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Rheology of silica suspensions stabilized by ethylenediamine

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The effect of ethylenediamine bridging, particle size and specific surface area of fumed silica on rheological properties of silica suspensions were studied with a cylinder rheometer. The apparent viscosity of suspensions of aerosils A-50, A-175, A-300 and A-380 irreversibly increases with shearing time at shear rates above a certain value. The critical shear rate for shear-induced bridging coagulation decreases with the increasing ethylenediamine concentration because of lowering of the energy barrier due to a compression of the electrical double layer. The suspensions become elastic pastes after the bridging coagulation.

Key words: silica; suspension; ethylenediamine; rheological properties; viscosity

1. Introduction

The colloidal silica dioxide finds more and more applications in various branches of science and technology: silica gels and glasses produced by the sol-gel method, hydrated cellulose, cellophane, paper, ceramics, for polishing optical and electronic components, etc.

Inter-particle forces determining the dispersion stability of silica particles can be of three types: the London–van der Waals attraction, electrostatic repulsion and forces of interaction of adsorbed long-chain polymer molecules with the silica particles. Important factors are also the bridging attraction and the steric repulsion since the energy barrier

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for the bridging is determined by the electrostatic contribution to the shear-induced bridging coagulation [1].

Disperse systems integrate the fundamental physicochemical features such as heterogeneity – the presence of an interface and dispersity. The role of these factors in disperse systems (in their aggregative and sedimentation stability) becomes more essential with the decrease of particles sizes and their concentration in a fluid medium.

The flocculation process is especially intensive in lyophobic (aggregative labile) disperse systems upon reaching a critical concentration of particles in the fluid dispersion medium. Main elements of the structural lattice in such systems are contacts between particles in an aggregate generator through the whole volume. The disperse system becomes structured and passes to a new state. In this contribution we explore rheological performances of silica suspensions stabilized by ethylenediamine which exhibit rheopexy and thixotropic properties.

2. Experimental

The suspensions were composed of fumed silica, ethylenediamine ($C_2H_8N_2$) and water. The medium was the solution of ethylenediamine in water. The $C_2H_8N_2$ concentration in aqueous solutions was 1.0–1.4 mol/dm^3. The silica samples were Aerosil A-50, A-175, A-300, A-380 from the Kalush Experimental Plant (KEP, Ukraine) and Aerosil MOX-80 from Degussa Co. (Germany). The particle diameters were 50–70 nm, 10–40 nm, 5–20 nm, 5–15 nm and 10–80 nm, respectively. Silica suspensions were prepared at concentrations up to 12.5 wt %. The technique of preparation of the stabilized aqueous dispersions of silica dioxide includes three stages [2]: stirring of starting components, ultrasonic dispergation and centrifugation. The suspensions were ultrasonicated for 60 min and centrifugated at 2000 min^{-1} for 15 min. Rheological properties of the dispersions were studied with a rotational viscosimeter Reotest 2.1 equipped with a cylindrical system in the range of detrusion rates from 9 to 1312.2 s^{-1}. The temperature of the samples was maintained at 20±0.5 °C.

3. Results and discussion

The study of coagulation of the suspended particles is presented in more detail in this paper than in the contribution by Hunter et al. [3] in which submicron particles are involved and van der Waals forces play an important role. To prevent agglomeration, the particles can be stabilized by ionic charges or a steric barrier if they are suspended in a liquid. Due to its high polarity and for the environmental reasons, water was chosen as the dispersion liquid. It has been observed that the stabilization with large molecules yields suspensions of high viscosity. The steric stabilization, in particular, needs much more space between the particles than the formation of an electric double layer in ionically stabilized suspensions. Consequently, the ionic stabilization is more convenient for low-viscosity aqueous suspensions with high silica concentrations.

According to the DLVO theory [3], the energy barrier between the primary and secondary minima which prohibits a spontaneous agglomeration depends on the ions, their concentrations and the surface potential ψ_0. If the kinetic energy of the particles at room temperature is of the order of the energy barrier, then the coagulation can occur between the dispersed particles if the shear stress vanishes. The agglomeration of the dispersed submicron particles can be described by a second-order kinetic equation [4]:

$$-\frac{dN}{dt} = \alpha_p \frac{4kT}{3\eta} N^2 \tag{1}$$

where N is the number of particles, η is the viscosity of the liquid, and α_p is an operational parameter for the stability ratio describing collisions that lead to permanent agglomeration. The physical meaning of the parameter α_p is the medium size of particles in the colloid. It can be calculated from Eq. (1). If $\alpha_p \leq 1$ then such a colloid system will be inconvertible. The system undergoes a spontaneous agglomeration for $\alpha_p > 1$.

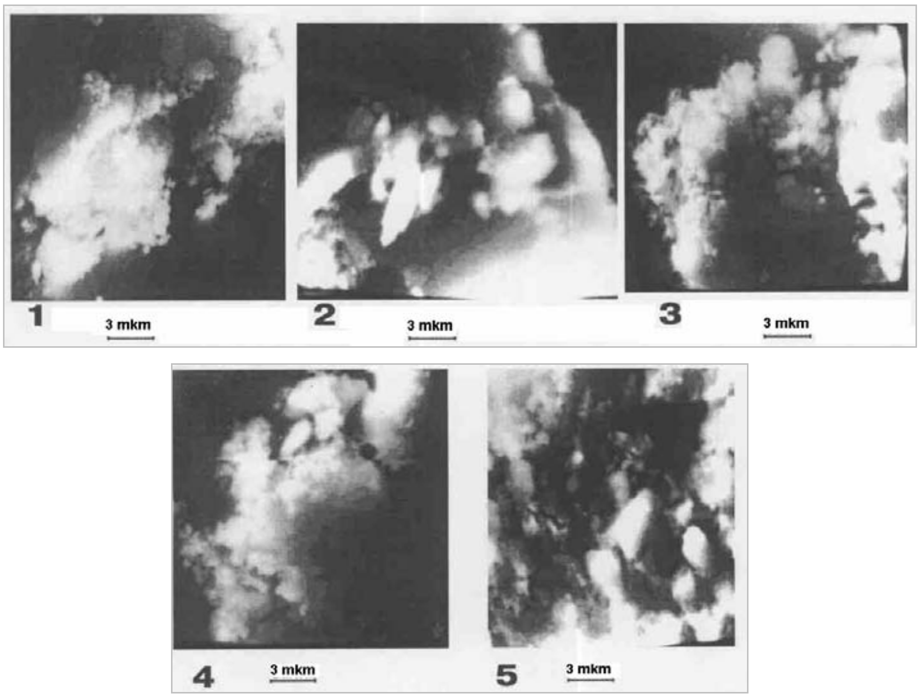

Fig.1. SEM of silica suspensions fabricated from fumed silica:
1 – A-50; 2 – A-175; 3 – A-300; 4 – A-380 (KEP, Ukraine);
5 – MOX-80 (Degussa Co., Germany)

Interacting particles initially connect via hydrogen bonds of the silanol groups on the silica surfaces. As long as only silanol groups are involved in bonding and the siloxane bonds are not formed, the increase of viscosity during the coagulation is reversible and shows a thixotropic behaviour. The thixotropy is largely influenced by the specific surface of silica and ethylenediamine particles because the bonds between the atoms are stronger in this case.

After addition of a small amount (about 6%) of ethylenediamine, low-viscosity suspensions can be prepared by the cross-linking within 3–6 months at room temperature. Figure 1 shows the SEM micrographs of silica particles in the suspensions. The silica particles in the dispersions obtained have a complex morphology.

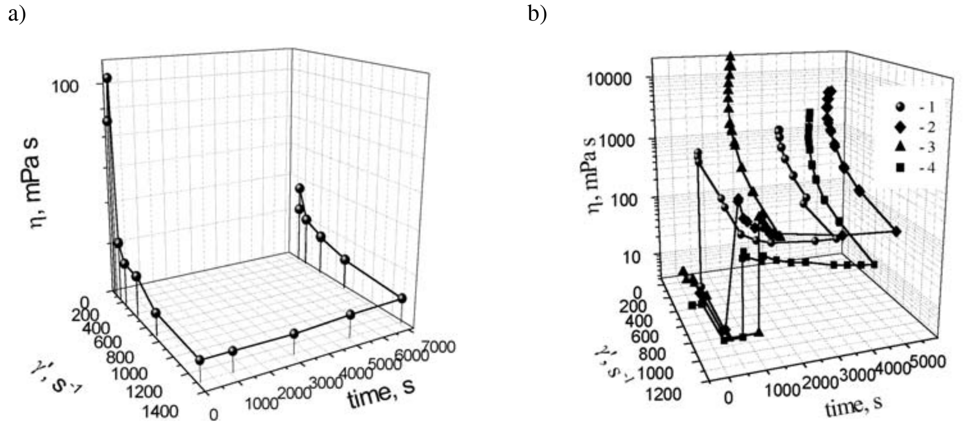

Fig. 2. Shear rate dependence of viscosity for suspensions containing 12.5 wt. % of fumed silica and stabilized by ethylenediamine: a) MOX-80 (Degussa Co., Germany), b) 1 – A-50, 2 – A-175, 3 – A-300, 4 – A-380 (KEP, Ukraine)

As can be seen in Fig. 1, the particles of the MOX-80 aerosil are least susceptible to agglomeration. This allows us to explain the thixotropic behaviour of the suspension prepared from the MOX-80 aerosil (Fig. 2a). The agglomeration of the initial silicas A-50, A-175, A-300 and A-380 with the increase of the shearing rate (γ') leads to irreversible changes in suspensions containing these aerosils (Fig. 2b). Thus, these suspensions exhibit rheopexy. The viscosity of the suspensions prepared increases with the decrease of the specific surface area of the aerosils.

4. Conclusions

We have demonstrated the possibility to process commercially available fumed silicas in order to obtain low-viscosity suspensions. The dispersions of silica nanoparticles (fumed silicas: A-50, A-175, A-300 and A-380 (Ukraine)) stabilized by ethylenediamine exhibit rheopexy. The effective viscosity of dispersions increases essentially at certain shearing rates. Aqueous, stabilized dispersions of the fumed silica MOX-80 (Degussa, Germany) have the thixotropic properties. The percolation transformation in the dynamic viscosity of silica dioxide dispersions can be important for polishing elements employed in fabricating optical and electronic devices with the silica colloids described in this work.

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