Colloid chemistry of clay minerals: the coagulation of montmorillonite dispersions

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Abstract

The transition between stable colloidal dispersions and coagulated or flocculated systems is a decisive process in practical applications of million of tons of bentonites (containing the clay mineral montmorillonite). Dispersion into the colloidal state requires the transformation of the original bentonite into the sodium form, for instance by soda activation. Therefore, we review here the coagulation of sodium montmorillonite dispersions by inorganic and organic cations and the influence of compounds of practical interest such as phosphates, cationic and anionic surfactants, alcohols, betaine-like molecules and polymers like polyphosphates, tannates, polyethylene oxides with cationic and anionic end groups, and carboxy methylcellulose. Typical properties of the sodium montmorillonite dispersions are the very low critical coagulation concentrations, the specific adsorption of counterions on the clay mineral surface, and the dependence of the c_K values on the montmorillonite content in the dispersion. In most cases coagulation occurs between the negative edges and the negative face. The phosphates Na_2HPO_4, NaH_2PO_4 and $Na_4P_2O_7$ increase the edge charge density and change the type of coagulation from edge $(-)$/face $(-)$ to face $(-)$/face $(-)$ with distinctly higher c_K values. Polyanions like polyphosphate and tannate stabilize in the same way. Carboxy methylcellulose causes steric stabilization. Montmorillonite particles with adsorbed betaine-like molecules provide an example of lyosphere stabilization.
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Keywords: Bentonite; Clay mineral aggregation; Coagulation; Dispersions; Montmorillonite; Polymer flocculation; Polymer stabilization

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1. Introduction

Clay minerals are distinguished from other colloidal materials by the highly anisometric and often irregular particle shape, the broad particle size distribution, the flexibility of the layers, the different types of charges (permanent charges on the faces, pH-dependent charges at the edges), the heterogeneity of the layer charges, see below), the pronounced cation exchange capacity, the disarticulation (in case of smectites) (Fig. 1) and the different modes of aggregation [1–5].

Montmorillonites (from Montmorillon, a town in the Poitou area, France) are the most abundant minerals within the smectite group of 2:1 clay minerals. They are the determinative components in bentonites. Montmorillonite particles may be as large as 2 μm and small as 0.1 μm in diameter with average sizes of ~ 0.5 μm. The particles are of irregular shape. They can be compact but, mostly, they are foliated and look like paper sheets torn into smaller pieces. The particles are never true crystals but are more like assemblages of silicate layers. These assemblages a few silicate layers contain coherent domains of equally spaced silicate layers. The domains are separated by zones of silicate layers in different distances. The contour lines of the particles are of irregular shape, the edges are frayed and layers or thin lamellae of a few layers protrude out of the packets and enclose wedge-shaped pores [3,6–11].

The permanent charges of the silicate layers result from isomorphous substitutions. However, the degree of substitution changes from layer to layer within certain limits so that the interlayer cation density also varies from interlayer space to interlayer
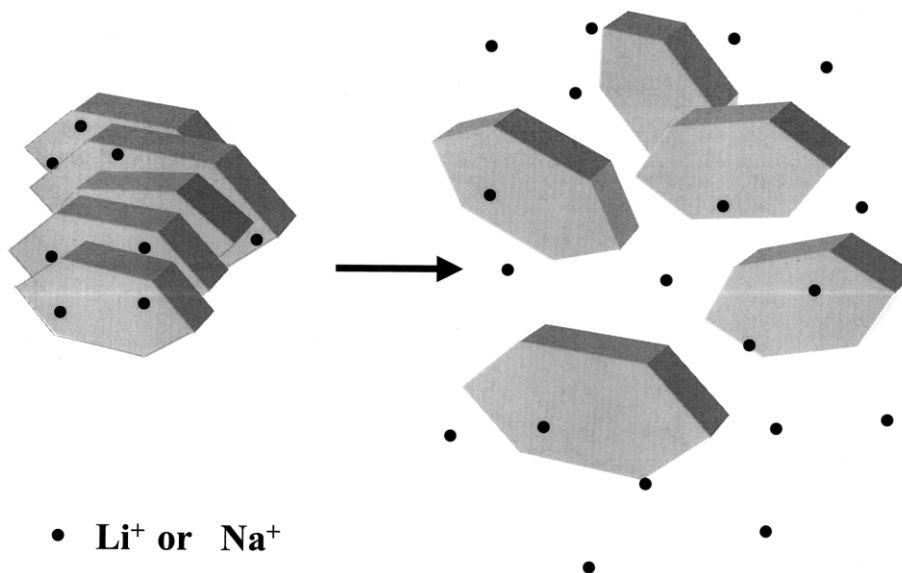

● **Li⁺ or Na⁺**

Fig. 1. Delamination of sodium montmorillonite crystals in aqueous dispersions.

Table 1
Important uses of dispersed bentonites

Large volume applications	Small volume applications
Foundry moulding sands	Paints
Oil well drilling	Adhesives (in asphaltic materials and latex)
Pelletising iron ore	Pharmaceutical uses
Sealing materials	Cosmetics
Civil engineering	Filling materials
	Water purification

New trends: porous heterostructures, nanoparticle engineering, nanocomposites

space and may also vary in directions parallel to the layers (heterogeneous charge distribution). The distribution of the interlayer cation density can easily be determined by the alkylammonium method [12,13]. The average layer charge of montmorillonites varies between 0.2 and 0.4 eq/formula unit $(Si, Al)_4O_{10}$ but most montmorillonites have layer charges around 0.3 eq/formula unit. This charge density corresponds to a surface charge of 0.10 Cm^{-2} [3,4]. On the basis of the high layer charge densities one calculates high surface potentials for the isolated particles, e.g. ~ 200 mV for a salt concentration of 10^{-3} mol/l and a surface charge density of 0.10 Cm^{-2}. Thus, high critical salt concentrations for face/face coagulation are expected [14].

The edges of the layers show aluminol and silanol groups and are positively charged at low pH and negatively charged at higher pH. The position of the point of zero charge of the edges is still uncertain but there are several colloid chemical arguments that it must be near pH~ 5 for montmorillonites [3,15,16]. Keren and Sparks [17] by potentiometric titration experiments found the p.z.c. of the edges of pyrophyllite (no permanent charges!) at pH 4.2.

An outstanding property of dispersed montmorillonite particles is delamination into the single silicate layers or thin packets of them when the counterions are alkali cations, preferentially lithium and sodium, and the salt concentration is sufficiently small (approx. <0.2 mol/l for sodium ions) (Fig. 1) [3,4,18–23].

Approximately 10 million tons of bentonites are used per year in innumerable applications [3,4,24]. Important uses are listed in Table 1. The colloidal state of the montmorillonite particles in the bentonite dispersion is decisive in many practical applications. Therefore, studies on the coagulation of montmorillonite dispersions were started many decades ago [25–33].

The coagulation of montmorillonite dispersions can be described by the DLVO theory, see for instance [1,17,30,34–40]. A different and, for a colloid scientist, strange opinion was put forward by Low and co-workers, see for instance [41–43]. The electrostatic interactions and the hydration of the counterions (interlayer cations) were considered being of minor importance, and non-specific interactions with the clay mineral surface (whatever this term means in these papers) is seen as the most important cause of swelling. Indeed, the structure of water in the interlayer space differs from bulk water [36,44–49] and is a decisive factor, but, as discussed by

Delville and Laszlo [36], it is the behavior of the water molecules in the interlamellar electrostatic force field which drives the swelling. Recently, Quirk and Marcelja [39] proved that the Poisson–Boltzmann and the DLVO double layer theory satisfactorily described the swelling of Li^+ montmorillonite in water and 10^{-4} to 1 M LiCl solutions at swelling pressures of 0.05–0.9 MPa. The DLVO theory with a 0.55-nm thick Stern layer indicated Stern potentials of -58 mV (1 M LiCl) to -224 mV (10^{-4} M LiCl) and a Gouy plane charge of 0.038 Cm^{-2} which is approximately 30% of the layer charge.

2. Materials and methods

Bentonite from Wyoming (Greenbond, M40 and M40A) and from Bavaria (Süd–Chemie Co., M 47) were purified by removal of iron oxides (reduction by dithionite and complexing Fe^{2+} by citrate) and humic materials (oxidation with H_2O_2) [50]. The <2-μm fraction of the sodium montmorillonite was then separated by sedimentation. The dialysed samples were freeze-dried. Usually, the freeze-dried samples were redispersed in water by intense shaking and ultrasound dispersion. The pH of the dispersions was 6.5. The sodium montmorillonite dispersion showed buffering behavior at this pH so that adjustment of pH was not required [51]. The layer charge of the montmorillonite from Wyoming was $=0.28$ eq/formula unit and that of the montmorillonite of Bavaria was 0.31 eq/formula unit.

The critical coagulation concentrations c_K were determined by visual inspection of the behavior of the 0.025% dispersions after salt addition (test-tube tests) [1,5]. These experiments gave more reliable results than turbididity measurements. With more highly concentrated dispersions (up to mass contents of approx. 0.5%) a clear distinction between the stable and the coagulated dispersion was often difficult and was impossible at still higher solid contents. In such cases c_K was derived from rheological measurements. At a certain salt concentration the viscosity of the dispersion increased sharply. This salt concentration was identified as c_K value [52,53].

The flow behavior of the dispersions was measured with a rotational viscometer (Physica, UDS 200) with plate–plate geometry (plate diameter 5 cm, gap 0.05 cm) at 15 °C. The shear stress τ was recorded at shear rates $\dot{\gamma}$ linearly increasing from 0 to 2000 s^{-1}. The plastic viscosity was derived from the slope of the linear section of the flow curves at $\dot{\gamma} \rightarrow 2000$ s^{-1} [52].

3. Results

3.1. Coagulation with sodium, calcium and aluminium salts

The c_K value of sodium, calcium and aluminium chloride was 5, 0.4 and 0.08 mmol/l for 0.025% sodium montmorillonite dispersions. Other montmorillonites showed similar c_K values of approximately 5–10 mmol/l sodium chloride. Even the more highly charged beidellite (Unterrupsroth, Germany, sample B 18/4, mean layer charge of 0.39 eq/unit) coagulated at ~ 6 mmol/l. The c_K value increased

Table 2
Critical coagulation concentration c_K of sodium, calcium and aluminium chloride for sodium montmorillonite dispersions (0.025, 0.5, 1.0% w/w solid content) at pH~6.5 (Na$^+$, Ca^{2+}) (test-tube tests). Montmorillonite from Wyoming (M 40A)

Counterion	c_K (mmol/l)		
	0.025%	0.5%	1%
Na$^+$	5	15	20
Ca^{2+}	0.4	2	3
Al^{3+}	0.08	1	1.5

with the solid content. The 0.5% dispersions of sodium montmorillonite (Wyoming) were coagulated by 20 mmol/l sodium chloride, 3 mmol/l calcium chloride and 1.5 mmol/l aluminium chloride (test-tube tests) (Table 2).

The critical coagulation concentration also depended on the type of anion (Table 3). Nitrate instead of chloride increased the c_K from 5 mmol/l to 16 mmol/l and sodium sulfate to 18 mmol/l (0.025% dispersion). The influence of certain phosphates was extremely strong. NaH$_2$PO$_4$ and NaH$_2$PO$_4$ coagulated the 0.025% dispersion at 1100 and 460 mmol/l, respectively. Sodium diphosphate Na$_4$P$_2$O$_7$ up to its solubility limit (~130 mmol/l) did not coagulate the dispersion. In contrast, sodium phosphate Na$_3$PO$_4$ showed a very low coagulation concentration, 25 mmol/l. NaOH coagulated at 20 mmol/l. In both cases the dispersion was highly alkaline (pH 11.5–12) at the point of coagulation. In contrast to the influence of chlorides and nitrates the critical coagulation concentration of NaH$_2$PO$_4$ and NaH$_2$PO$_4$ decreased with increasing solid content (Table 3).

The effect of phosphate was also seen when the montmorillonite dispersion was coagulated with NaCl in the presence of sodium diphosphate. Even an addition of 0.1 mmol/l Na$_4$P$_2$O$_7$ increased the c_K of NaCl from 5 to 195 mmol/l [16]. Larger quantities of this phosphate raised the c_K to approximately 300 mmol/l NaCl (Table 4). This effect was also observed for a 0.1% pyrophyllite dispersion at pH 5.3 which was coagulated by 0.4 mmol/l sodium nitrate but 100 mmol/l of this salt

Table 3
Critical coagulation concentration c_K of sodium salts for 0.025% and 2% dispersions of sodium montmorillonite (Wyoming M 40A)

	c_K (mmol/l)		pH		c_K (mmol/l)		pH
	0.025%	2%			0.025%	2%	
NaCl	5	30	6.5	Na$_2$HPO$_4$	1100	80	9
NaNO$_3$	16	12	6.5	NaH$_2$PO$_4$	460	40	~5
Na$_2$SO$_4$	18	35	6.5	Na$_3$PO$_4$	25	35[b]	11.5
NaHSO$_4$	4	4	~5	Na$_4$P$_2$O$_7$	–[a]	–[a]	10
				NaOH	20	30[b]	11.5; 12

[a] No coagulation up to the solubility limit of ~130 mmol/l.
[b] 0.5% dispersion.

Table 4

Critical coagulation concentration of NaCl in the presence of phosphates: 1. sodium montmorillonite dispersion (Wyoming) and sodium polyphosphates $(NaPO_3)_n$ [31]; 2. sodium beidellite (Unterrupsroth, Germany, fraction 0.1–2 μm, 0.025% dispersion) and sodium diphosphate $Na_4P_2O_7$ [30]

Phosphate	Phosphate concentration mmol/l	c_K mmol/l	pH
Sodium montmorillonite $(NaPO_3)_n$			
	0	12	
	0.01	20	
	0.1	80	
	1	120	
Sodium beidellite $Na_4P_2O_7$			
	0	6	6
	1.25[a]	230	6
	5	250	8.3
	10	270	9
	12.5	280	9.3
	25	310	9.7

[a] Sodium montmorillonite dispersion at 0.1 mmol/l $Na_4P_2O_7$: $c_K = 195$ mmol/l NaCl [16].

were required in the presence of 0.16 mmol/l sodium hexametaphosphate $Na_6P_6O_{18}$.

Acids like HCl, HNO_3, H_2SO_4 and H_3PO_4 coagulated the 0.025% dispersion (pH $\sim$ 2) at concentrations similar to the corresponding salts: $c_K(HCl, HNO_3) = 5.5$ mmol/l, $c_K(H_2SO_4) = 12.5$ mmol/l and $c_K(H_3PO_4) = 32$ mmol/l

3.2. Influence of alcohols

Addition of methanol, ethanol and propanol decreased the critical coagulation concentration of the 0.025% sodium montmorillonite dispersion from 8 mmol/l NaCl to 3.6 mmol/l NaCl (70% v/v methanol), 1.2 mmol/l NaCl (70% v/v ethanol) and 0.8 mmol/l NaCl (60% v/v propanol) (Fig. 2a) [16]. This effect was still more pronounced in the presence of 0.1 mmol/l sodium diphosphate. The c_K value decreased from 195 mmol/l to 7.5 mmol/l NaCl (70% methanol), 2.5 mmol/l NaCl (70% ethanol) and 5 mmol/l NaCl (60% propanol) (Fig. 2b).

3.3. Influence of surface active agents

It was surprising that small amounts, <1 mmol/l, of hexadecylpyridinium chloride (cetylpyridinium chloride, CPC) raised the critical coagulation concentration of NaCl from 8 mmol/l to 16 mmol/l (Table 5). At higher CPC concentrations the dispersion was coagulated by the surfactant itself. Addition of sodium dodecylsulfate SDS increased the c_K value of NaCl more strongly. In the presence of 100 mmol/l SDS a salt concentration of 136 mmol/l was required to coagulate the 0.025% dispersion [51].
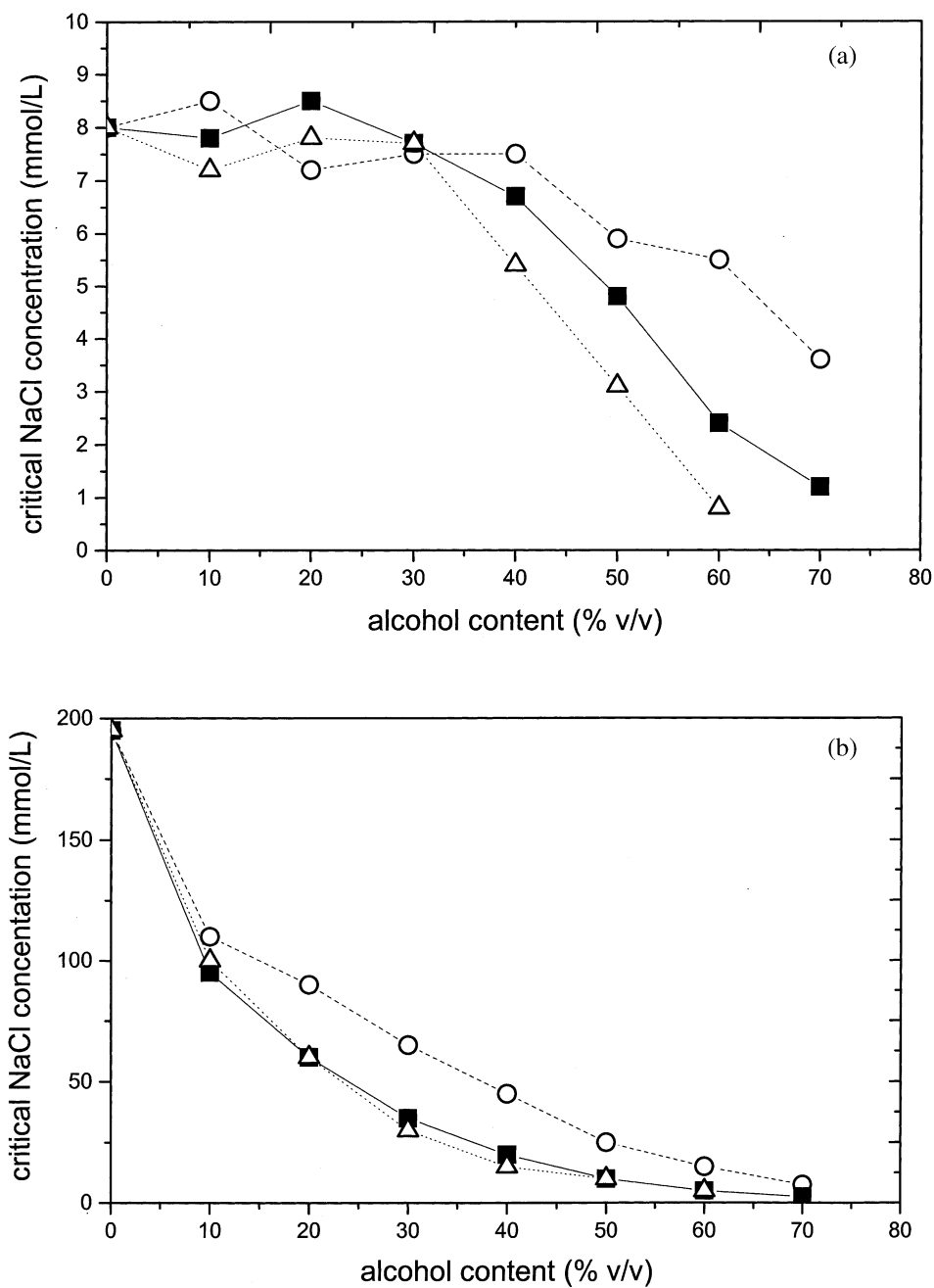
Fig. 2. The critical coagulation concentration of NaCl for 0.025% dispersions of sodium montmorillonite (from Wyoming) as a function alcohol content (in% v/v) at pH∼6.5 without (a) and in the presence of 0.1 mmol/l $Na_4 P_2O_7$ (b). o methanol, ■ ethanol, Δ n-propanol

Table 5
Critical coagulation concentration of NaCl for 0.025% dispersions of sodium montmorillonite (Wyoming, M 40) at pH ~ 6.5 in the presence of cetyl pyridinium chloride CPC and sodium dodecylsulfate SDS [51]

Surfactant concentration mmol/l	c_K (mmol/l)	
	CPC	SDS
0	8	8
$5 \cdot 10^{-4}$	9.5	
10^{-3}	9	10
10^{-2}	7	10
$2 \cdot 10^{-2}$	11	
10^{-1}	13	10
$2 \cdot 10^{-1}$	16	
1	[a]	12
10	[a]	81
100	[a]	136

[a] Coagulation by CPC itself.

3.4. Coagulation of betaine montmorillonites

Betaines as surface modifying agents

$$(CH_3)_3 \overset{\oplus}{N} - (CH_2)_n - COO^{\ominus}$$
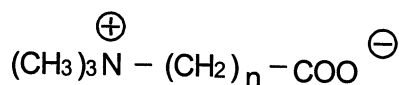
$$n = 3, 5, 7, 10$$

were synthesized to design organic derivatives which delaminate when dispersed in water. The quaternary ammonium groups replace the interlayer cations whereas the negative charges at the opposite end and their counterions initiate the separation of the silicate layers: Colloidal dispersions of single silicate layers with the attached betaines molecules are formed [54]. In contrast to the dispersions of Li^+ and Na^+ montmorillonite with yield values of ~400 mPa the dispersion showed Newtonian flow, and the viscosity of the dispersion (solid content 1.5% w/w, pH 7) approximated the viscosity of water.

LiCl coagulated the dispersion of Li montmorillonite and betaine montmorillonite with $n=3$ at a concentration of 8 mmol/l. The c_K value increased with n to a maximum of 60 mmol/l LiCl at $n=7$, then decreased slightly at $n=10$ (Table 6). The strong influence of small amounts of diphosphate was again noted. A maximum c_K value of 1320 mmol/l LiCl was reached for $n=7$.

The modification with betaines reduced the stability of the montmorillonite dispersions in water–alcohol solutions. Whereas the colloidal dispersions of Li^+ and betaine montmorillonite (in the absence of any salt) were stable up to a methanol molar fraction $\chi = 0.7$, dispersions of the long chain derivatives ($n=7$, 10) coagulated at $\chi = 0.1$, i. e. were only stable in water. In water/propanol mixtures
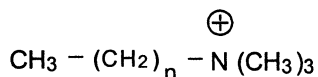
Table 6
Critical LiCl concentration for the coagulation of 0.05% dispersions of Li^+ and betaine montmorillonite (Wyoming M 40) in water and in the presence of 0.1 mmol/l $Na_4P_2O_7$ [54]

Counterion	c_K (mmol/l)	
	In water	With phosphate
Li^+	8	570
Betaine $n=3$	8	505
$n=5$	17	835
$n=7$	60	1320
$n=10$	50	1180

Li^+ and betaine montmorillonite ($n=3$) but also betaine montmorillonite ($n=10$) were stable up to a molar fraction of 0.3 propanol and the samples with $n=5$, 7 up to $\chi=0.5$ and 0.4 (Fig. 3).

3.5. Coagulation by organic cations

Tetramethylammonium chloride coagulated the sodium montmorillonite (Wyoming) dispersion at the same concentration as NaCl, 5 mmol/l. Monovalent long chain cations such as trimethyl alkylammonium ions

$$\overset{\oplus}{CH_3 - (CH_2)_n - N(CH_3)_3}$$

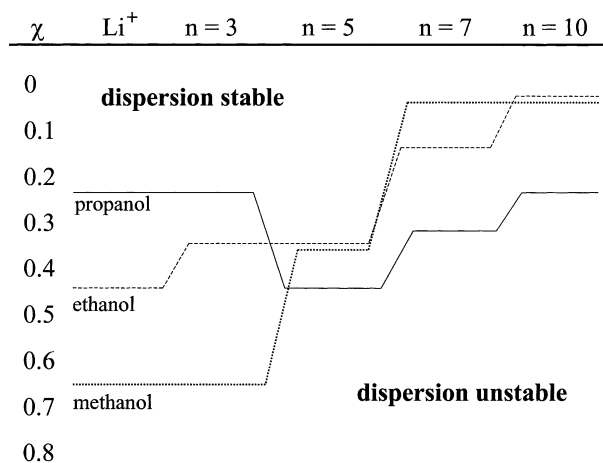trimethyl alkylammonium ions

Fig. 3. Stability fields of Li^+ and betaine montmorillonite dispersions in water/alcohol mixtures. $\chi=$ molar fraction of the alcohol, $n=$ alkyl chain length of the betaine. ------ methanol – – – – ethanol ——— propanol

Table 7
Coagulation of sodium montmorillonite dispersions by organic cations. Critical coagulation concentration of the 0.025% dispersions by test-tube tests, of the 0.5% (w/w) dispersions from rheological measurements, pH $\sim$ 6.5. Montmorillonite from Wyoming (M 40A) [52]

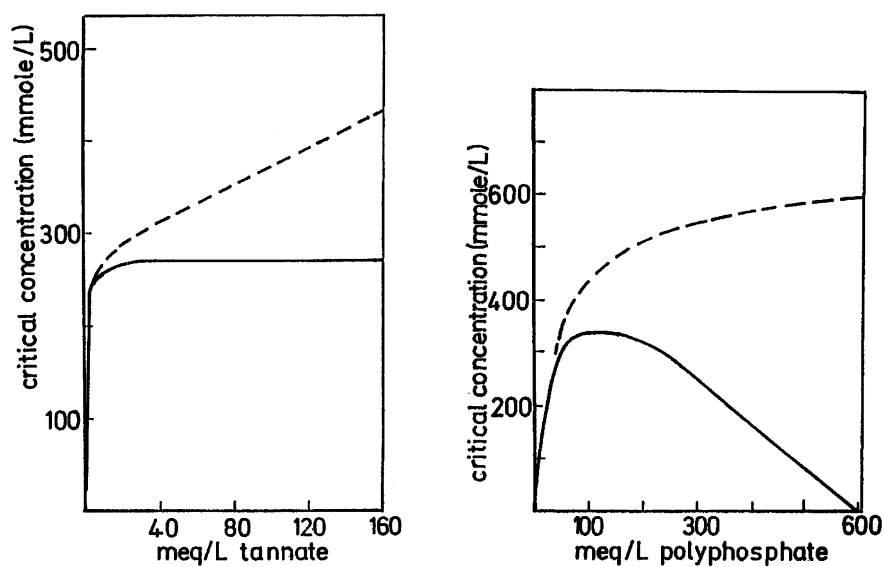| Cation	Valence	c_K (mmol/l)	
		0.025%	0.5%
TMM	1	5	5.8
TM 6	1	0.3	2
TM 12	1	0.15	0.76
TM 16	1	0.09	0.35
BP 1	2	0.2	0.85
BP 6	2	0.2	0.62
BP 12	2	0.1	0.18
CV	1	0.1	0.9
MG	2	0.2	0.9
TTP	3	0.05	0.09
PQ	2	0.08	0.4
DQ	2	0.1	0.45

Fig. 4. Stabilization of sodium bentonite dispersions by Quebracho tannate (sodium salt) (a) and sodium polyphosphate (b) ——— critical coagulation concentration of NaCl, ------ total Na$^+$ concentration at the point of coagulation from [3].

Table 8
Flocculation and restabilisation of sodium montmorillonite dispersions by cationic (TMA-PEO; DMDH-PEO) and anionic (S-PEO) polyethylene oxides. Montmorillonite from Bavaria (M 47)

PEO	Molecular mass[a]	Flocculation concentration (g/l)		
		0.05%	0.5%	1%
TMA-PEO 1500	1575	2	5	5
TMA-PEO 4000	4414	–[b]	–	8
TMA-PEO 20 000	17 985	–	–	–
TMA-PEO 35 000	37 113	–	–	–
DMHD-PEO 1500	1967	–	1 (8)[c]	2 (15)
DMDH-PEO 4000	4016	3	3	3 (15)
DMDH-PEO 20000	19 312	1	6	8
DMDH-PEO 35000	38 020	3	8	8
S-PEO 1500		7	8	6
S-PEO > 1500	–	–	–	

[a] Molecular weight from end group determination.
[b] – indicates: no flocculation.
[c] In parentheses: polymer concentration at restabilisation.

Table 9
Flocculation (by NaCl) of stable and restabilised dispersions of 1% sodium montmorillonite in solutions of modified PEOs. Montmorillonite from Bavaria (M 47)

PEO concentration (g/l)	c_K (mmol/l NaCl)				
	5	10	20	30	40
TMA-PEO 20000	12	16	25	32	
TMA-PEO 35000	18	24	40	45	
DMDH-PEO 1500[a]			∼500	50	25
DMDH-PEO 4000[a]			>500	>500	20
S-PEO 4000[b]	30	25	20	12	
S-PEO 20000	25	25	20	20	
S-PEO 35000	25	25	18	16	

[a] Restabilised dispersion.
[b] 2% dispersion.

coagulated at very low concentrations, $c_K \leq 0.3$ mmol/l (Table 7). Restabilization was observed when larger amounts of surface active agents (above the cation exchange capacity) were added.

Very small coagulation concentrations were also observed with large organic cations such as the monovalent cation crystal violet (0.1 mmol/l), the divalent methyl green (0.2 mmol/l) and trivalent TTP, tris(trimethylammonium phenyl) methane chloride, (0.05 mmol/l). Dispersions coagulated by crystal violet were restabilized by addition of CV in amounts > 1.5 mmol/g montmorillonite.

Paraquat and diquat were also strongly coagulating divalent cations with c_K values of ∼0.1 mmol/l. The divalent long chain cations hexyl and dodecyl bispyridinium chloride showed coagulation concentrations similar to the trimethyl alkylammonium
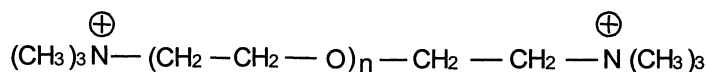
salts (Table 7). The valence of the organic cations was not as dominant as for inorganic cations. In all cases the c_K value increased with the montmorillonite content of the dispersion.

crystal violet

methyl green

tris (trimethylammonium phenyl) methane ions
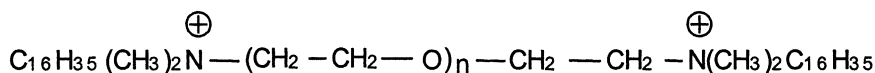
alkyl bispyridinium ions

paraquat

diquat
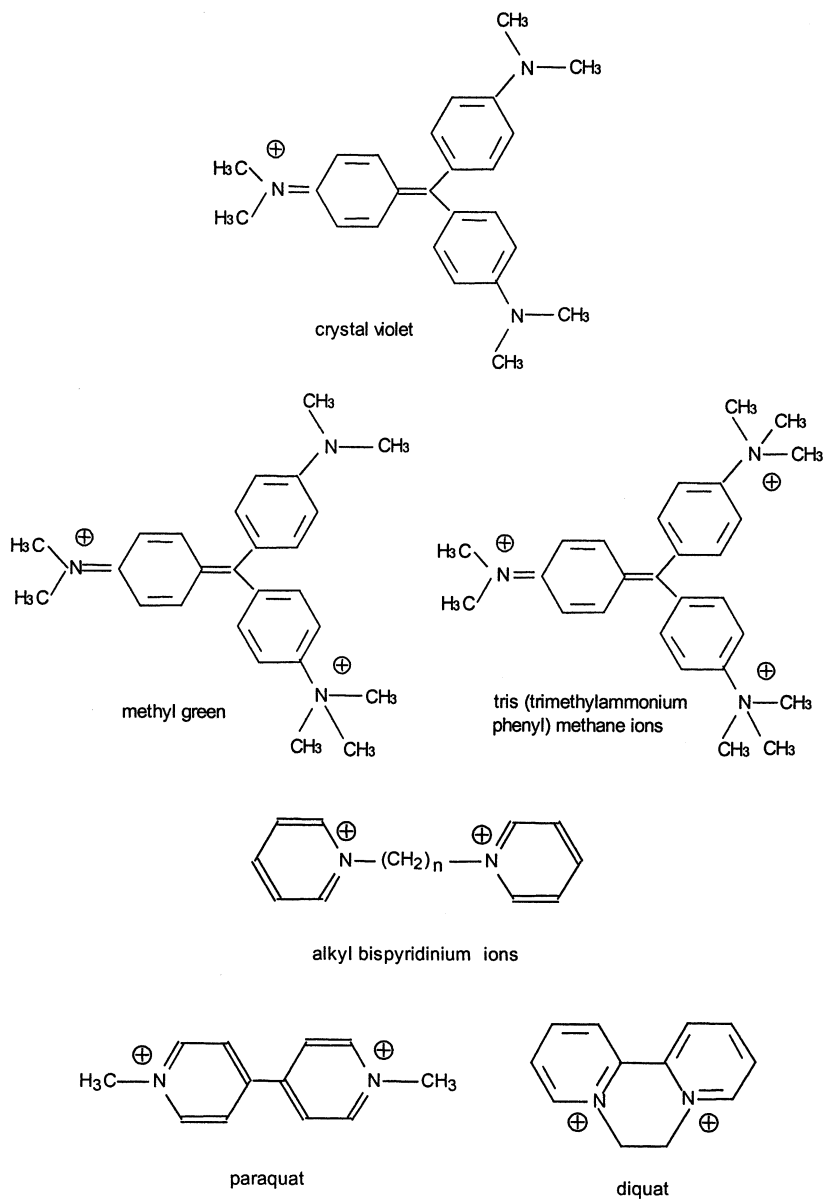
3.6. Coagulation in the presence of polymers

Instructive examples were reported long before [1]; see also [3,4]. The critical NaCl concentration for a sodium montmorillonite dispersion decreased slightly from 20 mmol/l to 11 mmol/l after an addition of 0.0003% sodium carboxy methylcellulose, CMC; then increased to 3100 mmol/l at 0.1% CMC. A common additive in drilling muds besides CMC is Quebracho tannate. The c_K value reached 270 mmol/l NaCl at ≥ 40 meq/l sodium tannate. The NaCl concentration needed to coagulate the sodium montmorillonite dispersion in the presence of polyphosphate increased to a maximum (320 mmol/l NaCl at ~ 100 meq/l polyphosphate), then decreased to zero at 600 meq/l polyphosphate, i.e. the dispersion was coagulated by polyphosphate itself (Fig. 4).
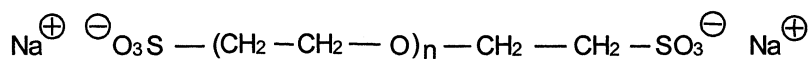
3.7. Influence of cationic and anionic polyethylene oxides

$$(CH_3)_3 \overset{\oplus}{N} - (CH_2 - CH_2 - O)_n - CH_2 - CH_2 - \overset{\oplus}{N}(CH_3)_3$$

TMA-PEO

$$C_{16}H_{35}(CH_3)_2 \overset{\oplus}{N} - (CH_2 - CH_2 - O)_n - CH_2 - CH_2 - \overset{\oplus}{N}(CH_3)_2 C_{16}H_{35}$$

DMHD-PEO

$$\overset{\oplus}{Na} \ \overset{\ominus}{O_3}S - (CH_2 - CH_2 - O)_n - CH_2 - CH_2 - SO_3^{\ominus} \ \overset{\oplus}{Na}$$

S-PEO

Polyethylene oxides (PEO) did not coagulate montmorillonite dispersions. However, when of cationic end groups such as trimethylammonium (TMA) or dimethyl hexadecylammonium (DMHD) are attached [55], the electrostatic interaction with the surface charges of the montmorillonite may compete with the good solvency of the PEO in water and initiate coagulation. Indeed, TMA-PEG with a molecular mass of ~ 1500 coagulated a 0.05% sodium montmorillonite dispersion at a concentration of 2 g/l (corresponding to 2.5 meq/l ammonium groups, from the experimental molecular weight, Table 8). The 1% (w/w) dispersion needed a TMA-PEO concentration of 5 g/l. TMA-PEOs with molecular masses >4000 did not coagulate the sodium montmorillonite (M47) dispersion (Table 8).

The dimethyl hexadecylammonium derivatives showed a complex behavior. DMHD-PEO 1500 did not coagulate the 0.05% dispersion but coagulated the 1% (w/w) dispersion at a concentration of 2 g/l (2 meq/l ammonium groups). This dispersion was restabilised at ≥ 15 g/l DMHD-PEO 1500 (15 meq/l N^+). Restabilisation was not observed for DMHD-PEO with molecular masses > 4000.

The anionic PEO with a molecular mass of ~ 1500 coagulated the montmorillonite dispersion at a concentration of 7 g/l (0.05% dispersion) and 6 g/l (1% dispersion). S-PEO with larger molecular masses did not coagulate the sodium montmorillonite dispersions (Table 8).

Sodium montmorillonite dispersions stabilized by cationic and anionic PEOs (TMA-PEO 20000 and 35000, S-PEO 4000, 20000 and 35000) were coagulated by 12–45 mmol/l NaCl, and c_K increased with increasing PEO content. In contrast, the DMHD-PEOs 1500 and 4000 needed much larger amounts of NaCl (Table 9). However, the usual range of NaCl concentrations was obtained at higher PEO concentrations (≥ 40 g/l).

The dispersions containing the anionic PEO were coagulated by ~ 20 mmol/l NaCl, and the c_K decreased slightly with increasing polymer concentration.

4. Discussion

4.1. Coagulation by inorganic salts

The critical coagulation concentration of 5–10 mmol/l sodium counterions for sodium montmorillonite dispersions is extremely low, compared with the usual values between 25 and 500 mmol/l [5,14,56,57]. Decades ago, this observation was explained by the interaction of positive edge charges with negative surface charges producing T-type contacts and aggregation in cardhouse type arrangements [1,58–60]. However, pH ≈ 6.5 is near or, more likely, above the p.z.c. of the edges i.e. positive edge charges are no longer present or their number is very small. An additional effect increases the negative field at the edges [61,62]: The edge thickness of the montmorillonite particles is small relative to the Debye–Hückel length at the critical salt concentration. The negative double layer extending from the basal plane surfaces spills over into the edge region. Even for an edge charge density of $+0.1$ C/m^2 (which is very high!) and a face charge density of -0.1 C/m^2 (typical of montmorillonite) the influence of the negative face charges is still significant at sodium salt concentrations $\lesssim 10^{-3}$ M. Therefore, coagulation occurs between edges $(-)$ and faces $(-)$ (Fig. 5). The importance of the edge surface in the coagulation process also follows from the coagulation experiments of Keren and Sparks [17] with colloidal pyrophyllite particles.

As the negative edge charge density is very small, coagulation requires low sodium salt concentrations. Pierre [63] calculated the electrostatic repulsion between an edge $(-)$ and a face $(-)$ on the basis of the DLVO theory. Assuming that the value of the charge density at the edges and the faces is identical, this repulsion is distinctly smaller than between faces.
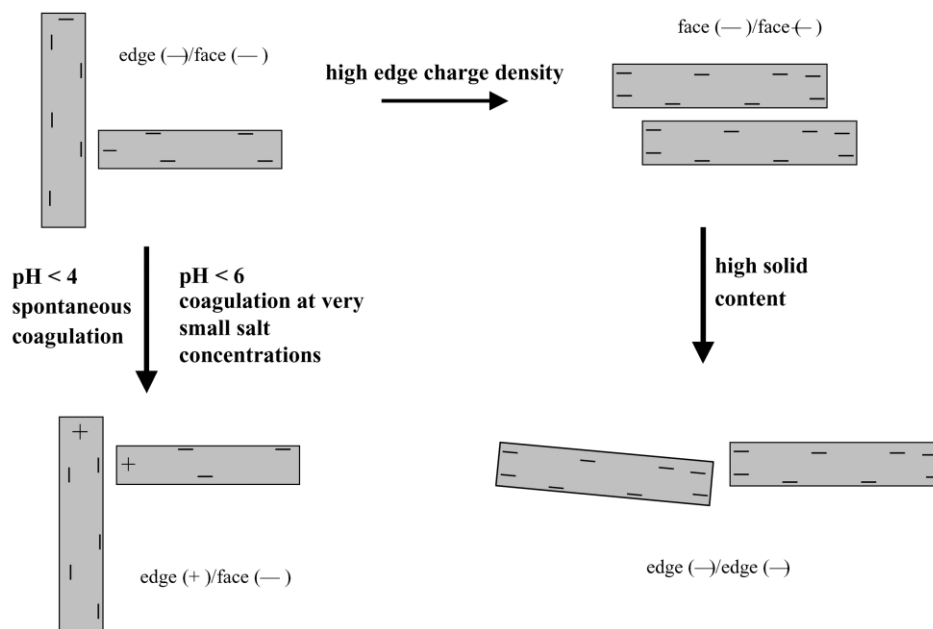
Coagulation by salts, pH > 6

Fig. 5. The different modes of aggregation of coagulated clay mineral particles.

As expected on the basis of the DLVO theory [14,56,64,65], the critical coagulation concentration of calcium and aluminium counterions, 0.4 and 0.08 mmol/l, is distinctly smaller than of sodium ions. The relation between the c_K values is

$$c_K \ (Na^+) \approx 12 \ c_K \ (Ca^{2+}) \approx 63 \ c_K \ (Al^{3+}).$$

These ratios correspond to the prediction of the DLVO theory [5,65]:

$$c_K \ (Me^+) = (4-64) \ c_K \ (Me^{2+}) = (9-729) \ c_K \ (Me^{3+})$$

The range of the predicted c_K values results from the dependence on the diffuse layer potential. The smaller value corresponds to potentials ≤ 50 mV, the large value to ≥ 150 mV. The observed ratios are near the values for lower potentials and indicate the pronounced Stern layer adsorption of the di- and trivalent counterions on the clay mineral surfaces [39,40,66–69]. The aggregation of clay mineral layers or lamellae in the presence of multivalent counterions is strengthened by ion–ion correlation forces [70,71].

The strong Stern-layer adsorption is also indicated by the c_K values increasing with the solid content (Tables 2, 3 and 7). When the salts solely regulate the

thickness of the diffuse ionic layer, c_K is independent of the solid content of the dispersion. It increases with the solid content when the counterions are adsorbed at the surface, for instance in the Stern layer. Instructive examples were reported by Stumm et al. [72] and Rooy et al. [73].

The slightly increased coagulation concentration of $NaNO_3$ in comparison with NaCl may result from the water structure breaking effect of nitrate ions. The consequence of structure breaking by the anion is an increased hydration of the cation which reduces the adsorption of the cation in the Stern layer. Coagulation then requires a slightly higher salt concentration. This effect was also observed in coagulation experiments with latex dispersions [5,74].

The 'liquefying' property[1] of phosphates is related to two effects. Phosphate anions are strongly adsorbed on oxide surfaces and also on the edges of the silicate layers. They replace structural OH groups by ligand exchange [3,4,75,76]. As multivalent anions, they increase the negative edge charge density with the consequence of an increased salt stability. As the electrostatic repulsive force is strongly dependent on the surface potential as long as this value is low (see, e.g. [5,14,77]), a weak increase of the edge charge density by phosphate adsorption can strongly increase the repulsive force and the c_K value.

The second effect is the transition of edge $(-)$/face $(-)$ coagulation into face $(-)$/face $(-)$ coagulation (Fig. 5). When the increased salt concentration required for edge $(-)$/face $(-)$ coagulation approximates the salt concentration for face $(-)$/face $(-)$ aggregation, the dispersion coagulates face-by-face because the area between two faces is larger than between an edge and a face. Keren et al. [32] suggested that the face/face aggregation between two platelets may be initiated at surface regions that, due to the charge heterogeneity, have a lower charge density than the average value ($=$layer charge).

Transition from edge $(-)$/face $(-)$ to face $(-)$/face $(-)$ coagulation, in particular at somewhat higher particle concentration, is promoted by the following effect. As discussed by Tateyama et al. [78], the edge $(-)$/face $(-)$ attraction depends on the angle between the two particles and the thickness of the particles. This potential is very small for delaminated montmorillonite because the layers are only 1-nm thick. Attraction becomes strong enough only for an almost perpendicular orientation of the two particles. Such contacts are only formed at low particle concentrations. At higher concentrations the strong repulsion between the faces disrupts the edge/face contacts more easily and the attraction must be enhanced to reach the face/face coagulation condition.

A striking effect is the pronounced decrease of the critical coagulation concentration of the sodium hydrogen phosphates at higher montmorillonite contents (Table 3). In dispersions with high clay mineral contents and a high negative edge charge density of the particles the strong repulsion between the faces forces the particles in parallel orientation [79–81]. This orientation promotes edge $(-)$/edge $(-)$

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[1] Liquefaction describes the decrease of the viscosity of kaolin dispersions after phosphate addition, which is very important for paper coating by kaolins. Phosphates can also decrease the viscosity of bentonite dispersions but an increase of viscosity was also observed at certain conditions [53].

coagulation [63,82] (Fig. 5) which is less likely in diluted dispersions. Coagulation is then initiated when the interaction between the edges $(-)$ becomes attractive. This process may include a certain overlapping of silicate layers or lamellae to band-type fragments. This type of coagulation needs lower coagulation concentrations than initiation by face $(-)$/face $(-)$ coagulation.

In comparison with the sodium hydrogen phosphates, Na_2HPO_4 and NaH_2PO_4, and sodium diphosphate, $Na_4P_2O_7$, the sodium phosphate Na_3PO_4 shows a very weak liquefying effect. The critical Na^+ concentration is $3•25 = 75$ meq Na^+/l and, therefore, higher than for NaCl, $NaNO_3$ and NaOH but distinctly lower than for the sodium hydrogen phosphates. The reason is the high pH value of 11.5 which reduces the adsorption of phosphate by ligand exchange [75,76]. Model calculations for the homologous anion arsenate showed a distinct adsorption maximum at $pH \sim 7$ [83]. The increase of the density of the negative edge charges due to the high pH value and a modest phosphate adsorption raises the c_K value for the edge $(-)$/face $(-)$ coagulation but is not strong enough to initiate the face $(-)$/face $(-)$ coagulation.

A modest liquefying effect is also observed with sulfate anions. The critical Na^+ concentration is 36 meq/l for Na_2SO_4 and, therefore, somewhat higher than for sodium chloride and nitrate. Wendelbo and Rosenqvist [84] considered that sulfate in soils supplied by rain or industrial effluents could promote the dispersion of clays in soils.

The adsorption of counterions on the particle surface generally increases when organic solvents are added to the aqueous dispersion. Several examples were reported by Rooy et al. [73]. A further example is the decreasing c_K of NaCl for sodium montmorillonite dispersions after addition of methanol, ethanol and propanol (Fig. 2). The effect is very strong for the phosphate stabilized dispersions where the c_K is reduced from 195 mmol/l NaCl to ≤ 7.5 mmol/l NaCl.

Surprising was a certain stabilization of the sodium montmorillonite dispersion by the cationic and anionic surfactants. We assume that the hexadecylpyridinium ions adsorbed at the surface change the distribution of the sodium counterions between the Stern layer and the diffuse ionic layer. The hydrophobic chains near the surface also influence the water structure in a certain region [85] with the consequence that some sodium ions are pushed away from the surface. The resulting weak increase of the Stern potential enhances c_K from 8 to 16 mmol/l.

The stabilizing effect of the dodecylsulfate anions is stronger. At $pH \sim 6.5$ a few surfactant anions can be adsorbed at sporadically occurring positive edge charges. These anions anchored at the particle edges can act as nuclei for the clustering of additional surfactants [86]. This reaction increases the number of negative edge charges and, therefore, the salt stability. It would be interesting to determine the salt stability as a function of SDS adsorbed. However, the adsorption of small amounts of anionic surfactants at $pH > 4$ is difficult to measure because of the pronounced volume exclusion effect for anions [66,87].

An interesting aspect of coagulation of clay mineral particles should be mentioned. Frens and Overbeek [64,88,89] introduced the distance of closest approach to explain the reversibility of coagulation. The existence of such a limiting distance of

approximately two water layers ($\sim$0.5 nm) is clearly proved by the behavior of montmorillonite. Even in concentrated NaCl solutions the basal spacing of sodium montmorillonite does not decrease below 1.4–1.5 nm, i.e. two layers of water are maintained between the coagulating silicate layers [3–5]. This water is only displaced when, in addition to the electrostatic forces, specific interactions become important. A well-known example is the collapse of more highly charged silicate layers in the presence of potassium ions [1,2,4].

4.2. Coagulation by acids

The edges of the clay mineral particles are positively charged in acidic medium at pH<5. Coagulation by edge($+$)/face($-$) contacts and formation of house-of-card aggregates is likely (Fig. 5). Because of this heterocoagulation process acidic dispersions are very sensitive against salts. A sodium montmorillonite dispersion coagulated spontaneously at pH<3.5. The c_K value of NaCl increased from approximately 1 mmol/l at pH$\sim$3.5 to a plateau of $\sim$2 mmol/l at pH$=$5–6 and, with the transition into edge ($-$)/face ($-$) coagulation at pH>6, raised to 10 mmol/l [28]. The pH-dependent colloidal stability was explained on the basis of an ionization model and the DLVO theory [90].

Acids like HCl and HNO$_3$ coagulate at 5.5 mmol/l. The coagulating acid concentration, evidently, corresponds to the proton concentration (pH$\sim$2.3) at which the positive edge charge density is high enough to initiate edge($+$)/face($-$) coagulation. In the presence of sulfuric and phosphoric acid, the stabilizing effect is also evident. When these acids or their anions like $H_2PO_4^-$ or HPO_4^{2-} are adsorbed at the edges, higher proton concentrations are required to recharge the edges. Therefore, the critical proton concentration increases from 5.5 meq/l for HCl and HNO$_3$ to 25 meq/l for H$_2$SO$_4$ and 32 meq/l for H$_3$PO$_4$ (which dissociates only one proton in acidic medium; pK_a values: 2.1; 7.2; 12.7).

However, the reaction with acids not only consists of protonating the edges. Interlayer cations are also exchanged by protons, and the protons initiate a slow decomposition of the silicate layers by liberating octahedral cations [4,91,92]. This process is much slower than protonation of the edges so that the reported values may be in the right order of magnitude.

4.3. Coagulation by organic cations

The reduced salt stability and dependence of c_K on the solid content as a consequence of the specific adsorption of the counterions (as defined by Lyklema) [93,94] is very pronounced for large organic cations. The c_K of long chain cations generally decreases with the chain length (Table 7). The adsorption of the organic cations can obscure the influence of the valence of the counterions. As evident from Table 7 increasing valence does not reduce c_K as it does with inorganic counterions. The adsorption of the organic counterions is not only regulated by the electrostatic forces but is enhanced by the stronger van-der Waals interaction between the organic cations and the surface compared with inorganic cations. In addition, their influence

on the surface properties, i.e. increasing hydrophobisation with increasing chain length [85] has to be considered. The disturbance of the water structure enhances the adsorption of the counterions and decreases the Stern potential and the electrostatic repulsion.

In case of strong counterion adsorption the amount of salt at the point of coagulation can approximate the total amount of adsorption sites on the particles ('equivalent coagulation' [73]). Because of tactoid formation in the montmorillonite dispersions the amount of organic cations is in the order of magnitude of the amount of surface charges but not identical to this value [52].

It is difficult to explain the smaller c_K of the monovalent crystal violet compared with the divalent methyl green. A reason may be the different orientation of the cations on the surface. The plane of the CV cations is inclined to the silicate layer whereas MG cations are parallel to the silicate layer [95]. Probably, the van der Waals contact is enhanced between the inclined CV cations of two adjacent montmorillonite layers and promotes coagulation. The higher yield value of CV containing montmorillonite dispersions compared with the corresponding dispersions with MG was explained in a similar way [52].

4.4. Stabilization by betaines

Adsorbed betaines show a pronounced stabilization effect when the negative edge charge density is sufficiently increased by phosphate adsorption (Table 6). As the number of betaine molecules corresponds to the cation exchange capacity [54], the total number of negative betaine end groups is identical to the number of layer charges (Fig. 6), and the enhanced stability cannot result from an increased charge density. It is also not very probable that steric stabilization occurs because the chains are too short to make this mechanism effective. As the negative charges are shifted away from the particle surface, the electrostatic interaction occurs over a smaller distance than the van der Waals interaction. This would increase the salt stability. However, the decisive effect seems to be caused by the formation of lyospheres composed of the betaine and water molecules around the particles (Fig. 6a) [96]. As the lyospheres include large amounts of water, the Hamaker constant of the envelope approximates the Hamaker constant of the dispersion medium water, and the van der Waals interaction becomes weak [14,97]. The dominance of the electrostatic repulsion then increases the salt stability. For the short chain betaine $(n=3)$ the lyospheres (if ever formed) are too thin to reduce the van der Waals interaction.

In the absence of phosphate a few betaine molecules can bridge between the surface charges and the sporadically occurring positive edge charges (Fig. 6b). For betaines $(n<7)$ which are too short to form bridges the above-mentioned shift of the charges may cause the slightly enhanced salt stability.

Replacement of water by organic solvents in the lyospheres can increase the van der Waals attraction which would reduce the stability of the (salt free) dispersions [98,99]. However, the Hamaker constants for water and the alcohols are not very different (water $3.7 \cdot 10^{-20}$ J, ethanol $4.2 \cdot 10^{-20}$ J), [100], and this effect will only
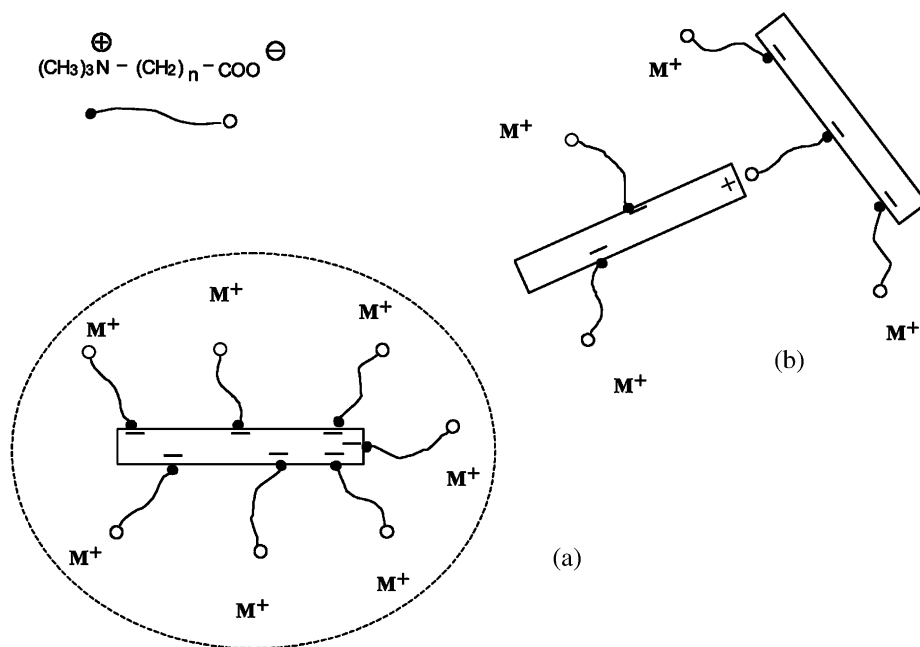
Fig. 6. Montmorillonite with adsorbed betaine molecules. (a) lyosphere composed of water and betaine molecules around the particles. (b) Betaine molecules bridging between surface charges and (positive) edge charges of two neighboring particles.

be weak. Thus, the decisive effect of alcohol addition is the compression of the diffuse layer [73] so that the betaine montmorillonite coagulates at a critical alcohol concentration (Fig. 3).

4.5. Influence of polymers

Sodium carboxy methylcellulose which increases the salt stability of sodium bentonite to 3000 mmol/l NaCl [1] provides an example of steric stabilization. The c_K values in the presence of tannate and polyphosphate are distinctly lower (Fig. 4). These polyanions stabilize the dispersion by increasing the edge charge density. The strange c_K maximum of the critical NaCl concentrations in the presence of polyphosphate disappears when the sodium ions are considered which are added to the system as the counterions of the polyphosphate anions. Thus, the sodium bentonite is stable up to approximately 600 mmol/l Na^+. The dispersions containing Quebracho tannate only tolerate total Na^+ concentrations up to ~ 450 mmol/l.

Cationic but also anionic polyethylene oxides show a certain stabilizing effect for montmorillonite dispersions. However, the presence of the charges at both ends of the polyethylene oxide chains reduces the extend of steric stabilization so that the salt stability is not pronounced (Table 9). The dispersions containing TMA-PEO

20000 and 35000 (and also the dispersions with anionic PEOs) are destabilised by less than 50 mmol/l NaCl. Probably, coagulation then occurs by PEO macromolecules bridging the particles, and the modest amounts of NaCl are required to bring the particle in somewhat closer distances. TMA-PEOs with the smallest molecular mass (~ 1500) flocculate the dispersion even in the absence of NaCl, probably by charge neutralisation. The flocculation concentration of 2 g/l TMA-PEO 1500 for the 0.05% dispersion (Table 8) corresponds to 2.5 meq/l N^+; the total charge of the montmorillonite (cation exchange capacity ~ 1 meq/g) is ~ 0.5 meq/l dispersion.

The DMHD-PEOs very likely coagulate by bridging. Flocculation of the montmorillonite by DMHDA-PEO 1500 with the shortest polyethylene oxide chains requires a minimum amount of solid particles of approximately 0.5% (w/w) as reported in many other systems [5,101]. Restabilisation was observed for DMHD-PEO 1500 and 4000 at polymer concentrations of 15 g/l (for the 1% dispersion). As long as the polymer concentration is not extremely high, the dispersion is stable up to NaCl concentrations ≥ 500 mmol/l (Table 9). The reason of this relatively high salt stability is seen in the presence of high amounts of macromolecules between the particles which impede bridging by these short chain macromolecules. The reduced salt stability at still higher polymer concentrations (30 or 40 g/l) reveals the influence of a beginning depletion destabilization. Note that each macromolecule has only two anchoring groups.

The influence of the anionic PEO is difficult to explain. There are only very few cationic sites at the particle edges where the anionic PEO can be bound. The amounts and the molecular mass of S-PEO 1500 may not be large enough for steric stabilization, and the montmorillonite dispersion is destabilised by the depletion effect. Steric stabilization becomes important for larger molecules (S-PEO 4000, 20 000, 35 000) but the dispersions still remain sensitive against salt.

5. Conclusion

Coagulation and flocculation of sodium montmorillonite dispersions (soda activated bentonites) reveal a diversity of destabilization processes. The anisometric shape and charge distribution of the montmorillonite particles cause very low critical coagulation concentrations of inorganic salts. Coagulation occurs between edges ($-$) and faces ($-$). The influence of the counterion valence corresponds to the DLVO theory. Adsorption of multivalent anions, especially of several phosphates increases the density of the negative edge charges and transforms the edge ($-$)/face ($-$) coagulation into face ($-$)/face ($-$) coagulation with distinctly higher critical salt concentrations. In dispersions of high montmorillonite contents ($> 1\%$) the coagulation is, probably, initiated by edge ($-$)/edge($-$) aggregation. Coagulation between the positive edges and the negative faces (cardhouse structure) only occurs at pH < 6.

Adsorption of the inorganic counterions at the surface plays an important role and is still more pronounced for organic cations which show very low coagulation concentrations. In these cases, the effect of the valence on the critical coagulation

concentration is obscured by the Stern layer adsorption, the different orientation of the organic counterions on the surface, and their influence on the solvent structure near the surface. As a consequence of the adsorption of inorganic and organic counterions on the clay mineral surface the c_K value depends on the montmorillonite content in the dispersion.

The substitution of the exchangeable cations by betaines provides an example of lyosphere stabilization: the betaine molecules anchored at the surface immobilize large amounts of water around the particles so that the van der Waals attraction between the particles in the aqueous dispersion becomes weak, the electrostatic repulsion dominates and increases the salt stability.

Polyethylene oxides with cationic and anionic end groups show the interplay between flocculation by charge neutralisation or by bridging and steric stabilization. However, pronounced stabilization of the sodium montmorillonite dispersions (c_K values of NaCl ≥ 500 mmol/l) was only attained for polyethylene oxides with smaller molecular masses (≤ 4000) and hexadecyl dimethylammonium end groups.

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