### INFLUENCE OF SOME NON-IONIC SURFACTANTS AND FLOCCULANTS ON STABILITY OF DILUTED DISPERSIONS OF KAOLIN AND HYDRO-MICA

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**Abstract:** The influence of some non-ionic surfactants and flocculants on aggregation and sedimentation stability of diluted dispersions of the argillaceous minerals has been investigated. This influence can be caused by some changes in physicochemical nature of the particles surface because of the surface adsorption layer formation. The substances with a branched structure of the molecules can disaggregate the dispersed phase particles, which causes a rise in the sedimentation stability of suspensions. The substances with a linear structure of molecules promote aggregation of particles, which leads to the opposite effect on the sedimentation stability. The interaction between particles is also affected by their size distribution. The wider this distribution is, the weaker the interaction between particles is. This effect is mainly caused by a smaller number of big particles, which can be packed in a volume unit and by some hydrodynamic effects, which result in flowing of smaller particles around the bigger ones with flux of liquid. The interaction between bigger and smaller particles ensures the most effective separation of disperse phase. The results can be applied to the enhancement of technologies of natural and waste waters treatment and cleaning from clay-like particles or used in the mineral raw materials refining and concentration.

Key words: sedimentation stability of suspension, hydrodynamic effect, mineral raw material

## Introduction

Separation of finely dispersed argillaceous particles from other minerals is often required in the technology of raw materials concentration. Some organic compounds can promote more effective separation through better aggregation and faster sedimentation of particles. The highest efficiency of aggregation can be reached for the mixed interaction between bigger and smaller particles when a smaller particle can be drawn into the field of attraction of a bigger one and mutual effect its molecular. electrostatic of and structurizing forces ensures formation of a more compact and stable aggregate. General stability of such an aggregate is governed by the balance of these forces [1, 2]. The characteristics of such mixed

suspensions can be regulated by addition of some organic agents.

## Experimental

Our investigation dealt with the following objects:

1. Hydro-mica (mineral illite) with general composition  $K_{1-1,5}Al_4[Si_{6.5-7}Al_{1-4.5}O_{20}](OH)_4*nH_2O$ . This mineral can be classified as an argillaceous mica-like mineral with a layered structure and close to the hexagonal lattice. The layers are built from continuous tetrahedrons SiO<sub>4</sub>. The granulometric composition of this material is represented in Fig. 1, line 2.

2. Kaolin with general composition  $Al_2O_3*2SiO_2*2H_2O$ . This mineral forms well-shaped plate-like hexagonal

crystals with well distinguished facets. All angles between facets are  $120^{0}$  and thickness of plates ranged between 0.1-0.3  $\mu$ m. The granulometric composition of this material is represented in Fig. 1, line 1.

3. The selection of organic modifiers has been carried out with regard to their surface activity towards particles of the disperse phase, chemical inertness and non-toxicity. According to [4], the following substances were found to conform to the above conditions: Non-ionic surfactant PEG-115 purchased from the Ukrainian firm "TOS". Molecular weight of this agent ranged within 5000-5100 atomic mass units (a.m.u.) and its formula is HO-(CH<sub>2</sub>-CH<sub>2</sub> -O)<sub>n</sub> –H, where n = 115.



2 - Illite-clay mixture.

4. Non-ionic surfactant OS-20 produced by the Ukrainian firm "TOS" with molecular weight of 1100-1200 a.m.u. and formula  $C_nH_{2n}$ -(O-CH<sub>2</sub>-CH<sub>2</sub>)<sub>m</sub>-H, where n=18; m=20. This agent can form micella with Critical Concentration of Micella Forming (CCM) = 0.2 kg/m<sup>3</sup>.

5. Non-ionic surfactant Twin-80 with molecular weight about 1100 a.u.m. This agent can form micella with CCM = 0.06 kg/m<sup>3</sup> and can be characterised by this formula:



6. Polyethylene-oxide (PEO) produced by the Novosibirsk branch of the Kemerovo firm "Carbolite" (Russia). Molecular weight is about  $2*10^6 - 3*10^6$  a.u.m. and formula: HO-[-CH<sub>2</sub>-CH<sub>2</sub>-O-]<sub>n</sub>-H. 7. Polyacrylamide (PAA) produced by the Kalush firm "Oriana" (Ukraine). Molecular weight is about  $4*10^6 - 5*10^6$  a.u.m.

An effective coefficient of adhering  $(C_{ad})$  was calculated as a slope tangent for a dependence of changes in the fine fraction concentration on the rough fraction content [4, 5] and used as a stability criterion for the interparticle

interaction in diluted systems. The details of influence of organic modifiers on sedimentation stability of the suspensions have been evaluated using a coefficient of sedimentation instability ( $C_{si}$ ), which was calculated as a slope tangent for a dependence of the optical density changes during the experiment ( $D_0 - D_{end}$ ) on concentration of the disperse phase particles [6].

### **Results and discussion**

Our experimental results proved that the physico-chemical properties of disperse phase particles have a significant influence on the interparticle interaction in suspensions. This interaction in kaolin suspensions ( $C_{ad} = 6.3 \times 10^{-2}$ ) is more intense than in the suspensions with hydromica ( $C_{ad} = 5.3 \times 10^{-2}$ ). This difference is caused by different surface hydrophily properties of kaolin and hydro-mica. Surface layers of both minerals are well water-retentive because of high content of

the hydroxyl groups on surface. On the other hand, this content on the surface of kaolin is higher, which causes a higher water retention value of this mineral.

Interparticle interaction also depends on the particles size and value of  $C_{ad}$ decreases with increase of difference between particles sizes (see Fig. 2). This process can be caused by a smaller amount of bigger particles, which can be allocated in the volume unit and some hydrodynamic effects, which results in flowing of smaller particles around the bigger ones with a flux of liquid.



Figure 2. Dependence of the effective coefficient of adhering (C<sub>ad</sub>) of the small particles ( $r = 10 - 15 \ \mu m$ ) with the big ones for: 1 - kaolin suspension; 2 - illite suspension.

Non-ionic surfactants and flocculants actively participate in the structures forming processes. Stability of argillite suspensions can be influences by addition of these compounds.

A characteristic of surfactants' and flocculants' influence on kaolin and illite suspensions is quite similar (see Tables 1 and 2). Low concentrated solutions of polymers (PAA and PEO, concentration below 0.01 kg/m<sup>3</sup>) and surfactants (OS-20 and PEG-115, concentration below 0.025 kg/m<sup>3</sup>) with linear structure cause more intense particles aggregation in the suspensions of kaolin. Further increase in

the surface agents' concentration causes decrease in the value of Cad. Such behaviour can be related to the properties of adsorbed molecules. Bigger macromolecules of PEO and PAA have comparatively high adsorption activity and can form bridge bonds between the disperse phase particles, which results in a more active mutual flocculation (see Table 1, columns 4 and 5). Further increase in the polymers concentration causes formation of relatively stable spatial structures with and particles particles aggregates embedded into their nodes. This process provides stabilizing effect а on

suspensions. Moreover, macromolecules of PAA can effectively stabilize both suspensions of kaolin: with rough particles only or a mixture of rough and fine particles.

Table 1.

				and polymers for kaoli			
Number	Agent	Concen tration	C <sub>ad</sub>	C <sub>si</sub> (rough fraction)	C <sub>si</sub> (fine fraction)	C <sub>si</sub> (rough and fine fraction)	
	Twin-80	0	0.063	0.098	0.108	0.158	
		0.0125	0.018	0.081	0.107	0.09	
Ι		0.025	0.012	0.076	0.106	0.096	
		0.05	0.02	0.071	0.105	0.101	
		0.075	0.021	0.076	0.102	0.103	
		0.1	0.022	0.079	0.1	0.105	
		0.15	0.022	0.082	0.099	0.106	
		0.2	0.22	0.083	0.098	0.107	
	OS-20	0	0.63	0.98	0.108	0.158	
		0.0125	0.075	0.14	0.105	0.166	
II		0.025	0.53	0.166	0.103	0.175	
		0.05	0.05	0.136	0.101	0.125	
		0.075	0.048	0.124	0.1	0.105	
		0.1	0.47	0.115	0.1	0.091	
		0.15	0.46	0.094	0.099	0.083	
		0.2	0.44	0.081	0.099	0.078	
	PEG-115	0	0.063	0.098	0.108	0.158	
		0.0125	0.107	0.468	0.11	0.504	
III		0.025	0.127	0.368	0.115	0.383	
		0.05	0.076	0.322	0.092	0.33	
		0.075	0.054	0.216	0.091	0.2	
		0.1	0.04	0.135	0.091	0.116	
		0.15	0.306	0.135	0.09	0.114	
		0.2	0.035	0.134	0.089	0.113	
	PEO	0	0.063	0.098	0.108	0.158	
		0.005	0.079	0.555	0.099	0.63	
IV		0.01	0.091	0.12	0.098	0.179	
		0.025	0.117	0.115	0.096	0.158	
		0.05	0.139	0.11	0.094	0.156	
		0.075	0.119	0.1	0.094	0.155	
		0.1	0.092	0.098	0.093	0.154	
		0.15	0.087	0.097	0.093	0.146	
		0.2	0.85	0.096	0.092	0.14	
	PAA	0	0.063	0.098	0.108	0.158	
		0.005	0.094	0.27	0.089	0.285	
V		0.01	0.117	0.29	0.076	0.313	
		0.025	0.134	0.41	0.052	0.477	
		0.05	0.077	0.346	0.015	0.40/	
		0.075	0.073	0.282	0.005	0.34	
		0.1	0.07	0.225	0	0.274	
		0.15	0.063	0.11	0	0.132	
		0.2	0.06	0	0	0	

Dependence of C<sub>ad</sub> and C<sub>si</sub> on concentration of non-ionic surfactants and polymers for kaolin suspensions

Any concentration of polymer within the experimental range provides a stabilizing effect on fine particles suspensions because they can be easily captured and embedded into spatial structures. The low-molecular surface agents PEG-115 and OS-20 provide a similar but weaker effect on kaolin suspensions because of the lower molecular weight of agents and some micelle formation activity of OS-20 (see Table 1, columns 2 and 3).

	Table 2.
Dependence of C <sub>ad</sub> and C <sub>si</sub> on concentrat	ion of non-ionic surfactants
and pol	ymers for illite suspensions

	Conce		$C_{si}$	Csi	C <sub>si</sub> (rough	
Number	Agent	ntratio	Cad	(rough	(fine	and fine
	8	п	- uu	fraction)	fraction)	fraction)
	Twin-80	0	0.053	0.254	0.105	0.364
		0.0125	0.028	0.209	0.103	0.282
T		0.025	0.029	0.198	0.101	0.262
-		0.05	0.036	0.194	0.102	0.250
		0.075	0.037	0.196	0.098	0.249
		0.1	0.038	0.200	0.095	0.248
		0.15	0.039	0.198	0.096	0.242
		0.2	0.039	0.201	0.095	0.234
	OS-20	0	0.053	0.254	0.105	0.364
		0.0125	0.066	0.278	0.112	0.375
П		0.025	0.037	0.289	0.103	0.379
		0.05	0.034	0.216	0.104	0.392
		0.075	0.032	0.196	0.102	0.352
		0.1	0.031	0.192	0.098	0.286
		0.15	0.03	0.191	0.1	0.272
		0.2	0.029	0.19	0.1	0.253
	PEG-	0	0.053	0.254	0.105	0.364
	115	0.0125	0.081	0.33	0.115	0.43
Ш	_	0.025	0.105	0.279	0.109	0.41
		0.05	0.118	0.257	0.1	0.408
		0.075	0.09	0.254	0.098	0.4
		0.1	0.065	0.25	0.09	0.395
		0.15	0.059	0.249	0.088	0.392
		0.2	0.053	0.248	0.085	0.388
	PEO	0	0.053	0.254	0.105	0.364
		0.005	0.102	0.313	0.102	0.528
IV		0.01	0.116	0.293	0.098	0.525
		0.025	0.132	0.273	0.097	0.493
		0.05	0.084	0.223	0.097	0.46
		0.075	0.078	0.222	0.096	0.45
		0.1	0.073	0.222	0.096	0.438
		0.15	0.068	0.215	0.096	0.425
		0.2	0.064	0.2	0.096	0.41
	PAA	0	0.053	0.254	0.105	0.364
		0.005	0.092	0.348	0.082	0.475
V		0.01	0.111	0.318	0.064	0.503
		0.025	0.111	0.192	0.031	0.208
		0.05	0.082	0.121	0.011	0.46
		0.075	0.065	0.085	0.003	0.35
		0.1	0.059	0.048	0	0.31
		0.15	0.055	0	0	0
		0.2	0.052	0	0	0

Low molecular weight of the non-ionic agents ensures wider concentration range of their activity but lower effect on the

aggregation and sedimentation stability of suspensions. This behaviour can be related to lower adsorption activity of such molecules and inability to form bridge bonds between particles. However, all changes in the suspensions characteristics cannot be limited to the influence of surface modification only. Modifying agents also can change an associative molecular structure of the disperse medium, which results in an influence on the above mentioned characteristics.

For example, a negative effect of turbulent pulsations on interparticle interaction can be diminished by the horizontally oriented adsorbed molecules of PEG-115. That is why the maximal values of Cad for PEG-115 and polymer agents are quite similar. The mechanism of modification with PEG-115 is similar to that of modification with polymers however; shorter molecules of PEG-115 can not form a well developed and stable structure. This causes specific pattern of dependence Cad - agent concentration, which passes through a maximum (see Tables 1 and 2, column 3). dependencies of sedimentation The stability on concentrations of PEG-115 or polymers are similar for the systems of rough only or rough and fine particles. However, in the case of systems of fine particles only these dependencies are different. Low concentration of non-ionic surfactant PEG-115 causes aggregation of the disperse phase particles and decrease in sedimentation stability. The increase in surfactant concentration results in some stabilization of suspension. The molecules of PEG-115 promote the aggregation of particles but formation of a stable structure is impossible even for a suspension of comparatively small and light particles.

An influence of OS-20 on aggregation and sedimentation stability is similar to the influence of PEG-115. OS-20 makes a lesser influence on the changes of  $C_{ad}$  and  $C_{si}$  because the molecules of this agent are smaller and lighter than PEG-115. The aggregation effect of OS-20 is very weak and the bridge bonds can not be formed by the molecules of this agent. Its activity is

based on the surface modification only. The effect of OS-20 on sedimentation stability of the suspensions containing fine particles only causes insignificant stabilization effect because this agent is unable to ensure the particles' aggregation in diluted argillite suspensions.

The effect of Twin-80 is very different from the effect of the agents with linear molecules. This agent causes lowering in  $C_{ad}$  and increase in sedimentation stability due to the better dispersion of particles. One can see a well-marked minimum in the dependence of  $C_{ad}$  on C(Twin-80). The spatial structure of Twin-80 molecules is responsible for such a specific effect of this agent. Twin-80 acts as a dispersion promoter if its concentration is below CCM while this activity experiences some decrease for the concentrations over CCM (see Tables 1 and 2, column 1).

A character of all dependencies for the illite-containing systems is similar to the dependencies for the systems with kaolin (see Table 2) but with a range of effective concentrations of the modifier. This range for PEO and PAA with kaolin suspensions is much wider comparing with the illite ones. The different granulometric disperse phase composition of and different properties of the adsorbed polymer layer can be responsible for this discrepancy. PAA can form a welldeveloped and stable spatial structure, which ensures quick stabilization of the system against sedimentation.

Structure forming properties are less typical for PEO and its higher adsorption value causes aggregation of hydro-mica even at higher PEO concentration. This results in decrease in sedimentation stability of the hydro-mica suspension. Decrease in  $C_{ad}$  values can be caused by prevailing interaction between rough particles at higher concentration of PEO (Table 1 and 2).

Non-ionic surfactant PEG-115 shows higher activity in the suspensions of illite

and in wider range of concentrations. It can be assumed that a higher value of adsorption ensures formation of a more stable and developed spatial structure of PEG-115 molecules in the illite-clay suspensions. This process results in a higher  $C_{ad}$  and lower sedimentation stability of suspensions.

A range of OS-20 effective concentrations for the illite suspensions is similar to a range for the kaolin ones. Similar results have also been registered for Twin-80. Both agents act on the suspensions of illite and kaolin in a similar way (see Tables 1 and 2, columns 1 and 2).

## Conclusion

It was proved that the aggregation and sedimentation stability of argillite minerals suspensions can be changed by addition of some surfactants and flocculants.

Those agents with linear molecules can significantly decrease the stability of

diluted argillite systems. The agents with branched molecules ensure higher stability.

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