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The rheological and colloidal properties of bentonite dispersions in the presence of organic compounds
III. The effect of alcohols on the coagulation of sodium montmorillonite

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Abstract: The critical coagulation concentration, c_K, of sodium chloride for sodium montmorillonite dispersed in water (solid content 0.025 percent) is 8 mmol/L. It remains virtually constant (7.5–8.5 mmol/L) in water-rich alcohol mixtures (below 50% (v/v) methanol and 40% ethanol and propanol). At higher alcohol contents the c_K decreases to 3.6 mmol/L (70 percent methanol), 1.2 mmol/L (70 percent ethanol), and 0.8 mmol/L (60 percent propanol). In the presence of 10^{-4} M sodium diphosphate the c_K in water rises to 195 mmol/L. In contrast to the behavior in the absence of diphosphate, even small amounts of alcohol reduce the critical coagulation concentration. In 70% methanol the c_K is 7.5 mmol/L, in 70 percent ethanol 2.5 mmol/L and in 60% propanol 5 mmol/L. The main mechanism is coagulation by contacts between negatively charged edges and faces.

At high alcohol contents montmorillonite-alcohol complexes (interlayer solvates) are formed and the colloidal dispersions become unstable even in the absence of salt. Transition from the state with diffuse ionic layers into the quasi-crystalline structure of the interlayer solvates is also evident from the sediment volume which changes with the alcohol content. Maxima are observed which are indicative of band-type structures as intermediate states between the colloidally dispersed particles with repulsive interaction and the discrete particles of the montmorillonite-alcohol complexes.

Key words: Alcohols – card-house – clay minerals – coagulation – edge/face aggregation – face/face aggregation – montmorillonite – salt stability – sedimentation

Introduction

Alcohol addition strongly influences the flow behavior of aqueous dispersions of sodium montmorillonite or sodium calcium bentonites. In the absence of salts, alcohol addition decreases the yield value and the apparent viscosity [1]. When sodium chloride is added (10^{-3}–10^{-1} mol/L) the flow parameters increase to a maximum at intermediate volume fractions of methanol, ethanol, and *n*-propanol. The alcohols influence the particle–particle*) interaction. They promote formation of network structures which stiffen the dispersion at certain alcohol and salt concentrations. The dominant type of interaction is face-to-face aggregation [2–7].

Coagulation of diluted sodium montmorillonite dispersions is often considered to occur by edge (+)/face (−) interactions (cf. [8–14]) because the critical coagulation concentrations are very low in spite of the high negative surface charge density. The critical concentration of sodium chloride required to destabilize sodium smectite dispersions ranges from 3 to 15 mmol/L

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*) The particles in diluted dispersions of sodium montmorillonite are single silicate layers (about 10 Å thick) or thin lamellae of a few such layers.

at pH 5–7.5 and increases to about 50 mmol/L at pH 9–10 (Table 1). The cause of this increase is seen in recharging of the edges so that higher salt concentrations are required for formation of edge (−)/face (−) contacts. In photon correlation spectroscopic experiments Novich and Ring [15] found an extremely high coagulation concentration of KCl for potassium montmorillonite ($c_K =$ 0.29 mol/L; 0.01 percent (w/w) dispersion, pH = 10).

In the case of heterocoagulation the electrostatic interaction energy becomes less negative when the dielectric constant is reduced (for instance, see [16–18)]. Thus, alcohol addition reduces the energy of edge (+)/face (−) contacts and may slightly increase the critical salt concentration. On the other hand, the electrostatic repulsion between likely charged particles is reduced which destabilizes the colloidal dispersion and decreases the critical salt concentration.

Table 1. Critical coagulation concentration, c_K, of sodium chloride for sodium montmorillonite dispersions

Smectite	c_K mmol/L	Conditions of coagulation[1])	Ref.
Montmorillonites			
Wyoming	3.5	0.025–0.8%	[45]
Upton, Wyoming		0.025%, pH = 6–7	[10]
	13	< 0.1 μm	
	10–15	0.1–2 μm	
Upton, Wyoming		< 2 μm, 0.1%	[5]
	10; 13	pH = 5; 7.5	
	31; 44	pH = 8.5; 9.8	
Crook County,		< 0.2 μm, 0.1%	[14]
Wyoming	10–33	pH = 6.3–9	
Ottay, Calif.		< 0.2 μm, 0.1%	[14]
	7–13	pH = 6–9.3	
Chambers, Arizona	1–10	0.025%, pH = 4–10	[46]
Cheto, Arizona		< 2 μm, 0.07%	[47]
	15; 24	pH = 6.4; 6.7	
	29; 32	pH = 8; 9	
Cyprous	8–12	0.1–2 μm, 0.025%	[10]
		pH = 6–7	
Cerro Bandera	8	0.09%, pH = 7.4	[48]
Putnam clay	14.8	0.15%	[49]
(origin unknown)	12–16	0.25%	[8]
Beidellite			
Unterrupsroth		0.025%, pH = 6–7	[10]
	7	< 0.1 μm	
	5–7	0.1–2 μm	
Silver City,		< 0.2 μm, 0.1%	[14]
Idaho	4–5	pH = 6.1–7.2	
	28–52	pH = 8.3–9.3	
Laponite	10	2%, pH = 8.5	[50]
	2–20	0.2%, pH = 7–12	[51]

[1]) Given are solid content, particle size fraction and pH at the coagulation point.

Materials and methods

Sodium montmorillonite was separated from Wyoming bentonite ("Greenbond") as the fraction < 2 μm. The bentonite was purifed by removing iron oxides with sodium dithionate in citrate containing solution and oxidation of organic materials with hydrogen peroxide (for details see [19–21]).

The critical coagulation concentration of sodium chloride, c_K, was measured for dispersions of sodium montmorillonite in water, methanol, ethanol, n-propanol and water-alcohol mixtures with volume fractions of 10, 20 .... 70% alcohol. It was determined by coagulation series in test tubes (cf. [9]) and turbidity measurements ($\log dt/dD$ vs $\log c$) [22]. The reported c_K values are from the test tube experiments, which are better reproducible than the photometric measurements. To avoid geometrical constraint, the solid mass content of the dispersions was 0.025% (w/w). The pH of the dispersions during the coagulation experiments was 6.5.

The sediment volume of dispersions of 2% sodium bentonite in water-alcohol mixtures was measured in closed cylindrical tubes (diameter 1.1 cm, length 10 cm) which were allowed to stand at room temperature up to 15 months. Care was taken to not disturb the sedimentation process. The sedimentation is expressed as the ratio of the height h of the sediment to the total height h_0 of the dispersion in the tube. The values are reported for sedimentation periods of 24 h and 15 months.

Results

The critical coagulation concentration of NaCl for the sodium montmorillonite dispersion in water is 8 mmol/L at pH ≈ 6.5 (Fig. 1a, Table 2). This value remains constant up to 30% alcohol and then decreases, more strongly for propanol than for methanol. Dispersions containing more than 70% (v/v) methanol (ethanol) or 60% (v/v) propanol are unstable, even in the absence of sodium chloride.

Addition of 10^{-4} mol/L sodium diphosphate increases the c_K of the aqueous dispersion from

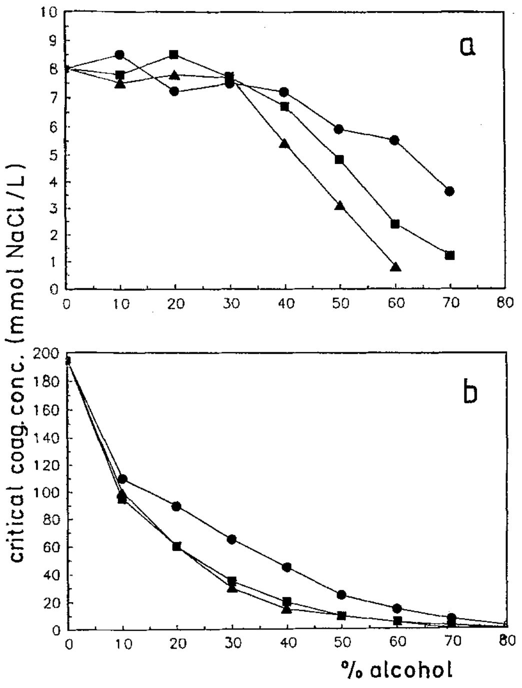

Fig. 1. The critical coagulation concentration of sodium chloride for dispersions of sodium montmorillonite (Wyoming, $< 2\ \mu m$ fraction, 0.025% w/w) in water-alcohol (pH ≈ 6.5) without (a) and in the presence of 10^{-4} mol/L sodium diphosphate. (b) Alcohol concentration in % (v/v). ● methanol, ■ ethanol, ▲ *n*-propanol

8 to 195 mmol/L NaCl (Fig. 1b, Table 2). The critical coagulation concentration decreases rapidly with increasing alcohol content. Slightly higher salt concentrations are required to coagulate the water-methanol dispersions than the water-ethanol and water-propanol dispersions. Striking is the form of the curves in Figs. 1a and b. At low alcohol concentrations, c_K remains constant with increasing alcohol content when phosphate is absent, but decreases strongly after diphosphate addition. Evidently, this behavior reveals two different coagulation mechanisms.

Highly dispersed sodium montmorillonite particles in water at pH ≈ 6.5 do not settle within 24 h. However, a voluminous sediment forms at alcohol concentrations above 70% methanol or ethanol and 60% propanol. The sediment becomes denser with increasing alcohol concentration (Fig. 2).

Table 2. Critical coagulation concentration, c_K, of sodium chloride for sodium montmorillonite dispersions in water-alcohol (0.025 percent (w/w), pH ≈ 6.5) at 20 °C

Alcohol conc. Percent (v/v)	mol/L	Dielectric constant	c_K mmol/L	c_K[1])
Methanol				
0	0	80.37	8.0	195
10	2.48	76.91	8.5	110
20	4.96	72.68	7.2	90
30	7.44	68.33	7.5	65
40	9.92	63.82	7.5	45
50	12.40	59.24	5.9	25
60	14.88	54.32	5.5	15
70	17.36	49.03	3.6	7.5
Ethanol				
0	0	80.37	8.0	195
10	1.71	75.72	7.8	95
20	3.42	70.74	8.5	60
30	5.13	65.46	7.7	35
40	6.84	59.24	6.7	20
50	8.55	53.90	4.8	10
60	10.26	47.96	2.4	5
70	11.97	42.00	1.2	2.5
Propanol				
0	0	80.37	8.0	195
10	1.34	74.75	7.2	100
20	2.68	68.80	7.8	60
30	4.02	62.40	7.7	30
40	5.36	55.50	5.4	15
50	6.70	48.26	3.1	10
60	8.04	41.09	0.8	5

[1]) c_K in the presence of 10^{-4} mol/L sodium diphosphate

Within 15 months a dense sediment accumulates at the bottom of the tube at $\leq 70\%$ methanol ($\leq 50\%$ ethanol, $\leq 40\%$ propanol). (The sedimentation time in water for particles with 0.1 μm Stokes equivalent diameter and a sedimentation height of 5 cm is about 2 months, neglecting the influence of the Brownian motion). At higher alcohol concentrations the sediments are again voluminous. The sediment height in water-methanol is distinctly smaller than after 24 h, but approximates the 24 h values in water-ethanol and water-propanol. The sediment formed at 60–80% ethanol is clearly separated from the supernatant. Szántó and Várkonyi [23], studying dispersions of 1 g sodium montmorillonite in 10 ml water-alcohol mixtures, observed decreasing sediment volumes from 10 to 100% alcohol.

Discussion

Coagulation of sodium montmorillonite dispersions by edge (+)/face (−) contacts provides

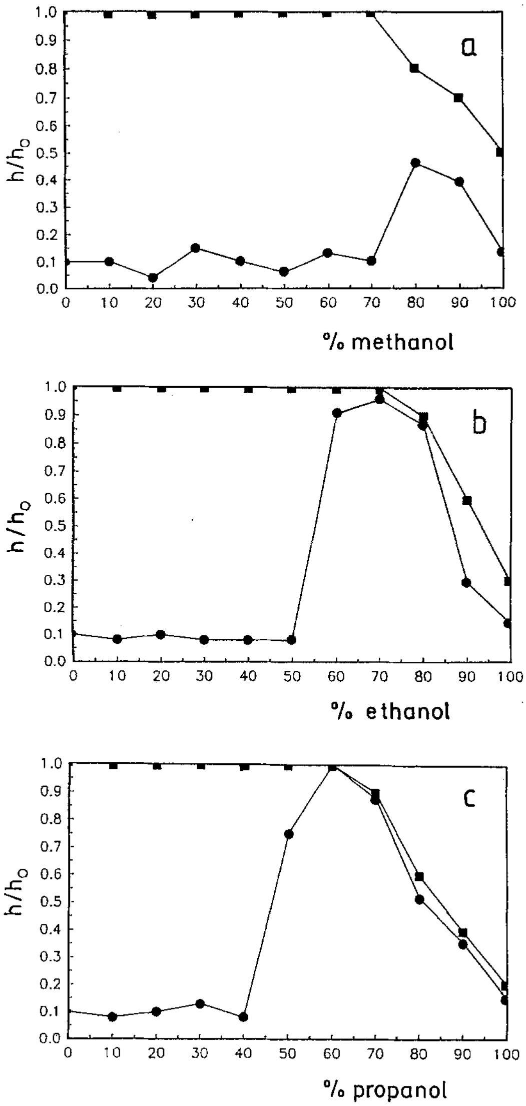

Fig. 2. Sedimentation of sodium montmorillonite dispersions in water-alcohol. Mass content 2% (w/w). The ratio h/h_0 is the relative height of the sediment after 24 h (■) and 15 months (●); $h/h_0 = 1$ signifies colloidal distribution (no sedimentation). Alcohol concentration in % (v/v). (a) methanol, (b) ethanol, (c) *n*-propanol

a very simple explanation of the low critical coagulation concentration. However, it is questionable if positive edge charges exist on montmorillonite particles at pH ≈ 6.5. The interlamellar cation exchange capacity measurable with the alkylammonium method is distinctly lower than the total exchange capacity. It must be assumed that a considerable part of the exchangeable cations (up to 20 percent) reside at the edges [24, 25]. This implies that the edges are negatively charged at pH$\gtrsim$6. Anderson and Sposito [26] measured the accessible edge charges by exchange reactions with cesium and lithium ions. About 14% of the total exchange sites were found to be related to the variable surface charges. Peigneur et al. [27], measuring the cation exchange capacity of several montmorillonites with the isotopic dilution method, found that the capacity increases by 9–15% between pH ≈ 4 to pH ≈ 6. At pH = 4, the equivalent fraction of hydrogen ions on the planar surfaces of the crystals is about 1% at most. Thus, the difference is considered to be the contribution of the edge charge density at pH = 6. In fact, the difference is higher for montmorillonites with smaller particle sizes than for coarser samples. The highest difference (15%) is observed for montmorillonite from Wyoming.

An important effect was noted by Secor and Radke [28]. For clay mineral particles whose edge thickness is small relative to the Debye–Hückel length, the negative double layer extending from the basal plane surfaces spill over into the edge region. Even for an edge charge density of $+10\,\mu\mathrm{Ccm}^{-2}$ and a face charge density of $-10\,\mu\mathrm{Ccm}^{-2}$ the influence of the face charge is still significant at salt concentrations below 10^{-3} N.

The rheological behavior of sodium montmorillonite dispersions between pH 4 and 7 is a further indication of the disappearance of positive edge charges. In acidic medium card-house networks with edge (+)/face (−) contacts form and cause high yield values and shear stresses (at a given shear rate). The sharp decrease of the flow parameters (apparent and plastic viscosity[1]), yield value, elastic modules) with increasing pH to a minimum [3, 4, 6, 29] reveals loosening of the edge/face contacts and break-down of the card-house structure. The Newtonian (or almost Newtonian) flow of the dispersions at moderate salt concentrations [1, 6] also indicates the absence of edge (+)/face (−) contacts.

When the edge charges are negative, coagulation could occur by face (−)/face (−) aggregation. However, it is very difficult to understand the

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[1]) for definitions see [31]

effect of phosphate ions which largely increase the critical salt concentration. Usually, it is assumed that binding of phosphate groups recharges the edges from positive to negative so that higher salt concentrations are required to overcome the repulsion between a face (−) and an edge (−).

Contacts between negatively charged edges and faces are formed when the interaction becomes attractive at a certain salt concentration. Pierre [32] showed on the basis of the DLVO theory that the electrostatic repulsion V_R between an edge (−) and a face (−) with the same charge density is distinctly smaller than between two faces:

$$V_R(\text{edge}\,(-)/\text{face}\,(-)) = \left(\frac{2\pi R}{\ae L^2}\right)^{1/2} V_R\,(\text{face}\,(-)/\text{face}\,(-)) \qquad (1)$$

The particles are assumed to have cylindrical edges with the radius R and the length L; $\ae$ is the Debye-Hückel length. Thus, low concentrations of salt which do not induce face (−)/face (−) aggregation, initiate edge (−)/face (−) contacts.

Phosphate, oligo- and polyphosphate anions are adsorbed on uncharged or negatively charged edges by replacing structural OH groups (ligand exchange). As multivalent anions they increase the negative edge charge density and enhance the salt stability. Very likely, this process induces face/face coagulation. When the increased salt concentration required for the edge (−)/face (−) coagulation in the presence of phosphates approximates the salt concentration for face (−)/face (−) aggregation, the dispersion coagulates by face/face contacts because the area between two overlapping faces is distinctly larger than between an edge and a face.

In dispersions with strong repulsion between the faces, i.e., at low salt concentration, attractive edge/face contacts can only be observed at very low solid contents. The attractive interaction between an edge and a face depends on the angle of inclination between the two particles and the thickness of the particles [33]. The potential energy is very small for 10 Å thick particles (as in case of delaminated montmorillonite particles) and attraction is strong enough only for almost perpendicular orientation of the two particles. Thus, the edge/face contacts are disrupted by the strong repulsion between the faces when the concentration of particles is increased. This is why edge/face contacts do not play a significant role in the flow behavior of bentonite dispersions under practical conditions, i.e., at pH ≥ 6 and higher solid contents (≥ 1 percent (w/w)). Only in stronger acidic medium do edge (+)/face (−) contacts become stable enough. The importance of face/face aggregation in gel formation is stressed by Keren et al. [5]. The authors also discuss that the gel strength may be enhanced by contacts between surface regions of low or even zero charge density as a consequence of the layer charge heterogeneity.

When edge/face contacts are absent, the particles assume a more or less parallel orientation in dispersions with higher solid content [34, 35]. Embedded in the matrix of parallel oriented particles, some particles can aggregate by edge/edge contacts, too. Some electron micrographs show hints of edge/edge or edge/corner contacts [32, 36, 37]. However, it is extremely difficult to distinguish these contacts from band-like contacts between very thin particles or silicate layers which overlap to a small extent only.

Alcohol addition reduces the electrical repulsion between the particles. Coagulation becomes still more sensitive against salts. The critical coagulation concentration decreases with increasing alcohol content in the absence and in the presence of phosphate. Remarkable is the different flexure of the curves in Figs. 1a and b. One may speculate that alcohol molecules are displaced from the contact area between an edge and a face. Therefore, the c_K values are similar to those in water as long as the alcohol concentration is not too high. Alcohol molecules are more difficult to displace from between face/face aggregations, i.e., in the presence of phosphate, and the c_K decreases more sharply with increasing alcohol content.

A further effect should be considered. The charge of the diphosphate anion

$$P_2O_7^{4-} \overset{H^+}{\rightleftharpoons} HP_2O_7^{3-} \overset{H^+}{\rightleftharpoons} H_2P_2O_7^{2-} \overset{H^+}{\rightleftharpoons} H_3P_2O_7^{-}$$

not only changes with the pH of the dispersion, but also with the concentration of alcohol. The decreasing dielectric constant of the medium shifts the equilibria to the right side and reduces the charge density at the edges. At high alcohol contents, the c_K values approximate the c_K values in the absence of phosphate.

The theoretical calculation of the critical salt concentration provides difficulties. The charge density of the basal planes of the particles is constant and face/face interactions should be described by the constant charge model with Stern layer adsorption. The flow behavior of sodium montmorillonite in water-alcohol dispersions can be explained on the basis of this model [1]. The charges at the edges are variable so that the potential related to this surface could remain constant with increasing salt concentration. There are several experimental hints that also on the basal plane surfaces the potential and not the surface charge remains virtually constant with increasing salt concentration in aqueous dispersions. Low and coworker (e.g., see [30]) deduced from various studies of the clay water system that the Stern potential is small and hardly changes with the salt concentration. Potentials independent of the salt concentration over the range 0.003 to 0.3 mol/L were derived from co-ion exclusion measurements (– 69 mV for sodium montmorillonite) [38]. Gan and Low [39] discussed the possibilities to explain the constancy of the potential. They showed by IR studies that the increasing negativity of the Stern layer charge density with increasing salt concentration must be due to the inward displacement of the Outer Helmholtz plane. The Stern layer thickness at low salt concentration must therefore be significantly larger than 5 Å which probably is the limiting thickness at high salt concentration. The variable Stern layer thickness must be related to the structural changes of the dispersion medium near the surface and should, therefore, also be influenced by the alcohol addition.

The relation between the c_K and the Stern potential Ψ_δ for plate-like particles is [40, 41]

$$\begin{aligned} c_K &= \frac{107.46(4\pi\varepsilon\varepsilon_0)^3\,(RT)^5\gamma^4}{F^6A^2\nu^6} \quad (\mathrm{mol/m^3}) \\ &= 17.173\cdot 10^{-45}\cdot\varepsilon^3\gamma^4/A^2\nu^6 \quad (\mathrm{mol/L}) \qquad (2) \end{aligned}$$

($\gamma = (e^{z/2} - 1)/(e^{z/2} + 1)$, $z = \nu F\Psi_\delta/RT$, ν = valency of the gegen ion; $\varepsilon_0 = 8.854\cdot 10^{-12}$ AsV^{-1} (permittivity); ε = relative dielectric constant, $F = 96485.31$ Cmol^{-1} (Faraday constant); $RT =$ 2437.37 Jmol^{-1} (at 20°C); $A = 0.2\cdot 10^{-19}$ J (Hamaker constant for clay minerals, cf. [1]).

More correctly, the relation between c_K and Ψ_δ should be elaborated on the basis of Eq. (1). However, even in this case only the order of magnitude of an average Stern potential is obtained because the two interacting surfaces (edge/face) do not have identical potentials. The maximum critical coagulation concentration, c_K = 195 mmol/L (without alcohol, in the presence of diphosphate) and the smallest value, c_K = 0.8 mmol/L (60 percent propanol) correspond to apparent average Stern potentials of 32 mV and 13 mV.

The critical coagulation concentration is measurable up to 70% methanol or ethanol and 60% propanol. At higher alcohol concentrations colloidal dispersions of sodium montmorillonite are no longer stable. The silicate layers condense to the discrete particles of the montmorillonite-alcohol complexes (interlayer solvates) with basal spacings between 13 and 18 Å [42]. Very likely, the complexes do not contain two compressed diffuse ionic layers, but one diffuse central sheet of gegen ions which makes the electrostatic interaction attractive. Presently, we do not know the mechanism of transition. Statistical calculations of the ion–ion correlations [43, 44] may provide an insight into this reaction.

In this regard, the variation of the sediment height is instructive (Fig. 2). In the water-rich alcohol mixtures the interaction is repulsive and the particles do not settle within a few days. When the montmorillonite-alcohol complexes begin to form at high concentrations of alcohol, the silicate layers stack together and a voluminous sediment forms which becomes denser with increasing alcohol concentration. Within longer periods (here 15 months) the particles settle under the gravitational force when the alcohol content is below 80% (methanol) or 60 and 50% (ethanol, propanol). A dense sediment accumulates at the bottom of the tube because the force between the particles is repulsive [9]. At higher alcohol contents the voluminous sediment of aggregated particles persists. It is distinctly denser than after 24 h when the alcohol is methanol, but hardly contracts with time in water-propanol. In the pure alcohols dense sediments are again created consisting of the particles of the montmorillonite-alcohol complexes.

Sedimentation is dependent on the solid content of the dispersion. In diluted dispersions the particles settle independently from each other when the interaction is repulsive, and a dense sediment forms. At higher solid content the particles are subjected to geometrical constraints. They cannot separate to minimize the influence of the repulsive force. The strong repulsion holds the particles in their position and retards or impedes rotational and translational movements (electroviscous effect). Therefore, Szántó and Várkonyi [23] found high sediment volumes in water which decreased with increasing alcohol content. The solid content was extremely high (1 g sodium montmorillonite in 10 mL water or water-alcohol). The decrease of the sediment volume reflects the compression of the diffuse ionic layer with increasing alcohol concentration and, eventually, continuous transition into the montmorillonite-alcohol complexes.

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