

# THE EFFECTS OF Na-SALICYLATE AND Na-FULVATE ON THE STABILITY AND RHEOLOGICAL PROPERTIES OF Na-MONTMORILLONITE SUSPENSIONS

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Na-salicylate and Na-fulvate in small quantities adsorb on the edges of Na-montmorillonite particles (adsorption capacities: 20 and  $14.5 \mu\text{eq g}^{-1}$ ).

The negative zeta potentials (determined by microelectrophoresis) and the critical coagulation concentrations increase with increase in the quantity of the organic anions. These anions interact with the octahedral aluminium ions on the edges of the montmorillonite particles, the charge of the edges thereby being reversed, and the negative charge of the particles increases. The experimental results are supported by calculations made according to the DLVO theory and Stern's theory.

In the presence of organic anions, the neutralization of the edge charge means that only face-to-face aggregation and no edge-to-face aggregation can be formed. These various structures are shown in scanning electronmicroscopic pictures.

The changes in the structure of the suspensions are proved by rheological measurements. As an effect of the small quantity of organic anions, the Bingham yield stress of the suspensions decreases significantly.

## *Introduction*

The peptizing effects of various anions, mainly phosphate, polymetaphosphate and carbonate, which influence the stability and rheological properties of clay mineral suspensions, have been examined mainly from a practical point of view. Relatively few systematic studies have been carried out on the effects of organic anions, although many polyanions of natural origin are used to increase the suspension stability and to modify the flow properties.

The questions arise as to whether organic anions are bound to certain surface parts of clay mineral particles in a similar way to inorganic anions and have a similar effect as a result of this, and whether a more negative charge, *i.e.* the complete dissociation of more functional groups of the molecule, is needed for the above effects to occur.

There are extreme opinions in the technical literature about the interactions between clay minerals, mainly montmorillonite, and organic acids and their salts. Certain authors [1, 2] question the occurrence of adsorption altogether or regard it as very slight, while others [3, 4], who have examined mainly humic substances of natural origin, describe significant adsorption. The problem is that, as a result of isomorphous substitution in their crystal lattice, the clay mineral particles have a negative charge and thus repel organic anions.

However, interaction may occur in the case of a highly retarded dissociation state (e.g. in the case of a weak acid at low pH) [3]. Further, if the lattice charge is compensated by multivalent cations, then interaction may also occur through these [4] and with the broken bonds on the edges of the particles, which (depending on the circumstances) can be in a given hydrated and charged state [5, 6, 14].

Depending mainly on the pH, but to a smaller extent on the electrolytes [7], phosphate anions bind to the aluminium ions on the edges of clay particles [6, 7]. They reverse the positive charge of the edges and may increase their negative charge, thereby impeding the formation of edge-to-face aggregation [8]. In the presence of multivalent anions (e.g. diphosphate anions), the stability of clay suspensions increases considerably, since only a face-to-face aggregated structure can be formed and this needs a considerably greater quantity of coagulating electrolytes [8].

The flow improving effects of various supplementary anionic materials on ceramic meshes were examined by WEIAND [9] from a practical aspect.

The present paper considers the interactions between Na-montmorillonite and the Na-salts of salicylic acid (as a simple aromatic oxycarboxylic acid) and synthetic fulvic acid (as a model of natural humic substances), as well as their effects on the stability and rheological properties of a Na-montmorillonite suspension.

#### *Experimental materials and methods*

Montmorillonite was obtained from Kuzmice bentonite by fractionation following  $\text{Na}_2\text{CO}_3$  peptization. From this, H-montmorillonite was produced with the Barshad method [10], and the monocationic Na-montmorillonite was made by neutralization with an equivalent quantity of NaOH. Particle size:  $d \leq 1 \mu\text{m}$ , cation exchange capacity:  $800 \mu\text{eq g}^{-1}$ .

For the experiments Na-salicylate of analytical purity was used. The fulvic acid was made from gallic acid in the presence of Ca-montmorillonite as heterogeneous catalyst [11]. The number-average molar mass of the product was 840, calculated by means of vapour pressure osmometry with the pH correction method of HANSEN and SCHNITZER [12]. The total acidity of the fulvic acid was  $10.1 \text{ meq g}^{-1}$ ; this is the quantity of negatively charged functional groups in the material. From these data it can be seen that an average of 8.5 acidically dissociating functional groups are to be found on the molecules of fulvic acid.

Adsorption isotherms were determined under the following conditions:

Na-montmorillonite concentration:  $5 \text{ g dm}^{-3}$

Adsorption time: 2 days at room temperature

Initial concentration of adsorptives:  $0.1\text{--}1.0 \text{ meq dm}^{-3}$ .

So that the results could be compared, we calculated in terms of concentration units (given in equivalents) referred to negative charges, and not in terms of molar concentrations. The two different concentration units are the same for Na-salicylate since the dissociation of Na-salicylate gives one negative charge per molecule if the pH of the medium is not too high (dissociation constants of salicylic acid:  $K_1 = 1.06 \cdot 10^{-3}$ ,  $K_2 = 3.6 \cdot 10^{-14}$ ).

The equilibrium concentrations were determined spectrophotometrically following sedimentation of the montmorillonite particles in a preparative ultracentrifuge

(20 000 RPM, 30 minutes). The Fe(III) salicylate complex was measured at 525 nm, and Na-fulvate at 450 nm.

The zeta potentials of  $1 \text{ g dm}^{-3}$  Na-montmorillonite suspensions containing Na-salicylate or Na-fulvate in increasing quantities were measured with a Japanese-made Laser Zee Meter microelectrophoresis apparatus. In parallel with this, the critical coagulating concentrations (*c.c.c.*) of suspensions of the same type were determined by observing coagulation series with increasing NaCl concentrations. The results were measured on materials after a 96-hour standing. This differs from the customary 24 hours in the literature [6, 8]. The reason is that after a 24-hour standing the examined structures were not close to the equilibrium state, whereas after 96 hours the observations did not change quantitatively compared to those throughout the total observation period of 240 hours.

The edge-to-face or face-to-face aggregated structures formed by coagulation of the suspensions were examined with a scanning electron microscope (JEOL, Japan). The samples were made from  $5 \text{ g dm}^{-3}$  Na-montmorillonite suspensions which contained 0 or  $1 \text{ meq dm}^{-3}$  Na-salicylate or Na-fulvate, as well as  $200 \text{ mmol dm}^{-3}$  NaCl, with the freeze-drying technique proposed by O'BRIEN ET AL. [13]. The suspension-film on the disc was dipped into isopentane cooled with liquid-air to approx.  $-140^\circ\text{C}$ , and the water was then sublimed in a freeze-drying instrument. With this method the suspension structure can be preserved even in the solid state.

Rheological examinations were carried out with a Rheotest-2 (GDR) rotational viscometer. To  $7.4 \text{ g}/100 \text{ g}$  Na-montmorillonite suspensions, 0, 16, 33 or  $66 \mu\text{g g}^{-1}$  Na-salicylate or Na-fulvate was added. The flow curves were measured after a 2-day standing.

### Results and discussion

The adsorption isotherms in Fig. 1 show the quantitative relationships of the interactions of Na-salicylate and Na-fulvate with Na-montmorillonite. Figure 1 also gives the equilibrium pH values, which do not display a monotonous change with increasing concentration of the adsorptives; they are about  $\text{pH}=7$ . In the case of Na-salicylate the isotherms is of regular Langmuir-type, while it is a little different for Na-fulvate. The linear regression data and the adsorption capacity values calculated from the linearized form of the Langmuir isotherms equation are listed in Table I.

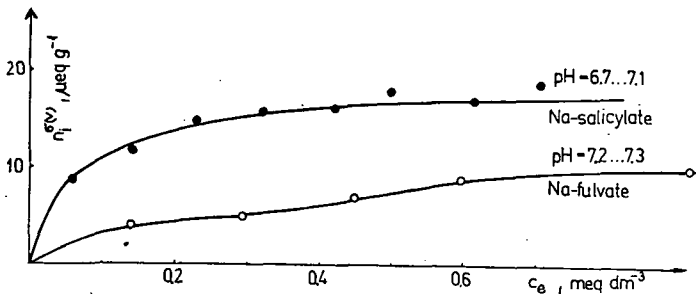


Fig. 1. Isotherms for the adsorption of Na-salicylate and Na-fulvate by Na-montmorillonite at room temperature

Table I

Adsorption system	Equilibrium pH	Adsorption capacity $\mu\text{eq g}^{-1}$	Linear regression
Na-montmorillonite + Na-salicylate	6.7—7.1	20.0	0.989
Na-montmorillonite + Na-fulvate	7.2—7.3	14.5	0.951

The degree of adsorption is small; it is only a few per cent of the quantity of adsorbed organic cations. GREENLAND and MOTT [14] describe the amounts of positive and negative charge on various clay minerals and oxides in their review. In the case of montmorillonite prepared from Wyoming bentonite, the quantity of negative charge was  $980 \mu\text{eq g}^{-1}$ . The pH-dependent positive charge at  $\text{pH}=7$  was  $2 \mu\text{eq g}^{-1}$ , and at  $\text{pH}=3$  was  $12.5 \mu\text{eq g}^{-1}$ . These data suggest that the very low adsorption capacities we calculated are realistic. We made calculations of whether, on purely quantitative considerations, bonds on the edges are possible. The approximate quantity of octahedral Al ions on the edges of 500—100 nm montmorillonite particles is  $3.12\text{--}31.3 \mu\text{mol g}^{-1}$ . The magnitude of the calculated adsorption capacity (see Table I) is the same. Thus, the salicylate anions are most likely to be bound to the Al ions on the edges (as we described in detail in our previous study [15]), probably by complex bonds. Since fulvic acid is a polycondensed aromatic oxycarboxylic acid, fulvate is bound to the surface in a similar way to salicylate.

We confirmed the bonding of salicylate and fulvate anions on the edges of montmorillonite particles by various examinations and calculations. Depending on their nature and quantity, the adsorbed anions change the stability of the montmorillonite suspension. In connection with this, the change in the structure of the electric double layer can be followed macroscopically by measurement of the zeta potential.

The measured zeta potentials are presented in Fig. 2 as functions of the concentration of salicylate and fulvate. It can be seen that both anions increase the negative zeta potential to a small extent (about 1.15—1.20 of the original). In our estimations the effect of Na-fulvate is higher. Because of the several (8.5) negatively charged functional groups, only a few can bind by adsorption (steric block); the others increase the negative charge of the particle. In the case of salicylate, even if only the coverage of the positive

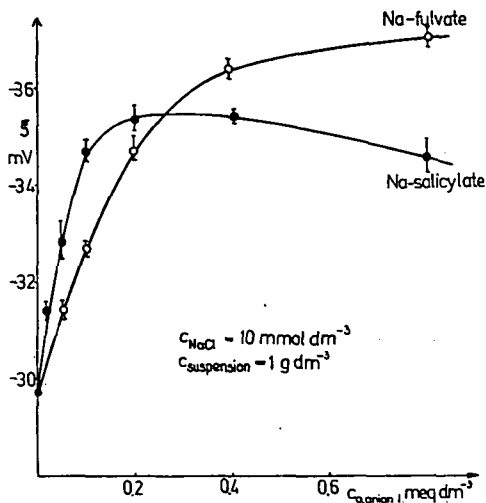


Fig. 2. The zeta potential of montmorillonite suspensions as a function of Na-salicylate and Na-fulvate concentration

charge of the edges is assumed, the small increase in the gross charge of the particle, and macroscopically the increase in the zeta potential, become understandable. If the negative surface or Stern potentials are calculated from the original surface charge density of the montmorillonite and from the increased charge density, taking into consideration the adsorption data, the difference will be similar to the experimental zeta potential increase. In the case of Na-hexadecyl-sulphate kaolin systems, similar results (the increase of the electrophoretic mobility of the particles) were reported by FLEGMANN and OTTEWILL [16].

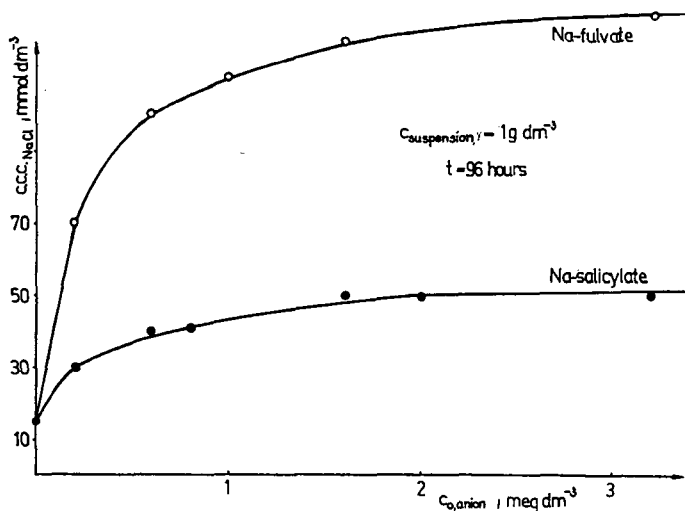


Fig. 3. The critical coagulation concentration of montmorillonite suspensions as a function of Na-salicylate and Na-fulvate concentration

The *c.c.c.* values (see Fig. 3) show the increased stability of montmorillonite suspensions following treatment with salicylate and fulvate. The stabilizing effect of salicylate was much smaller than that of fulvate. This contradicts VAN OLPHEN'S [6] results. Van Olphen considers that there must be at least 3 phenolic hydroxyl groups in the aromatic molecule for it to have a stabilizing effect. FREY and LAGALY [8] determined a *c.c.c.* of 200 mmol dm<sup>-3</sup> for montmorillonite suspensions stabilized by diphosphate. This value is roughly 1.5 times the *c.c.c.* of a suspension stabilized by Na-fulvate.

Taking into consideration the results of adsorption measurements on the basis of the zeta potential and the coagulation data, the stabilizing effects of Na-salicylate and Na-fulvate can be explained analogously to that of multivalent phosphate anions [8].

The organic anions bound on the edges of the particles modify their charge. The Stern potential of montmorillonite ( $\psi_{sl}^*$ ), which is characteristic of a double layer of the platelets, was calculated at various electrolyte concentrations on the basis of the Stern model by means of the following equations referring to a flat double layer [6]. The surface charge density ( $\sigma$ ) is the sum of the charge densities of the Stern layer

$(\sigma_1)$  and the diffuse layer  $(\sigma_2)$ :

$$\sigma = \sigma_1 + \sigma_2$$

$$\sigma = (\varepsilon'/4\pi\delta_{St})(\psi_0 - \psi_{St})$$

where  $\delta_{St} = 5 \text{ \AA}$  (the thickness of the Stern layer)

$\varepsilon'$  = dielectric constant of the medium in the field of the molecular condenser

$\psi_0$  = surface potential

$\psi_{St}$  = Stern potential

$$\sigma_1 = \frac{N_1 ve}{1 + (N_A/Mn) \exp(-(ve\psi_{St} + \varphi)/kT)}$$

where

$N_1 = 10^{15}/\text{cm}^2$ , the number of adsorption sites on  $1 \text{ cm}^2$  of the wall,

$\varphi$  = specific adsorption potential of the counter-ions (with our calculations  $\varphi=0$ )

$e$  = elementary charge ( $e=4.77 \cdot 10^{-10}$  esu)

$v$  = valency of the ion

$N_A$  = Avogadro number

$M$  = molecular weight of the solvent

$$\sigma_2 = (2\varepsilon nkT/\pi)^{1/2} \sinh(ve\psi_{St}/2kT)$$

where

$\varepsilon$  = dielectric constant of the medium

$k$  = Boltzmann constant

$T$  = temperature

$n$  = ion concentration in number of ions/ $\text{cm}^3$

The average surface charge density of montmorillonite was calculated from the cation exchange capacity (*c.e.c.* =  $800 \mu\text{eq g}^{-1}$ ) and the dimensions of the unit cell (surface:  $F=46.5 \cdot 10^{-16} \text{ cm}^2$ , relative weight:  $M=720$ ):

$$\bar{\sigma} = Mc.e.c.10^{-6} e/2F = 2,954 \cdot 10^4 \text{ esu/cm}^2$$

The condition of coagulation at the *c.e.c.* is the equality of the differential quotients of the attractive and repulsive potentials with respect to distance [17]:

$$\frac{dV_R}{dd} = \frac{d(-V_A)}{dd} \quad \text{and} \quad V_R = -V_A$$

where

$$V_R = \frac{64nkT}{\kappa} \gamma^2 e^{-2\kappa d}$$

$$V_A = -\frac{\delta^2 A}{32\pi d^4} \quad (\text{in the case of plates } \delta \text{ thick})$$

where

$\delta=6.6 \text{ \AA}$  (the thickness of montmorillonite plates) in the case of  $\kappa d=2$  condition it can be deduced [18].

$$c.e.c. = 4.1 \cdot 10^{-6} \frac{\gamma^{4/3}}{A^{2/3} \sqrt{10/3}} \quad (\text{mmol dm}^{-3})$$

$A$  = Hamaker constant ( $10^{-12}$  or  $2 \cdot 10^{-12}$  erg)

$$\gamma = \frac{\exp(z/2) - 1}{\exp(z/2) + 1} \quad \text{and} \quad z = \frac{ve\psi_{St}}{kT}$$

The Stern potential ( $\psi_{St}^{**}$ ) which can be calculated from the experimental *c.c.c.* data using the above equations shows the realistic behaviour of the systems. The *c.c.c.* values determined at  $3.2 \text{ meq dm}^{-3}$  anion concentrations, the Stern potentials ( $\psi_{St}^{**}$ ) calculated from the *c.c.c.* values, and the potentials ( $\psi_{St}^*$ ) calculated on the basis of Stern's theory at the same electrolyte concentrations, are given in Table II.

Table II

System	c.c.c. mmol dm <sup>-3</sup>	$\psi_{St}^*$ mV	$\psi_{St}^{**}$ , mV	
			$A = 10^{-12}$ erg	$A = 2 \cdot 10^{-12}$ erg
Na-montmorillonite	15	-109	-8.4	-11.9
Na-montmorillonite + Na-salicylate	50	-80.3	-20.9	-30.1
Na-montmorillonite + Na-fulvate	130	-56.5	-45.1	-68.9

A comparison of the data in Table II; clearly reveals the differences. The montmorillonite particles can be aggregated by edge-to-face (low *c.c.c.*) and face-to-face (high *c.c.c.*) interactions [8, 18], depending on the electrolyte concentration and the charge of the edges. In the case of montmorillonite, from the high Stern potential ( $\psi_{St}^* = 109 \text{ mV}$ ) characteristic of a double layer of the plates a significantly greater stability could be expected. The difference in magnitude of  $\psi_{St}^*$  and  $\psi_{St}^{**}$  (the latter can be calculated from the *c.c.c.*) is a contradiction which can only be solved by assuming formation of the edge-to-face heterocoagulation structure. Edge-to-face aggregation is blocked in the presence of materials which adsorb on the edges and recharge them [6, 8]. It can be supposed that in the case of salicylate this occurs partially, but with fulvate the edges become negative and hydrated completely due to the non-bound, ionized and therefore negatively charged functional groups. Thus, in the presence of fulvate, only a face-to-face aggre-

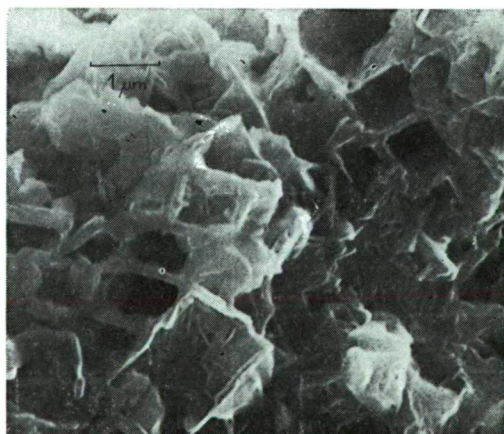


Fig. 4. Scanning electronmicrograph of house-of-cards structure in montmorillonite suspension (uncompressed, freeze-dried sample of montmorillonite suspension coagulated with  $200 \text{ mmol dm}^{-3}$  NaCl)



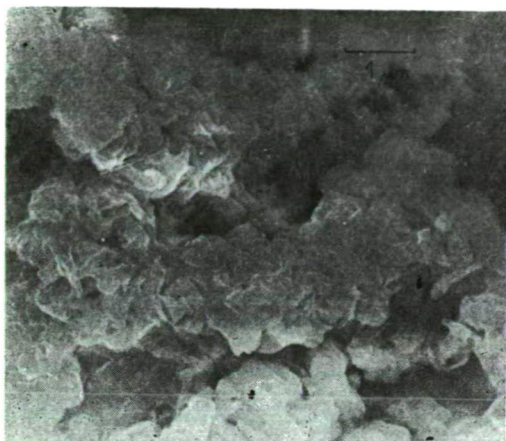


Fig. 5. Scanning electronmicrograph of montmorillonite suspension in the presence of Na-salicylate (uncompressed, freeze-dried sample of montmorillonite suspension containing  $1 \text{ meq dm}^{-3}$  Na-salicylate, coagulated with  $200 \text{ mmol dm}^{-3}$  NaCl)

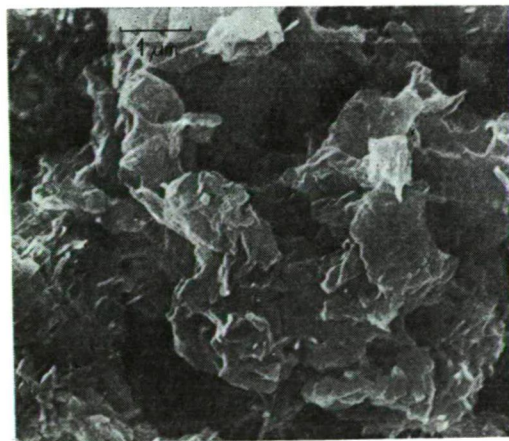


Fig. 6. Scanning electronmicrograph of montmorillonite suspension in the presence of Na-fulvate (uncompressed, freeze-dried sample of montmorillonite suspension containing  $1 \text{ meq dm}^{-3}$  Na-fulvate, coagulated with  $200 \text{ mmol dm}^{-3}$  NaCl)

gated structure can be formed and therefore the  $\psi_{st}^*$  value characterizing the double layer of the plates is quite near the  $\psi_{st}^{**}$  values characterizing the real stability of the system. Similar results were given in the case of Na-gallate and Na-humate in earlier examinations [19].

Marked evidence for the formation of structures aggregated in different ways is provided by the electronmicroscopic photographs shown in Figures 4–6. The house-of-cards structure formed by an edge-to-face connection can be seen very well in the sample which does not contain any organic material. On the other hand, the picture of the sample containing salicylate and fulvate is rather indistinctive and furry; one can only guess that the plates have slid on top of each other.

We examined the effects of Na-salicylate and Na-fulvate on the rheological properties of a montmorillonite suspension. The flow curves of suspensions containing different specific quantities of organic anions are shown in Figures 7–8.

The shearing stress ( $\tau$ ) plotted as a function of the rate of shear ( $D$ ) is the highest for suspensions which do not contain organic anions. At higher velocity gradients ( $D$ ) the flow curves become linear and run almost parallel with each other. By extrapolation of these straight lines the Bingham yield stress ( $\tau_B$ ) can be obtained.  $\tau_B$  is shown in the  $a$ – $\tau$  plane of spatial Figures 7 and 8 as a function of the specific amount of organic material ( $a$ ,  $\mu\text{eq g}^{-1}$ ). It can be seen that with increasing amount

of organic material  $\tau_B$  first decreases significantly, then reaches a minimum and subsequently increases slightly. The yield-stress minima exhibited quite good agreement with the adsorption capacities (for Na-salicylate: approx.  $20 \mu\text{eq g}^{-1}$ ; for Na-fulvate: lower than  $20 \mu\text{eq g}^{-1}$ ). These materials also cause a reduction of the



Bingham yield stress, similarly to inorganic and some natural organic compounds used in the ceramics industry [9]. This effect is a result of the bonding of the anions on the edges. The completely negatively charged particles repel each other,

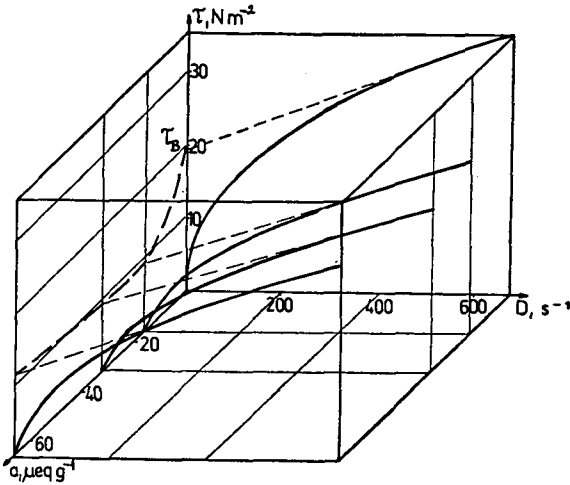


Fig. 7. Flow curves of Na-montmorillonite suspensions with different Na-salicylate contents, and the Bingham yield stress as a function of the specific amount of added Na-salicylate

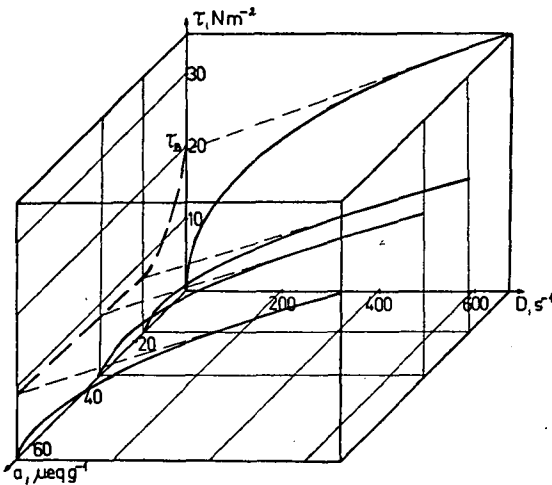


Fig. 8. Flow curves of Na-montmorillonite suspensions with different Na-fulvate contents, and the Bingham yield stress as a function of the specific amount of added Na-fulvate

and therefore an edge-to-face house-of-cards structure cannot be formed; thus, a smaller shearing force is enough to form independent flow units.

To summarize, it can be stated that a uniform interpretation of results obtained from different experimental methods is possible if adsorption on the edges is assumed, similarly as for inorganic anions.

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## ВЛИЯНИЕ САЛИЦИЛАТА И ФУЛЬВАТА НАТРИЯ НА СТАБИЛЬНОСТЬ И РЕОЛОГИЧЕСКИЕ СВОЙСТВА НАТРИЕВОГО МОНТМОРИЛЛОНИТА

Э. Томбац, М. Гильде и Ф. Санто

Значения зета потенциалов и критических концентраций коагуляции возрастают с увеличением адсорбированного количества названных соединений. Экспериментальные данные подтверждены расчетами произведенными на основании модели Штерна и теории ДЛВО. Представлены скэнинг электронно-микроскопические снимки полученных образцов. Реологические свойства суспензий подтверждают предполагаемые структурные изменения в суспензиях.