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RHEOLOGICAL BEHAVIOR OF MONTMORILLONITE WATER SUSPENSIONS IN THE PRESENCE OF SURFACTANTS

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Abstract. In this thesis the features of rheological behavior of ultrasonic-activated water dispersions of montmorillonite in the presence of surfactants of anionic and non-ionic type are considered. It was determined that the strength of coagulation structure changes depending on the type of surfactant.

Keywords: montmorillonite, suspension, surfactant, adsorption, spatial aggregation, mesopores.

1. Introduction

Montmorillonite clays are widely used in paint and coatings industry as thixotropic additives and thickeners for waterborne varnishes and paints. During the water dilution they produce stable viscous suspension with noticeable thixotropic properties. Montmorillonite mineral is the representative of layered silicates group and possess developed surface. Contact of mineral with liquid water causes the penetration of water molecules into interlayer space of montmorillonite with subsequent hydration and thus, causes swelling [1]. This process can be essentially accelerated with the use of ultrasonic treatment, which reduces hydration time from 6–9 h to 20–40 min. During the activation, the secondary aggregates separation takes place, chemical composition and crystallinity of mineral remains unchanged. Ultrasonic treatment enhances dispersity grade and structure strength of the suspension. They become more viscous and thixotropic through increase of the quantity of contacts between particles themselves and between the particles and disperse phase [2].

It is known that in low-concentrated suspensions of montmorillonite, coagulation with subsequent sedimentation of particles aggregates takes place (Fig 1b). On reaching of the defined suspension concentration (1.5–4 mas %), spatial aggregation (flocculation) of particles takes place. This leads to the formation of “card house

structure”, in which particles are forming, at first sight, unstable structure (Fig 1c) [3].

Cross-particle contacts arise in consequence of interaction between positively charged particle edges and negatively charged basal surfaces (planes). Free space which is formed between interacting particles possess significant part of system volume and by convention is called mesopores [4].

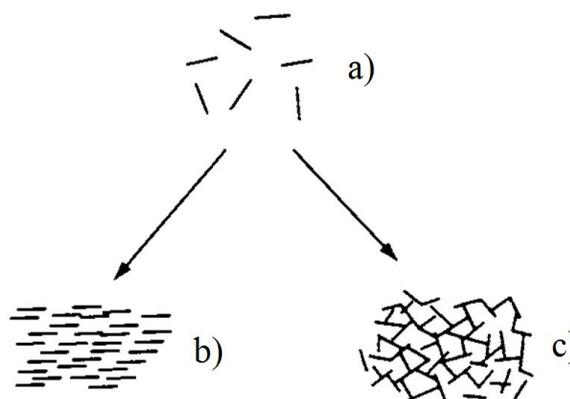


Fig. 1. Possible states of montmorillonite particles structure depending on concentration of the water dispersion: particles of montmorillonite in suspension (a); precipitate formation (b) and cardhouse structure formation (c)

Electromolecular forces are particularly strong on edges of particles, thus determining high strength of such microstructures. It is known that due to non-stoichiometric cation exchange in crystal lattice, excess negative charge appears on this particle regions and it is compensated with exchange cations inside interlayer volume. The condition of the formation of positive charge on the mineral particle edges is acid or neutral environment [5].

The strength of montmorillonite-containing dispersion systems can be regulated by introduction of surfactants. A great number of papers are devoted to the

interaction between montmorillonite and cationic surfactants, which come into interaction only with negatively charged particle edges [6]. Meanwhile, the use of anionic and non-ionic surfactants has not been fully studied.

The aim of this paper is the study of the influence of anionic and non-ionic surfactants on the rheological behavior of montmorillonite water suspensions.

The object of the study is water based montmorillonite-containing dispersions structure parameters and the effect of surfactants of different types on these parameters.

2. Experimental

As the basic material for research the bentonite powder from Dashukivske deposit (product "PBA-22 Extra" of "Dashukivski bentonity" JSC) was selected (see Table 1). The material is composed of montmorillonite (up to 60 mas %) and the residues are presented by quartz and feldspar. This material is the product of treatment of natural calcium bentonites through chemical activation with sodium carbonate and subsequent drying and grinding.

As surfactants in this study we used the following substances: polyether-siloxane polymer (No.1) as non-ionic surfactant and sodium methyl silicate (No.2) and ammonium polyacrylate (No.3) as anionic surfactants. All the substances were used as industrial products, supplied by BYK Chemie GmbH (Germany).

As the basic method for research of montmorillonite water suspensions properties rheometry was selected (viscometer Rheotest II); sorption measurements were conducted accordingly to BET method (argon gas), Deryagin method, and Khodakov device was used for measuring specific geometrical surface.

The suspensions were obtained in laboratory mixer of anchor type (mix. velocity 120 min^{-1} , engine capacity 0.5 kWph). Dispergation process was conducted on ultrasonic disperser UZDN-Ab for 5–7 min (frequency 19.5 kHz, amplitude of variable sonic pressure 0.588 MPa, amplitude of particle oscillation $2.42 \mu\text{m}$, amplitude of particles acceleration $3.6 \cdot 10^4 \text{ m/s}^2$).

Surfactants were introduced into cooled sonicated systems montmorillonite-water. Mixing was conducted during 15 min, and after that the suspensions were

conditioned during 1 h under the temperature of 293 K before rheological measurements.

Static parameters of rheometry were decided to be taken as characteristics of the structure strength, namely – shear limit and value of maximal (Shvedov) viscosity. Dynamic parameters of rheometry were decided to be taken as characteristics of the system's ability to rearrangement in shear conditions, namely – shear limit and value of minimal (Bingham) viscosity [7].

The "card house" model was used as the basic model of montmorillonite water systems structure for explanation of surfactant introduction effect on structure.

3. Results and Discussion

It was shown through the analysis of static parameters (Fig. 2), that surfactants of anionic types have the most essential influence on the shear limit and viscosity, while the structure strength and static viscosity rapidly decreases from the concentration 0.2 mas % of the surfactant. It can be explained with a sorption of the substances on active centers of positively charged particle edges [8]. In turn, this weakens strength of coagulation contacts of "edge-plane" type and, as the result – overall strength of system. Due to the active centers blocking, the hydration of montmorillonite particles also decreases.

The introduction of nonionic surfactant to the system is accompanied by an even and almost linear increase of shear limits and viscosity. It can be assumed that this surfactant in solution is adsorbed on montmorillonite particles without disturbing structure formation. As stated in Ref. [9], surfactant molecules, in case of spatial aggregation of the clay, can occupy free volume in mesopores, which can be a possible explanation of viscosity increase together with the increase of surfactant concentration. This assumption can be proven by the character of relationship between shear limit and surfactant concentration. The strength of the dispersion spatial structure grows due to the presence of surfactant in the pore volume.

Relationships between dynamic parameters and surfactant concentration (Fig. 3) prove conclusions made on the basis of static relationships analysis.

Table 1

Clay powder properties

Parameter	Value
Specific surface (BET), m^2/g	700
Specific geometrical surface, m^2/g	1.6
Surface development coefficient S/S	437.5
Water vapour sorption, mg/g	10.6
Water contact angle, deg	46
Density, g/cm^3	1.8

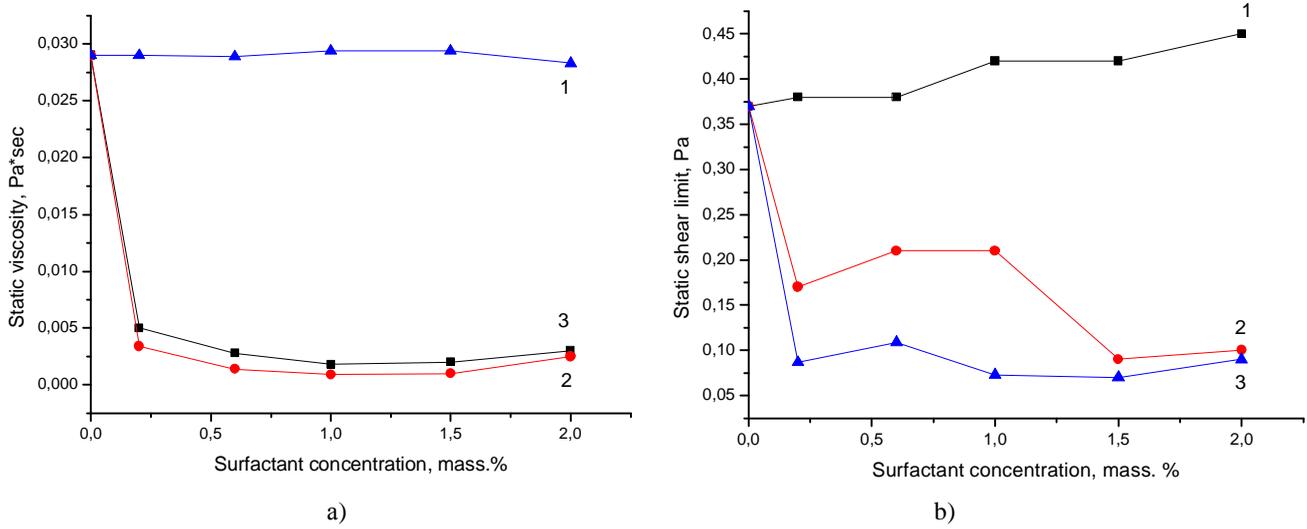


Fig. 2. Relationships between static viscosity (a), shear limit (b) and surfactant concentration: No.1 (1); No.2 (2) and No.3 (3)

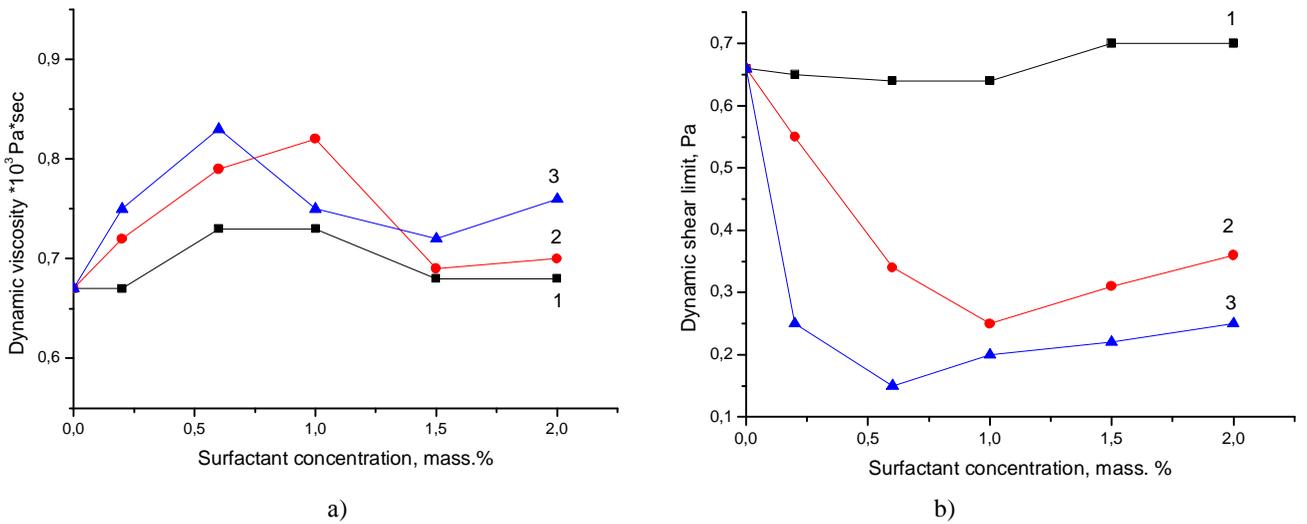


Fig. 3. Relationships between dynamic viscosity (a), shear limit (b) and surfactant concentration: No.1 (1); No.2 (2) and No.3 (3)

The plot of relationship between dynamic viscosity of the system and surfactant concentration have maximum that corresponds to concentration between 0.6 and 1.0 mas % (Fig. 3a). The shear limit at the same concentration has minimal values (Fig. 3b). It can be assumed that in the case of medium concentration of surfactant, a part of mesopores is filled up with it. The other part remains unfilled, so the dynamic shear resistance (characterized by Bingham viscosity) in such structure increases, but in general, such structure possesses low strength and thus, less values of shear limit [10].

In case of surfactant concentration increase, the value of viscosity decreases (returns to initial values) due to the equalizing of surfactant concentration in the entire pore volume. As the result – the viscosity essentially decreases and shear limit increases.

Anion surfactants raise the value of dynamic viscosity of suspensions; the relationship have maximums at 1.0 mas % for sodium methyl siliconate and 0.6 mas % for ammonium polyacrylate (Fig. 3a) [11]. This may be due to the cluster formation, which hinders orientation rebuilding in the system under shear. This assumption is proved by the nature of dynamic shear limit curves (Fig. 3b). During the cluster formation, the structural properties of the system in general decrease [12].

4. Conclusions

It was determined that the strength and dynamic parameters of the coagulation structure of montmorillonite suspensions are depending on the nature of the introduced surfactants.

Addition of non-ionic surfactants to the system does not result in significant change of rheological parameters. Activity and hydrophilic nature of montmorillonite surface during the interaction with the surfactant of this type does not decrease. This surfactant does not block the spatial structure formation and, most likely, sorbs in mesopores, slightly increasing coagulation stability of the structure.

Anion surfactants show essential effect on rheological parameters of the mentioned structures even when added in small concentrations. Clay particles, having on their edges mixed, mainly positive charge, interact strongly with dissociated surfactant molecules. This process leads to the weakening of connections in coagulation structures

Results of this study can be used in such branches of chemical industry as petrochemical, paint and coatings, ceramic, etc. Further researches will be dedicated to the influence of polymer surfactants on rheological properties of montmorillonite water slurries.

References

- [1] Onikata M., Kondo M. and Yamanaka S.: Clays and Clay Minerals, 1999, **47**, 678.
- [2] Introzzi L., Blomfeldt T. *et al.*: Langmuir, 2012, **28**, 11206.
- [3] Osipov V., Sokolov V. and Rumjanceva N.: Microstructura Glinistykh Porod. Nedra, Moskwa 1989.
- [4] Park H.-M., Kim T.-W., Hwang S.-J. and Choy J.-H.: Bull. Korean Chem. Soc., 2006, **27**, 1323.
- [5] Tombácz E. and Szekeres M.: Appl. Clay Sci., 2004, **27**, 75.
- [6] Hower W.: Clays and Clay Minerals, 1970, **18**, 97.
- [7] Permien T. and Lagaly G.: Clays and Clay Minerals, 1995, **43**, 229.
- [8] Auerbach S., Carrado K. and Dutta P.: Handbook of Layered Materials. Marcel Dekker, New York 2004.
- [9] He H., Zhu J., Yuan P. *et al.*: Proceed. ICAM 2008 – Ninth International Congress for Applied Mineralogy, Brisbane 2008, 321.
- [10] Wang C., Juang L., Lee C. *et al.*: J. Colloid Interface Sci., 2004, **280**, 27.
- [11] Chen D., Zhu J., Yuan P. *et al.*: J. Thermal Analysis & Calorimetry, 2008, **94**, 841.
- [12] Armando G., de la Torre L, García-Serrano L. and Aguilar-Elguézabal A.: J. Colloid Interface Sci., 2004, **274**, 550.

РЕОЛОГІЧНА ПОВЕДІНКА ВОДНИХ СУСПЕНЗІЙ МОНТМОРИЛОНІТУ В ПРИСУТНОСТІ ПОВЕРХНЕВО-АКТИВНИХ РЕЧОВИН

Анотація. Розглянуті особливості реологічної поведінки активованих ультразвуком водних суспензій монтморилоніту в присутності поверхнево-активних речовин аніонного та нейоногенного типів. Визначено, що міцність коагуляційної структури змінюється в залежності від типу поверхнево-активних речовин.

Ключові слова: монтморилоніт, суспензія, ПАВ, адсорбція, просторова агрегація, мезопори.