Structural transitions in aqueous suspensions of natural graphite

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The electric conductivity $\sigma$ and plastic viscosity $\eta$ of aqueous suspensions at different volume fraction of graphite $\varphi$ and concentration of nonionic surfactant (Triton X-305) are investigated. The correlations between conductivity and rheological properties are discussed. A model of structural transitions in aqueous graphite suspensions is discussed. Two structural transitions, corresponding to changes in electrical and rheomechanical properties, are identified as percolation and sol-gel transitions, respectively. An unusual initial decrease of the bulk electrical conductivity with graphite volume fraction $\varphi$ increase was observed in surfactant solution. This fact is explained as a result of isolating coating formation around the graphite particles.

Keywords: Aqueous graphite suspensions, Electric conductivity; Viscosity; Percolation transition; Sol-Gel transition

I. INTRODUCTION

Colloidal suspensions of carbon have many industrial applications and are used for production of conducting composite materials, liquid electrophotographic toners, pigments in inks and paints, rubber reinforcing and fillers, electrodes and conducting films [1-7]. The highly dispersed carbon materials (natural graphite, carbon black etc.) display a strong tendency to agglomerate and form highly disordered ramified aggregates with the fractal structures [8-10]. Recently, the properties of these systems are intensively studied experimentally, but here remain many problems in understanding of correlations between morphology of the aggregates and physical properties. Especially, we may note the practically important problem related with electrical percolation behavior of the carbon-based composite materials [11-15].

In this work we studied the structural transitions in the aqueous suspensions of natural graphite in the presence of nonionic surfactant by means of electrical conductivity and viscosity measurements. Because of high hydrophobicity of graphite, it particles tend to aggregate in water suspensions and to form a gel phase, but addition of a surfactant allows to achieve fine adjustment of aggregation processes through changes in surfactant concentration.

II. MATERIALS AND METHODS

A. Materials

The natural graphite (product of Zavalie Plant, Ukraine, carbon content 99.5%, type C-0) was chosen for investigation. An example of the transmission electron micrograph of the natural graphite sample is presented in Fig. 1. The electron microscopy data confirm the presence of particles with plate-like geometry. The granulometric composition of dispersions was studied by laser diffraction microanalyzer Analysette-22 (Fritsch). The distribution curves cover the size range 1-10 $\mu$m and have a narrow maximum at $\approx 5 \mu$m (Fig.2).

Table. Some properties of the natural graphite sample

| Property                        | Value |
|---------------------------------|-------|
| Diameter of particle, $d$ ($\mu$m) | $\approx 5$ |
| Plate thickness, $h$ ($\mu$m)   | 0.1-0.5 |
| Particle aspect ratio, $d/h$     | 10-50 |
| Specific surface area, $S$ ($m^2/g$) | 20 |
| Exchange capacity, $q$ (meq/g)   | 0.05 |
| Surface charge density (pH=10), $\sigma_s$ (C/m$^2$) | 0.12 |
| Specific heat wetting, $w$ (J/m$^2$) | 0.09 |

The Table presents the main properties of our sample of natural graphite. Here, the value of the specific surface area $S$ was determined from the water vapor adsorption isotherms using the vacuum microbalance apparatus and from the dye (methylene blue) adsorption isotherms in water solutions. The exchange capacity, $q$ and the surface charge $\sigma_s$ were determined using the conductometric and potentiometric titration of dispersions by 0.1 M KOH solution and 0.2 M KCl solution. The heat of wetting $w$ was determined with the help of DAK-1M microcalorimeter (Pribor, Moscow).
We used Triton X-305, CH_{3}-C(CH_{3})_{2}-\text{CH}_{2}-C(CH_{3})_{2}-
C_{6}H_{5}O-(\text{CH}_{2}\text{CH}_{2}O)_{n}H, where n=30, as a non-ionic surfactant. The background electrolyte concentration of 0.01 M KCl was present in all the cases. The stated values of pH and ionic strength of dispersions were adjusted by the combination of 0.01 M HCl, KCl and KOH solutions. The water, used in this study, was double distilled and had conductivity 5x10^{-6} S/cm at 20°C. All the reagents were of analytical grade. The suspensions were prepared by sonicating (UZDN-2T sonifier, Russia) during 1 minute. The sonifier was operated at a frequency of 22 kHz, with the output power 150 w. Then, after cooling, the sample was placed into the thermo-stabilized cells for measurements of conductivity and rheological parameters.

B. Experimental methods

The electrical conductivity, zeta potential and rheological parameters of natural graphite in aqueous suspensions were measured at fixed temperature \( T=293 \, \text{K} \).

1. Electrical conductivity

The electrical conductivity measurements were made using -5021 (Tochelectropribor, Kiev, Ukraine) at the frequency of \( f=1 \, \text{kHz} \) in a cell with platinum electrodes with the surface area of 1 cm^2.

2. Zeta potential

The zeta potential measurements were made using microelectrophoresis technique at the electric field strength \( E = 5-6 \, \text{V/cm} \) and the volume fraction of graphite particles \( \varphi \sim 10^{-4} \). The average of, at least, three measurements for each sample was recorded. No corrections were made for polarization and relaxation effects of the electrical double layer, as far as in our case the condition \( d/\lambda \geq 100 \) (where \( d \) is the average particle diameter and \( \lambda \) is Debye screening length) is fulfilled [16].

III. RESULTS AND DISCUSSION

Electrical conductivity and rheological properties of suspensions are very sensitive to their structural organization, which is controlled by the balance of interparticle
forces [17]. An important information about the structural transitions and mechanisms of particle aggregation in water suspensions may be obtained from analysis of experimental data on these characteristics. Figure 4 shows electrical conductivity $\sigma$ and plastic viscosity $\eta$, measured at shear rate $\dot{\gamma} = 1312$ s$^{-1}$ versus volume fraction of the natural graphite $\varphi$ in water at different concentrations $C_s$ of Triton X-305. In the absence of any surfactant, the electrical conductivity $\sigma$ and viscosity $\eta$ increase sharply even at very small volume fractions $\varphi \approx 0.01 - 0.02$ (1-2 vol.%). It reflects existence of a strong aggregation between the carbon particles and formation of a highly interconnected network between the particles of anisotropic geometry [18-20]. In the presence of a surfactant, the fluidifying effect is observed, it results from decrease of the aggregation of particles. The surfactant molecules form the stabilizing layers on the surfaces of the graphite.

Because of a high electrical contrast of these systems (specific conductivity of graphite particles is of an order $\sigma \approx 10^3 - 10^5$ S/cm [21] and is very high as compared with conductivity of water solutions, $\sigma \approx 10^{-5}$ S/cm) the typical percolation behavior of conductivity $\sigma$ is observed [22]. A considerable increase of the conductivity of suspensions begins only after the certain threshold value of $\varphi = \varphi_c$ is exceeded (Fig. 4). The similar behavior was observed for other highly conductive carbon-based composites [8,10,11,13,15,18,19]. The viscosity of suspensions continuously decreases with volume fraction $\varphi$ increase. However, as rule, the observed $\eta$ versus $\varphi$ dependencies are step-like (Fig.4). The viscosity begins to increase sharply only at concentrations $\varphi > \varphi_v$, and $\varphi_v$ value is noticeably high than value of $\varphi$. As surfactant concentration $C_s$ increases, both threshold values, $\varphi_c$ and $\varphi_v$, also increase. For example, in Fig. 4, two concentrations of $\varphi$ and $\varphi_v$ are shown for the case when $C_s = 0.001$ mol/dm$^3$. The similar step-like behavior $\eta(\varphi)$ was observed also for other values of $\dot{\gamma}$ (Fig. 5). In the region where $\varphi$ do not exceed the threshold value $\varphi_c$, the initial linear decrease of the bulk electrical conductivity $\sigma$ with $\varphi$ increase is observed (Fig. 6)

$$\sigma(\varphi) = \sigma_i = \sigma(0)(1 - \alpha \varphi), \quad \text{at} \quad \varphi \leq \varphi_c. \quad (1)$$

Here, $\sigma(0) = 1.23$ mS/cm is the conductivity of the 0.01 N aqueous solution of KCl at $T = 293$K and $\alpha = 2.05$ is the fitting parameter.

This behavior is rather unusual, as far as electrical conductivity of the system decreases with increasing of the ratio of more conductive component. In fact, Maxwell obtained first the Eq. (1) for dilute dispersions of isolating spherical inclusions in a conductive host matrix [23]. It is valid for $\varphi < 0.1$ and the coefficient $\alpha$ is equal to 1.5.

The initial decrease of electrical conductivity may be interpreted in view of the low effective conductivity of
such as periodical colloid structures and random statisti-
cal properties, depending on the volume fraction of the
tures of disperse systems may display different topolog-
cal networks formed from chains of aggregated particles,
or compact aggregates linked by coagulation chains.

The structural transitions at \( \phi_c \) and \( \phi_v \) correspond to changes in electrical (conductivity \( \sigma \)) and rheomechanical (viscosity \( \eta \)) properties of a system, and we believe that they may be identified as percolation and sol-gel transitions, respectively.

An illustration of our model of structural transitions in aqueous suspensions of graphite is presented in Fig. 8. At low concentration of solid phase, the long-range type mechanism of structure formation prevails. We can assume that surfactant molecules form nonconductive films on the hydrophobic surface and stabilize a graphite sus-
pension through modification of the hydrophilicity and zeta potentials of colloidal particles. These films have low conductivity, and the coated graphite particles behave effectively as nonconductive. With \( \phi \) increase at given \( C_s \) the isolation of particles destroys. At the critical concentration \( \phi = \phi_c \) an infinite percolation cluster of the conducting graphite particles appears for the first time. The critical concentration \( \phi_v \) corresponds to the critical concentration of the structure formation. At this point \( \phi = \phi_v \), an infinite cluster with non-local elastic properties appears for the first time, and this point may be identified as the sol-gel transition point.

\[
\sigma = \sigma_i + \beta(\phi - \phi_c)^t, \quad \text{at} \quad \phi > \phi_c, \tag{2}
\]

FIG. 7: Critical volume fractions of particles \( \phi_c \) and \( \phi_v \) (estimated from measurements of electrical conductivity and vis-
cosity, respectively) versus surfactant concentration \( C_s \).

FIG. 8: Illustration of a model of structural transitions in aqueous graphite suspensions. Black circles represent the carbon particles and gray shells represent the low-conducting surfactant layers.

IV. CONCLUSIONS

Experimental data on electric conductivity and plastic viscosity of aqueous natural graphite suspensions as function of solid volume fraction and nonionic surfac-
tant concentration were presented. Electric conductivity and plastic viscosity displays different sensitivity to structural transitions in suspensions. Two different concentration points, corresponding to changes in electrical and rheomechanical properties, were identified as percolation and sol-gel transitions, respectively. We obtained the critical index value as close to \( t = 2.0 \), which corresponds a classical random percolation case. The surfac-
tant molecules may form isolating coating around particles of conductive graphite, and it results in initial decrease of suspension conductivity with increase of solid
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