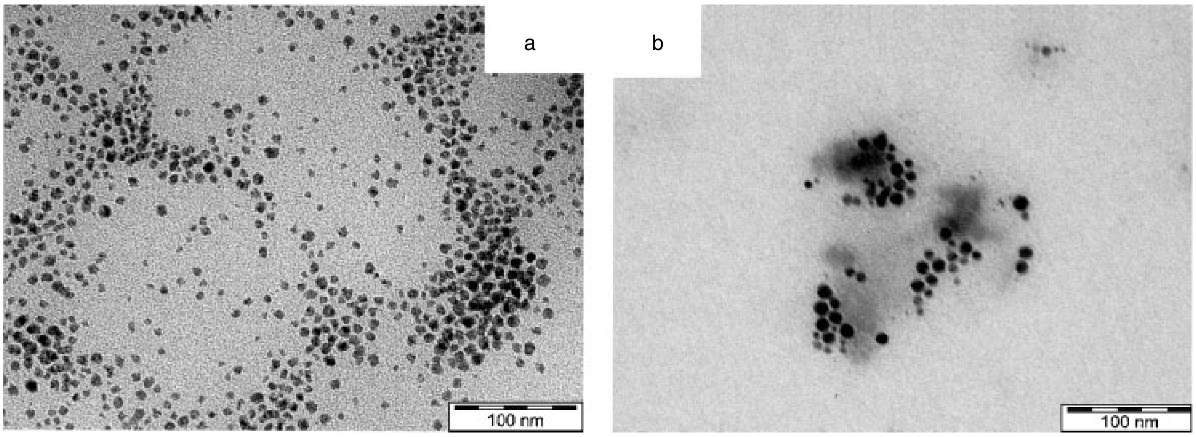

Figure 1. TEM micrographs of (a) Korantin-stabilized copper colloid and (b) cashew stabilized copper colloid.

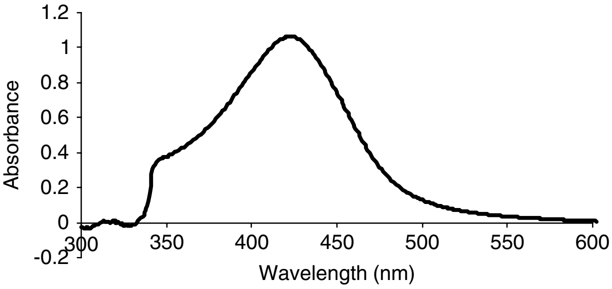

Figure 2. Silver colloid stabilized by Korantin (0.5 mM).

agreement with the literature.[20] This implies that the colloid system is monodisperse with a narrow size distribution. TEM results further support this result (Fig. 3).

The TEM micrograph in Fig. 3 shows that the monodisperse nanocrystals self-assembled into superlattice structures. Fig. 3b provided evidence for the tight size distribution, which was necessary for the superlattice formation. A particle size distribution of 9.5 ± 0.7 nm was obtained (Fig. 3b). This is a narrower size distribution than the 5–20 nm diameter silver particles prepared by Yase and co-workers.[21] The particles presented here are well separated from each other, thereby demonstrating the interaction between the particles and the surfactant.

Effect of Korantin concentration on particle size

A much lower concentration of Korantin (Ag/Korantin = 4/1) was used to determine the degree of aggregation. Figure 4 shows the resulting TEM micrograph of a Korantin-stabilized silver colloid with a reduced surfactant ratio. Some smaller and larger particles are visible. The particle size distribution was 8.18 ± 4.4 nm. Although a broader size distribution was obtained at a much lower concentration of surfactant, the particles remained well separated.

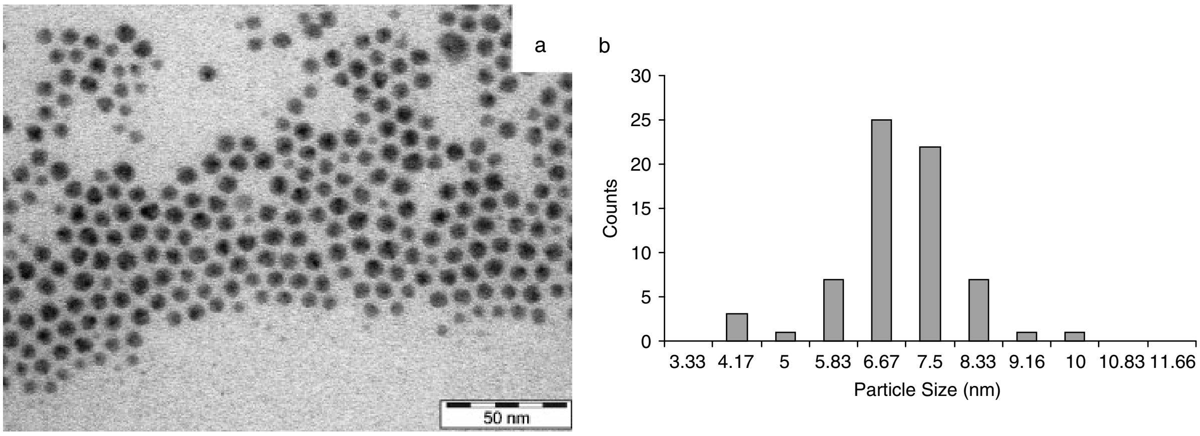

Figure 3. (a) TEM micrograph of Korantin-stabilized silver colloid (3 : 1) and (b) the corresponding particle size distribution based on 67 particles counted.

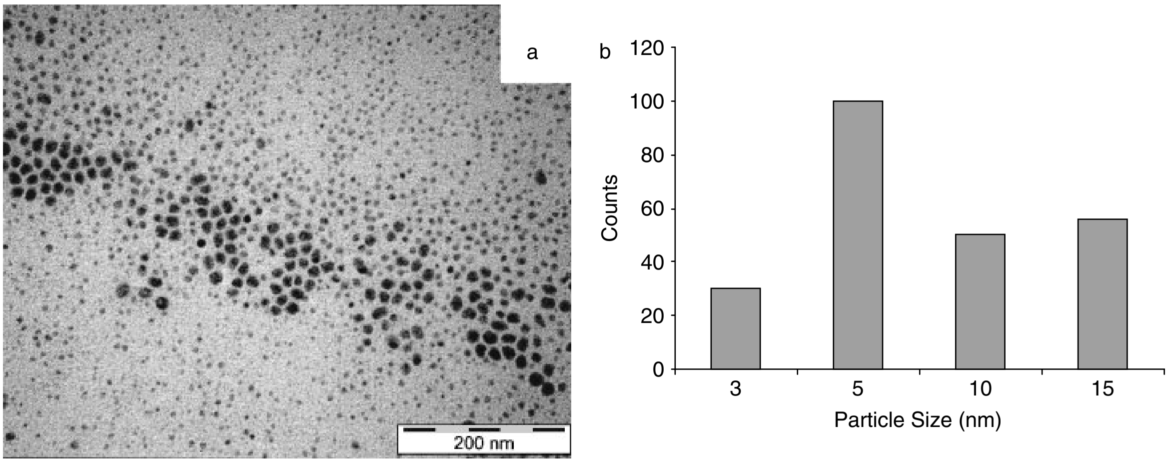

Figure 4. TEM micrograph of (a) Korantin-stabilized silver colloid (Ag/Korantin = 4/1) with (b) corresponding particle size distribution based on 236 particles counted.

It has been reported that long-chain carboxylic acids form close-packed monolayers on the surface of silver nanoparticles.[22] Tao reported that the two oxygen atoms of the carboxylate bind to the silver surface nearly symmetrically, and the molecular chain extends trans zigzag.[23] In order to gain insight into the interaction between Korantin and the silver surface, FTIR was employed.

FTIR

Owing to the lower concentration of the samples prepared (see Table 1) the absorption spectrum of the Korantin-stabilized silver colloid was similar to that of mineral oil. Furthermore, mineral oil consists of a high concentration of hydrocarbons; these absorb in the same region as some of the functional groups of Korantin and, hence, cover many peaks in the absorption spectrum. However, the most noticeable difference in these complex spectra were the $-COO^-$ and the $-NCOO^-$ stretching frequencies. The strong band at $1736\ cm^{-1}$ was assigned to the C=O stretching vibration ($\nu_{C=O}$) of free Korantin. A shift was observed to lower frequency ($1725\ cm^{-1}$) once the surfactant coordinated itself to the silver surface via the two oxygen atoms. In addition, a shift in the amide I band ($1613\ cm^{-1}$) to higher frequency was observed ($1635\ cm^{-1}$). Combining all the results thus far, it is clear that colloidal silver nanoparticles were successfully synthesized directly in mineral oil. The reaction could be explained as follows. In the presence of Korantin, silver lactate was oxidized to pyruvic acid, which in turn caused the silver ions to be reduced to silver(0). It should also be noted that a much shorter reaction time was observed when the reaction was performed in air. Hence, in this case, the presence of oxygen plays an active role in silver nanoparticle formation.[24] Upon reduction, the carboxylate head group of Korantin adsorbed onto the silver surface, thereby preventing aggregation. This assumption could also provide an indirect explanation to the amount of silver nanoparticles lost through precipitation (Table 1). The oxidation of silver lactate into pyruvic acid could result in a lowering of the pH. At lower pH the charges on the particles are weaker, hence lowering the stability of the dispersions. At high surfactant concentration the pH is even lower and, hence, more unstable dispersions are obtained.

Formation studies

The formation of silver particles of different concentration (0.3 vol.% and 0.011 vol.% silver) was followed by absorbance measurements. Initially, more than one absorption band was visible (Fig. 5a and b). This is a clear indication of the polydispersity of the system at that stage. According to Mie's theory, small spherical nanocrystals should exhibit a single surface plasmon band, whereas larger metal colloid dispersions can have broad or additional bands in the UV–VIS range. This is due to excitation of plasmon resonances or higher multipole plasmon excitation.[25,26] At 90 °C (Fig. 5c) the asymmetrical peak blue-shifted as smaller particles started to form. Hence, larger particles were formed at the beginning of the reaction, which were later decomposed into smaller particles. Approximately 1.5 to 2 h later at 90 °C, only one symmetric absorption peak was observed at the wavelength characteristic for spherical silver nanoparticles with a narrow size distribution (Fig. 5d). This was confirmed with TEM (see Fig. 3). After stirring for 1–2 days at room temperature (Fig. 5e), no further change was observed, which implies that the reaction reached completion.

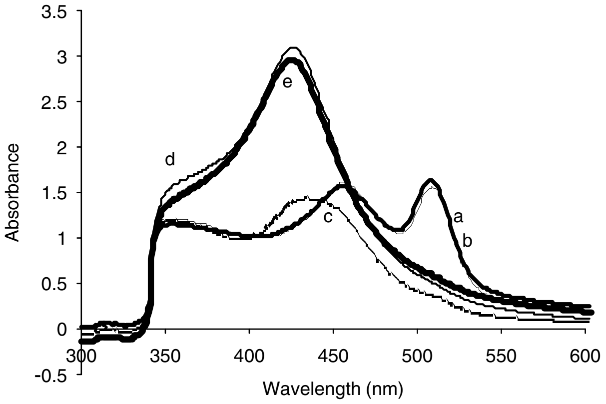

Figure 5. UV–VIS spectra of 0.3 vol.% silver particles at different times during the reaction: (a) and (b) correspond to samples taken at room temperature and 60 °C respectively, and (c) and (d) correspond to samples taken at 90 °C, but during different times. Sample (e) was collected at room temperature 1–2 days later.

Figure 6 shows the UV–VIS spectra obtained during the silver colloid formation studies with a lower concentration of silver. From the spectra, it is clear that the reaction should be stopped after no later than 2 h (Fig. 6c) once the above-mentioned temperature is reached. This will ensure a narrow size distribution of spherical silver nanoparticles, since from (d) to (g) there is a gradual increase in the FWHM observed due to agglomeration.

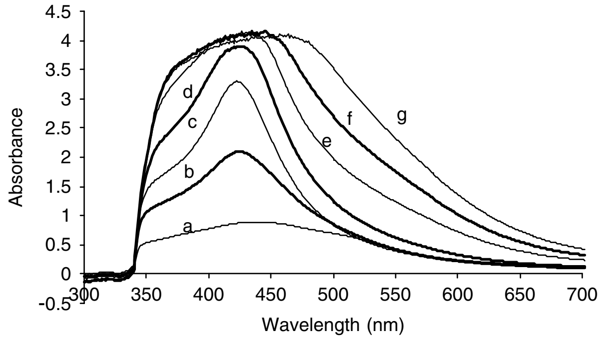

Figure 6. UV–VIS spectra of 0.011 vol.% silver particles in mineral oil at different times during the reaction at 90 °C: (a) 20 min, (b) 1 h, (c) 2 h, (d) 4 h, (e) 5 h and (f) the next day (room temperature).

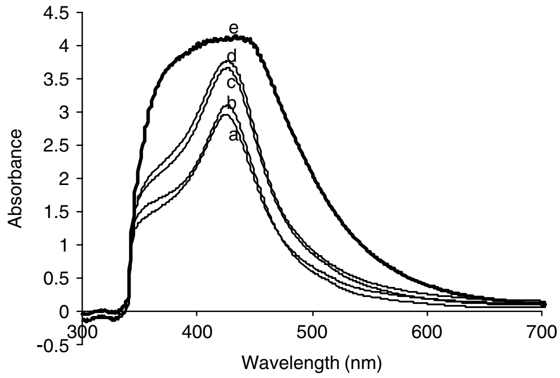

Figure 7. Stability studies of Korantin-stabilized silver nanoparticles, where (a) and (b) correspond to freshly prepared and 2-day-old samples respectively. Samples (c) and (d) refer to time intervals of 1 week and 2 weeks respectively. Sample (e) was measured 1 month later.

Stability studies

To detect the stability of the Korantin-stabilized silver nanoparticles in mineral oil, the absorption spectra were recorded at different times. From Fig. 7, no obvious difference was detected in the shape or position of the absorption peaks during the initial 2 weeks (Fig. 7a–d). However, an increase in intensity is observed that could be due to the formation of larger particles. The silver nanoparticle suspensions prepared were stable for about 1 month, since at that time the symmetrical peak broadened showing the onset of agglomeration (Fig. 7e).

CONCLUSIONS

Copper colloid suspensions were successfully peptized with Korantin SH and CNSL, resulting in particles with sizes less than 10 nm in the former and 7–15 nm in the latter. Mineral-oil-based nanofluids containing silver nanoparticles with a narrow size distribution (9.5 ± 0.7 nm) were prepared by a one-step process. The particles remained well separated even when a much lower surfactant concentration was used. Furthermore, a higher concentration of surfactant yields monodisperse spherical silver particles with a narrow size distribution. However, a high concentration of silver leads to a higher loss of silver during the reaction due to Brownian motion. The particles are stabilized by Korantin, which coordinates to the silver surface via the two oxygen atoms forming a dense layer around the particles. The silver suspensions were stable for about 1 month.

Acknowledgements

We wish to thank Mr Dreier (MPI) for TEM and Mr Wassmuth (MPI) for FTIR measurements. The National Research Foundation (SA) and the DFG Priority Program SPP 1072 (grant no. BO 1135/3-3) are acknowledged for financial assistance.

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