

Cryochemical synthesis of bimetallic nanoparticles in the silver-lead-methyl acrylate system

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Combined condensation of silver, lead and methyl acrylate vapours in a vacuum onto a glass reactor surface cooled by liquid nitrogen followed by melting and heating of the co-condensate results in the formation of organosols consisting of bimetallic particles capable of aggregation; the size of these particles does not exceed 5 nm.

Bimetallic nanoparticles with a uniform or lamellar distribution of metals in the bulk attract attention due to their application in catalysis and as model objects in studies of alloy formation.¹ Bimetallic nanoparticles are usually obtained by reduction of salts of two metals in solution or by condensation of metal and organic solvent vapours in a vacuum onto a cooled surface.² The latter technique was also used in this work. The choice of the silver-lead-methyl acrylate system is based on the results of our previous studies³ and on a quantum-chemical estimation of the properties of bimetallic nanoparticles. The binding energies of mixed metal clusters $(M_1)_m(M_2)_n$ ($m + n \leq 4$) have been calculated. These values are obtained as the energy differences of the equilibrium structures of clusters and of all possible fragments in their equilibrium geometries. The silver-lead systems are found to be the most stable ones.⁴

We showed previously³ that combined condensation of methyl acrylate (MA) with silver is accompanied by initiation of methyl acrylate polymerisation by silver. The adsorption of the resulting macromolecules on the surface of the silver nanoparticles provides the high stability of the organosols and the possibility of concentrating them, to the extent of obtaining solid poly(methyl acrylate) films containing several percent of silver. In the present work, we describe the results of cryochemical synthesis of dispersions of Ag/Pb bimetallic particles in methyl acrylate. Vapours of silver and lead were obtained by means of two independent evaporators mounted in a semi-preparative reactor. The concentration of the metals in the organosols was determined by atomic emission spectroscopy with an inductively coupled plasma and by X-ray fluorescent analysis.

The Ag/Pb/MA organosols formed by slow (*ca.* 1 h) heating of low-temperature co-condensates are reddish-brown and are stable for several days in an argon atmosphere. The Pb/MA system studied simultaneously behaves similarly. The methyl acrylate evaporated during the cryosynthesis of Pb/MA and Ag/Pb/MA organosols can be quantitatively removed from them, which indicates the absence of polymerisation under the experimental conditions. Thus, unlike silver, lead does not initiate the polymerisation of methyl acrylate. Moreover, as regards methyl acrylate polymerisation, the system containing both metals behaves as Pb/MA rather than as Ag/MA. In our opinion, such a behaviour is caused either by a non-additive change of nanoparticle properties on transition from binary systems, Pb/MA and Ag/MA, to a ternary system (Ag/Pb/MA), or by efficient inhibition by lead of MA polymerisation initiated by silver atoms.

Methyl acrylate is obviously a less efficient stabiliser of nanoparticles than poly(methyl acrylate), which creates on their surface a polymeric shell preventing aggregation. For this reason, lead and lead/silver nanoparticles form aggregates in organosols. This is easily seen in the electron microscopic photographs shown in Figure 1. In both cases, the particle size does not exceed 5 nm, *i.e.* they are smaller than the diameter of the silver nanoparticles (7–15 nm) obtained previously under similar conditions.³ Figure 2 (curve 1) shows an absorption

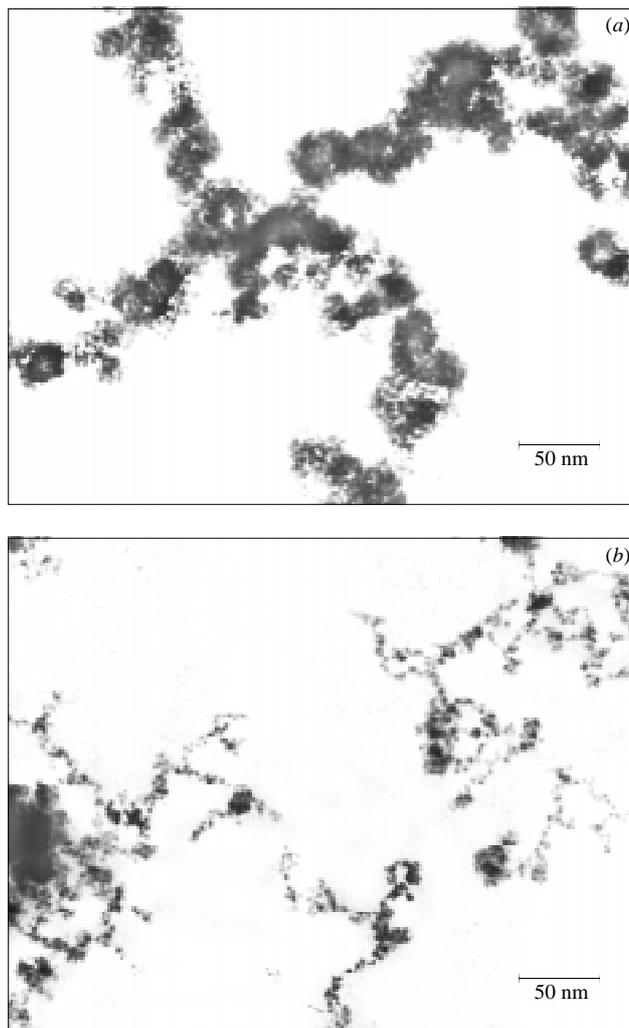


Figure 1 Microphotographs of nanoparticles in Pb/MA (a) and Ag/Pb/MA (b) organosols.

spectrum of cryochemically synthesised Pb/MA organosol. The spectrum shape is determined by the fact that the maximum of the lead plasmon absorption band is located at *ca.* 220 nm.^{5,6} As a result of oxidation of lead particles with air oxygen, organosol absorption in the visible range decreases rapidly, and opalescence appears. The Pb/C₂H₅OH system behaves similarly.⁵ The silver plasmon absorption band in the Ag/MA organosol has a maximum at 416–420 nm.³ In the spectrum of the freshly prepared Ag/Pb/MA organosol recorded immediately after it was transferred (in argon atmosphere) from the reactor chamber into a cylindrical ampoule (internal diameter $d = 5$ mm) and sealed (Figure 2, curve 2) this band is red-shifted ($\lambda_{\max} = 438$ nm).

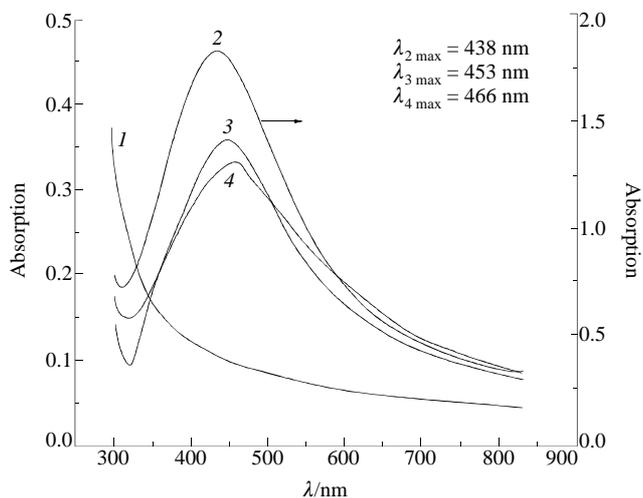


Figure 2 Absorption spectra of cryochemically synthesised organosols: 1, Pb/MA (recorded immediately after completion of the co-condensate melting and its transfer into a 1 mm spectrophotometric cell in air); 2, Ag/Pb/MA (sample in a sealed cylindrical ampoule, internal diameter 5 mm, in an argon atmosphere); 3–4, the same as 2 immediately after unsealing the ampoule in air and pouring the sample into a 1 mm spectrophotometric cell (curve 3) and 1–1.5 h later (curve 4). Metal content (mg ml^{-1}): 1.12 lead in Pb/MA; 0.14 lead in Ag/Pb/MA; 0.09 silver in Ag/Pb/MA.

When the ampoule was unsealed and the sample exposed to air and placed in a spectrophotometric cell ($l = 1 \text{ mm}$) λ_{max} sharply increased to 453 nm (Figure 2, curve 3). During the subsequent 1–1.5 h, λ_{max} gradually approaches 466 nm (Figure 2, curve 4). At the same time, the intensity of the band decreases somewhat, possibly due to oxidation of lead involved in bimetallic particles. The interpretation of the absorption spectra of dispersions of metal colloidal particles is known to be a multi-factor problem.⁷ Taking this into account, it is unlikely that an exhaustive explanation of the spectral changes occurring on transition from the Ag/MA and Pb/MA systems to Ag/Pb/MA can be given at present. On the other hand, the electron microscopic data presented in this work allow us to consider the aggregation of nanoparticles as the main, theoretically substantiated^{7,8} cause of the red shift (416–420 nm \rightarrow 438 nm) in an inert environment. The oxidation of lead with air oxygen can affect the stability of bimetallic nanoparticles. In this case, the long-wave shift of λ_{max} , 438 nm \rightarrow 453 nm and 453 nm \rightarrow 465 nm (Figure 2, curves 2–3 and 3–4), indicates the development of the aggregation processes and, possibly, a change in the electronic state of the bimetallic particles due to lead oxidation.⁹

Further studies will make it possible to estimate how the composition of the bimetallic nanoparticles and the structure and properties of the surface layer of an organic ligand affect the optical and chemical properties of cryochemically synthesised nanoparticles and their organosols.

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