

Sistema Argila-Água

Parte II



PMT 5846 – Ciência e Tecnologia de Argilas

Prof. Antonio Carlos Vieira Coelho

**Departamento de Engenharia Metalúrgica e de Materiais
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Colloid chemistry of clay minerals: the coagulation of montmorillonite dispersions

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Montmorilonitas

- Tamanhos de partículas
- Morfologia
- Carga (origem, distribuição e magnitude)

- Cristais? Finos ou espessos?

- Como são as faces?
- Como são as arestas?



Montmorillonitas

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 $\sim 0.5 \mu\text{m}$. 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 space and may also vary in directions parallel to the layers (heterogeneous charge distribution).



Montmorillonitas

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 $(\text{Si, Al})_4\text{O}_{10}$ 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. $\sim 200 \text{ mV}$ 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 $\text{pH} \sim 5$ for montmorillonites [3,15,16].

Montmorillonitas

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].

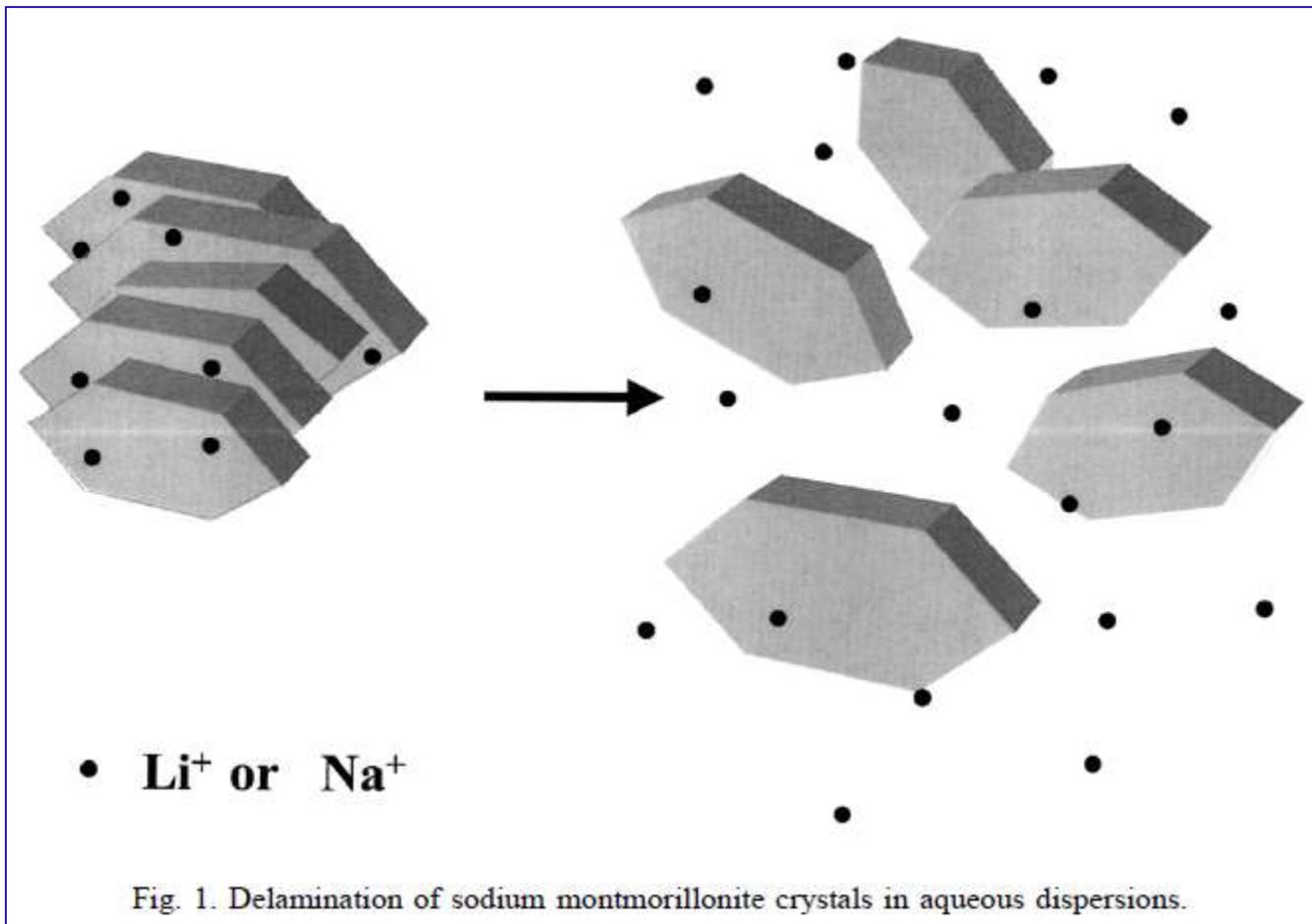


Fig. 1. Delamination of sodium montmorillonite crystals in aqueous dispersions.



Montmorilonitas

- Tamanhos de partículas
 - Faixa entre $2\mu\text{m}$ e $0,1\mu\text{m}$; tamanho médio $\approx 0,5\mu\text{m}$
- Morfologia
 - Irregular; “papel amassado”, com bordas “esgarçadas”
- Carga (origem, distribuição e magnitude)
 - Substituições isomórficas, possíveis tanto na folha octaédrica, quanto na folha tetraédrica
 - CARGA: varia entre 0,2 e 0,4 eq/fórmula unitária $(\text{Si,Al})_4\text{O}_{10}$
- Cristais? Finos ou espessos?
 - Quando **delaminadas**: (1) mais “conjuntos” (“*assemblages*”) de camadas 2:1 do que cristais; (2) partículas MUITO FINAS
- Como são as faces?
 - Grupos Si-O-Si; carregadas negativamente.
- Como são as arestas?
 - Grupos silanol e aluminol; carregadas positivamente em pH baixo (abaixo do pzc das arestas; $< \approx 5$), e negativamente em pH alto.



Quando **delaminadas**:

- (1) mais “conjuntos” (“*assemblages*”) de camadas 2:1 do que cristais;
- (2) partículas MUITO FINAS

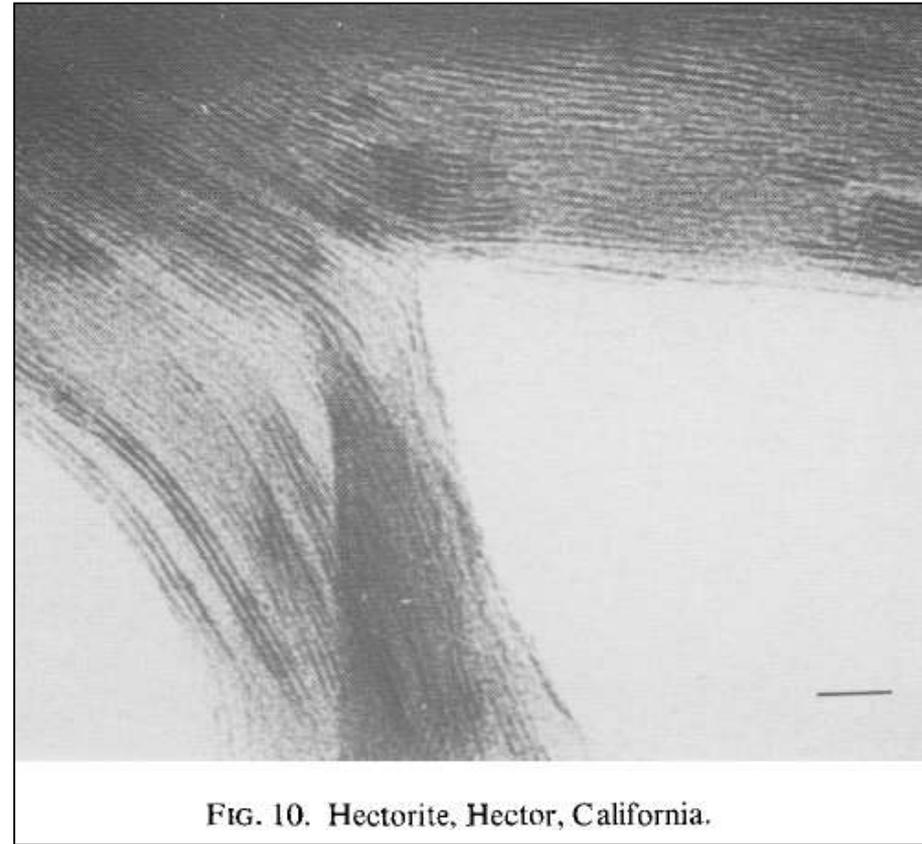
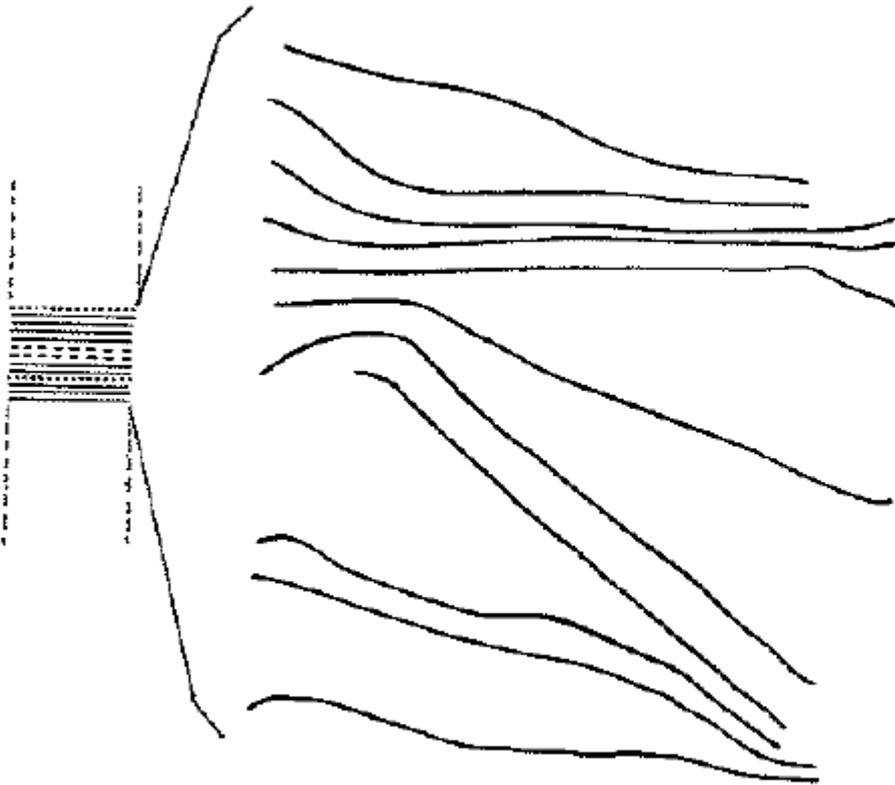


FIG. 10. Hectorite, Hector, California.

Vali, H.; Köster, H.M. *Clay Minerals* 21, 827-859 (1986)

FIG. 10 Schematic representation of the structure of a smectite-water gel.

ARESTAS

pH



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Developments in Clay Science, Vol. 1
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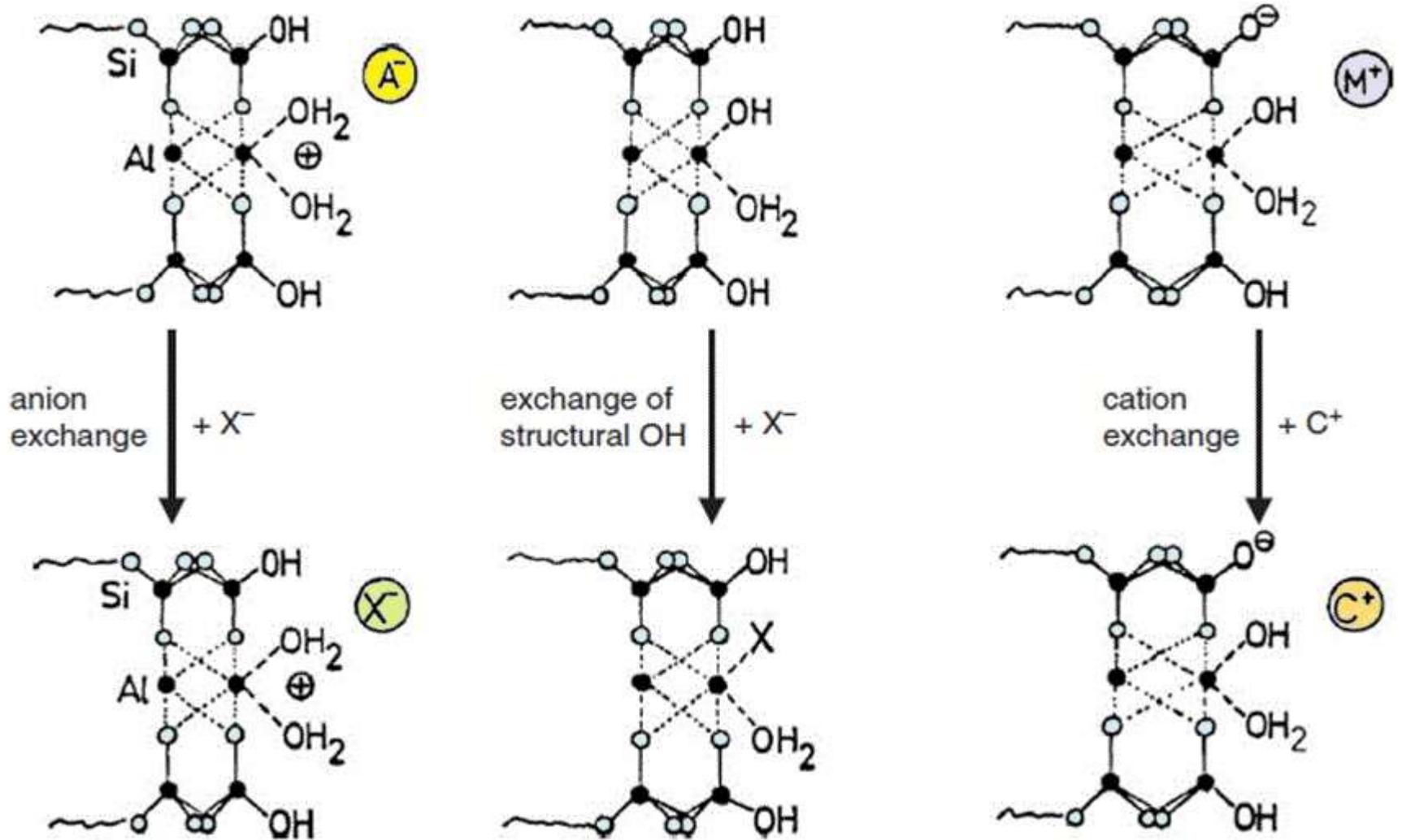


Fig. 5.2. The pH-dependent ion and ligand exchange reactions at the edges of the clay mineral layers, shown for 2:1 clay minerals. From Lagaly (1993).



Coagulation by inorganic salts

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 $<2\text{-}\mu\text{m}$ 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 turbidity 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

Coagulation by inorganic salts → o que se observa?

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

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_2HPO_4	1100	80	9
NaNO_3	16	12	6.5	NaH_2PO_4	460	40	~ 5
Na_2SO_4	18	35	6.5	Na_3PO_4	25	35 ^b	11.5
NaHSO_4	4	4	~ 5	$\text{Na}_4\text{P}_2\text{O}_7$	– ^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.



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 $\text{pH} \sim 6.5$ (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

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

$\text{pH} \approx 6.5$ 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 $+0.1 \text{ C/m}^2$ (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 $\leq 10^{-3} \text{ M}$. Therefore, coagulation occurs between edges (–) and faces (–)



As the negative edge charge density is very small, coagulation requires low sodium salt concentrations. 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, $\text{pH} > 6$



edge (-) / face (-)



Coagulation by inorganic salts → **valência do cátion**

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)

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Ca^{2+}	0.4	2	3
Al^{3+}	0.08	1	1.5

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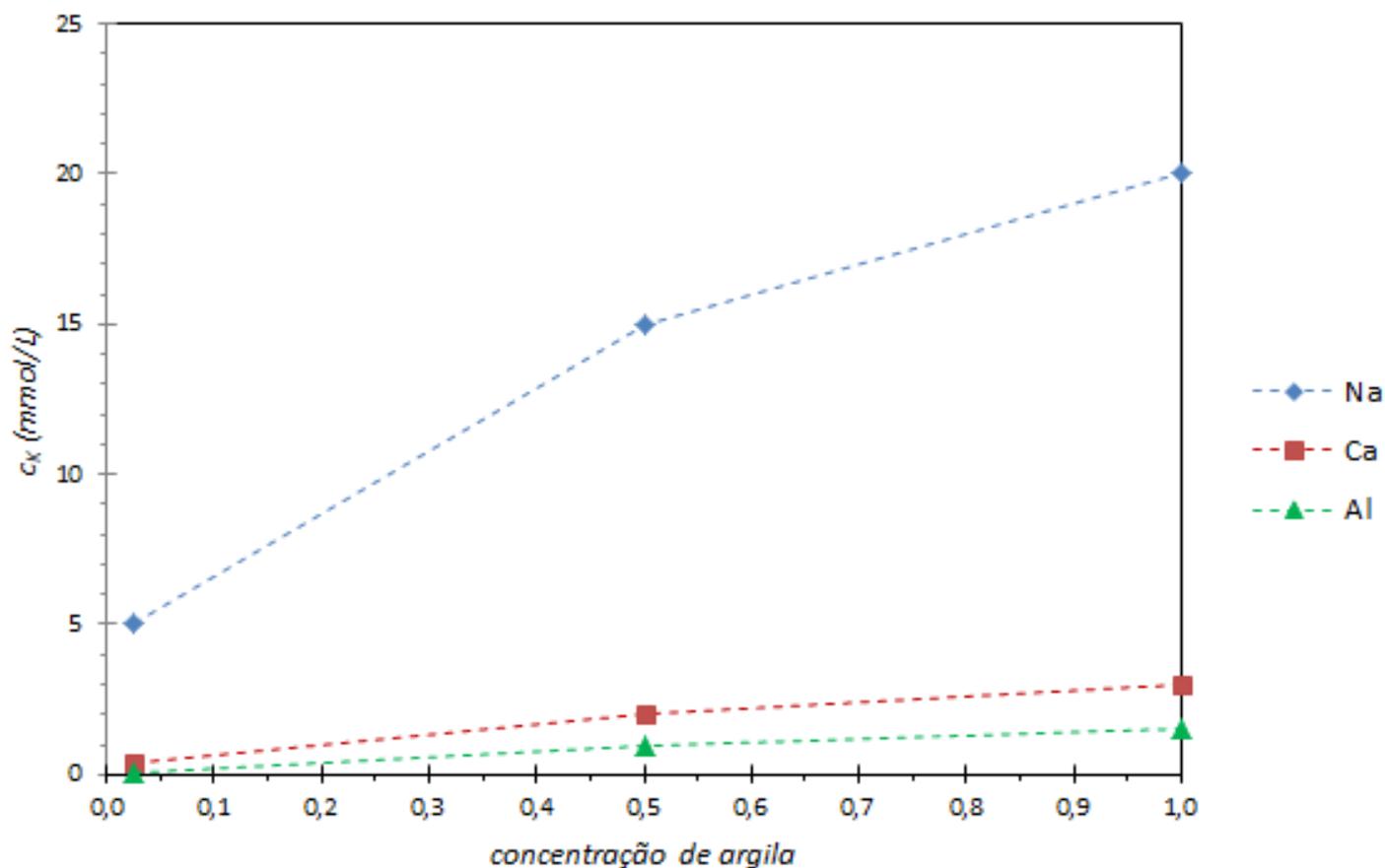
	c_K (mmol/l)		pH		c_K (mmol/l)		pH
	0.025%	2%			0.025%	2%	
NaCl	5	30	6.5	Na_2HPO_4	1100	80	9
NaNO_3	16	12	6.5	NaH_2PO_4	460	40	~ 5
Na_2SO_4	18	35	6.5	Na_3PO_4	25	35 ^b	11.5
NaHSO_4	4	4	~ 5	$\text{Na}_4\text{P}_2\text{O}_7$	– ^a	– ^a	10
				NaOH	20	30 ^b	11.5; 12

^a No coagulation up to the solubility limit of ~ 130 mmol/l.

^b 0.5% dispersion.

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)

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	0.025%	0.5%	1%
Na^+	5	15	20
Ca^{2+}	0.4	2	3
Al^{3+}	0.08	1	1.5

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

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

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

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

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).
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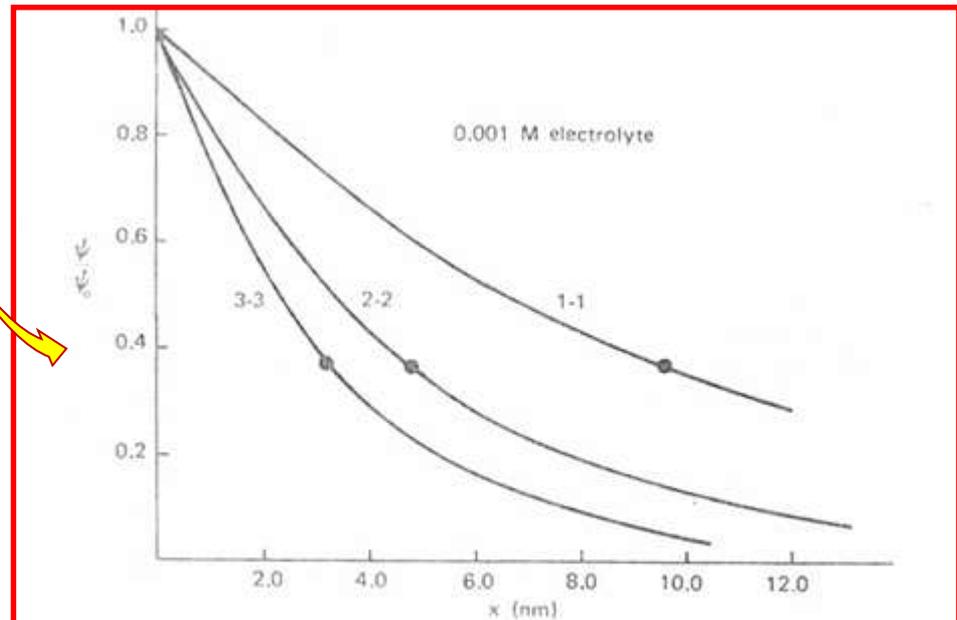
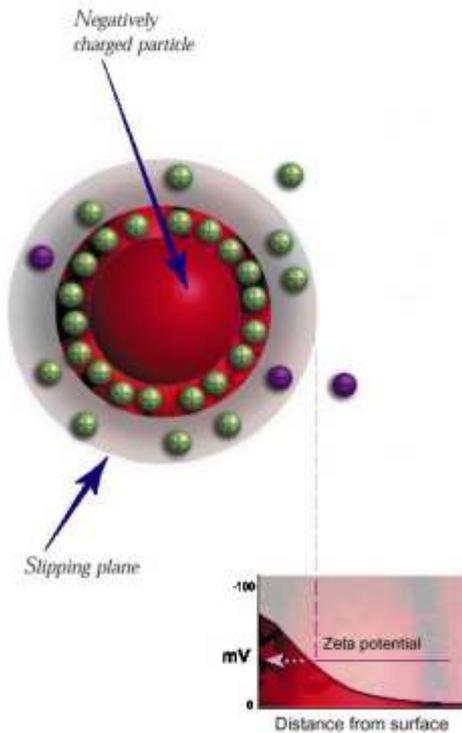


Figure 12.4 Fraction of double layer potential versus distance from a surface according to the Debye-Hückel approximation, Eq. (37):
curves drawn for 0.001 M symmetrical electrolytes of three different valence types.

Coagulation by inorganic salts → natureza do ânion

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)

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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_2HPO_4	1100	80	9
NaNO_3	16	12	6.5	NaH_2PO_4	460	40	~ 5
Na_2SO_4	18	35	6.5	Na_3PO_4	25	35 ^b	11.5
NaHSO_4	4	4	~ 5	$\text{Na}_4\text{P}_2\text{O}_7$	— ^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.



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.

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.

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_2HPO_4	1100	80	9
NaNO_3	16	12	6.5	NaH_2PO_4	460	40	~5
Na_2SO_4	18	35	6.5	Na_3PO_4	25	35 ^b	11.5
NaHSO_4	4	4	~5	$\text{Na}_4\text{P}_2\text{O}_7$	— ^a	— ^a	10
				NaOH	20	30 ^b	11.5; 12

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Coagulation by inorganic salts → **fosfatos** (“liquefying property” - defloculação)

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

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NaHSO_4	4	4	~ 5	$\text{Na}_4\text{P}_2\text{O}_7$	— ^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.



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].

The 'liquefying' property¹ 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.

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

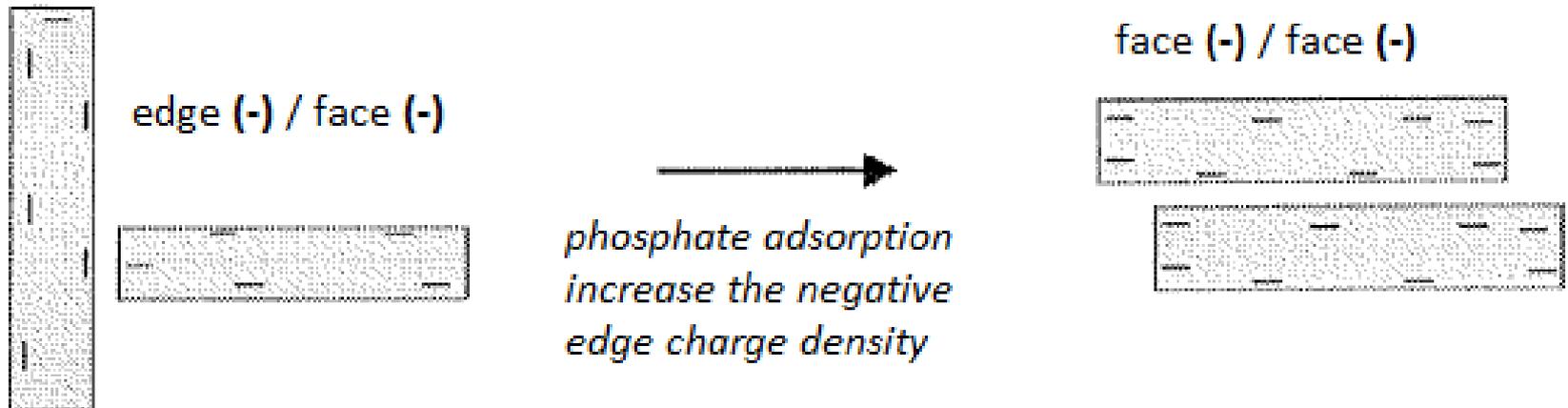
	c_K (mmol/l)		pH	c_K (mmol/l)		pH	
	0.025%	2%		0.025%	2%		
NaCl	5	30	6.5	Na ₂ HPO ₄	1100	80	9
NaNO ₃	16	12	6.5	NaH ₂ PO ₄	460	40	~5
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^b 0.5% dispersion.



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.





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 (–) 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.

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

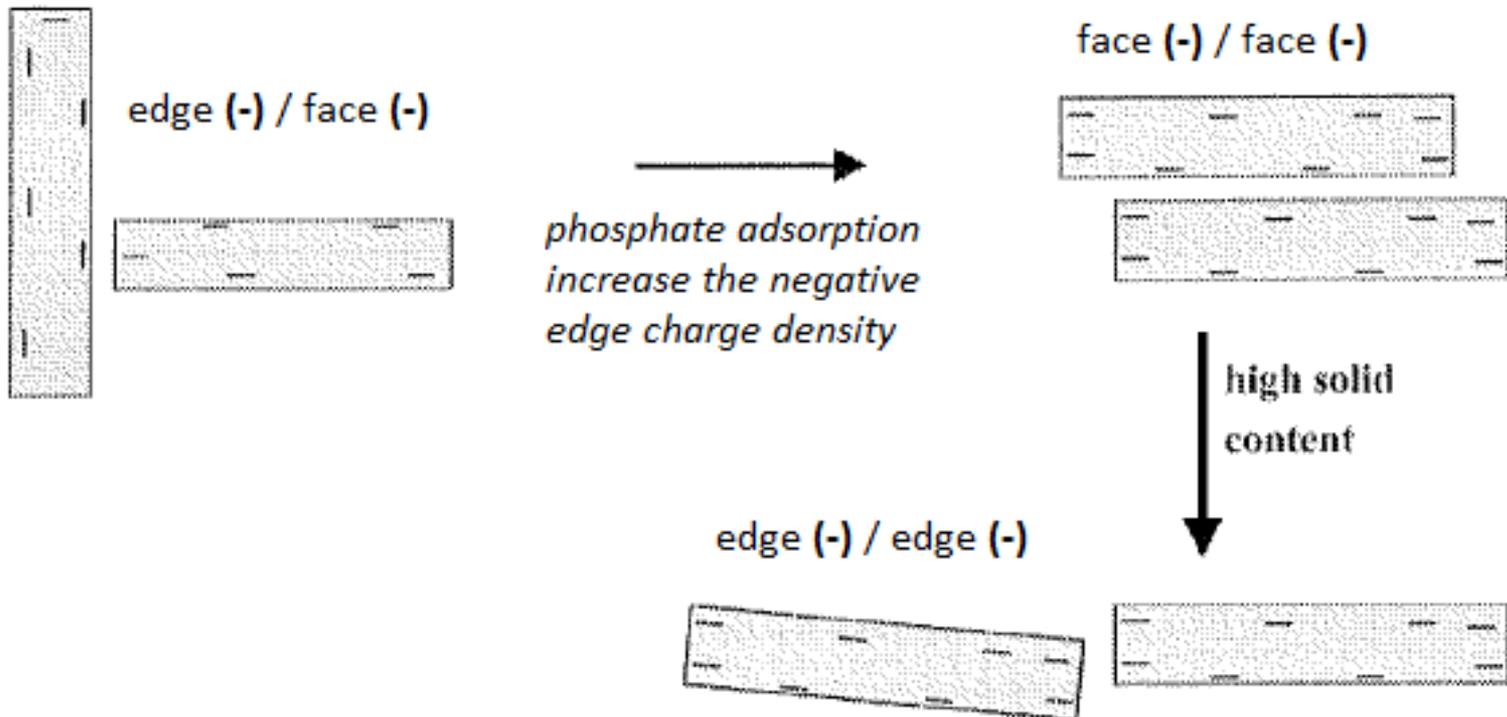
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Coagulation by inorganic salts

→ Concentração de argila na suspensão

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%
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NaCl	5	30	6.5	Na_2HPO_4	1100	80	9
NaNO_3	16	12	6.5	NaH_2PO_4	460	40	~ 5
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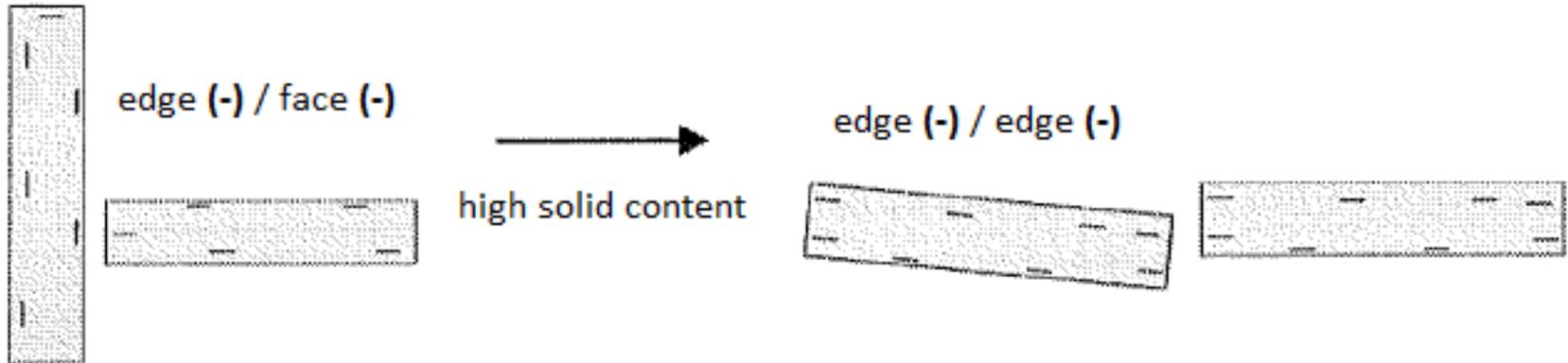
^b 0.5% dispersion.

Coagulation by inorganic salts

→ **Concentração de argila na suspensão**

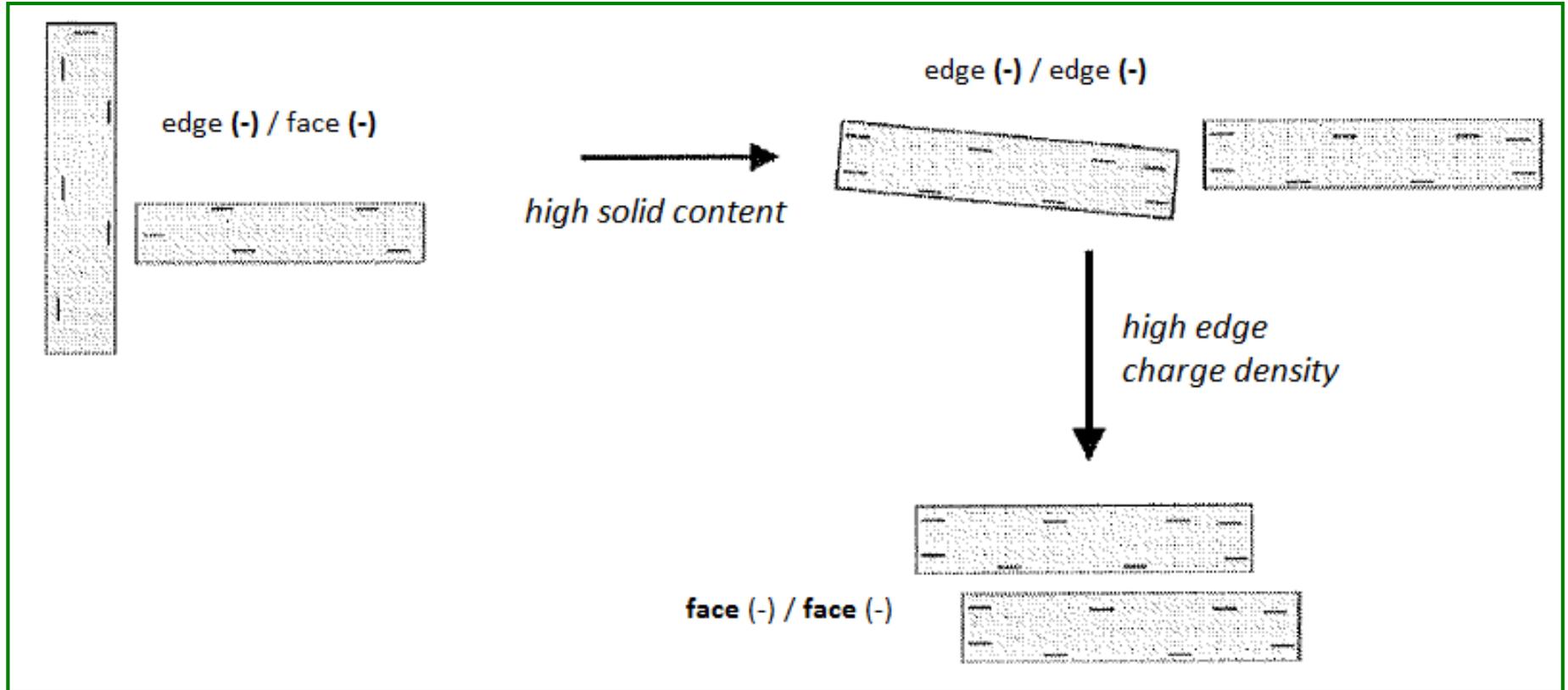
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Coagulation by inorganic salts

→ **Concentração de argila na suspensão**



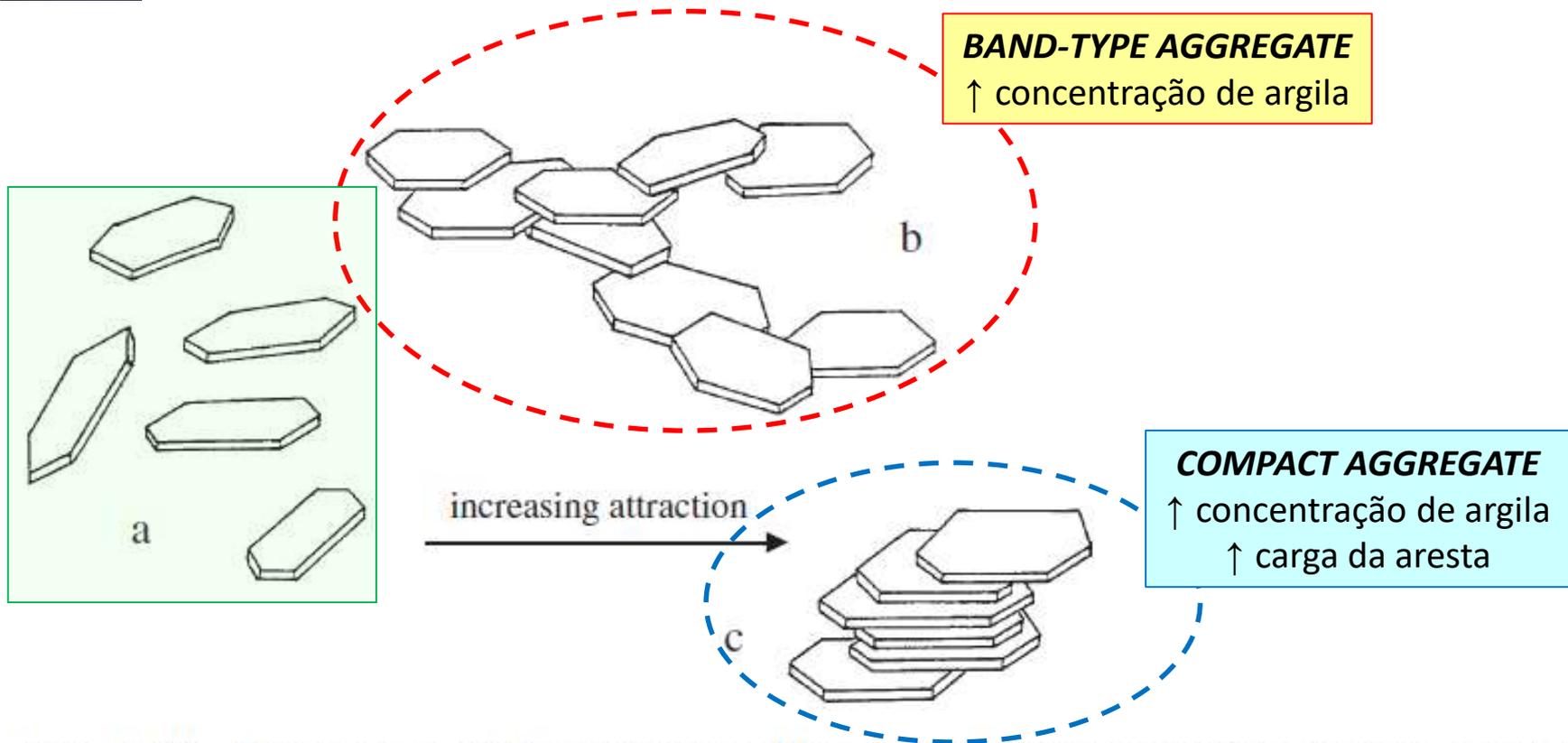
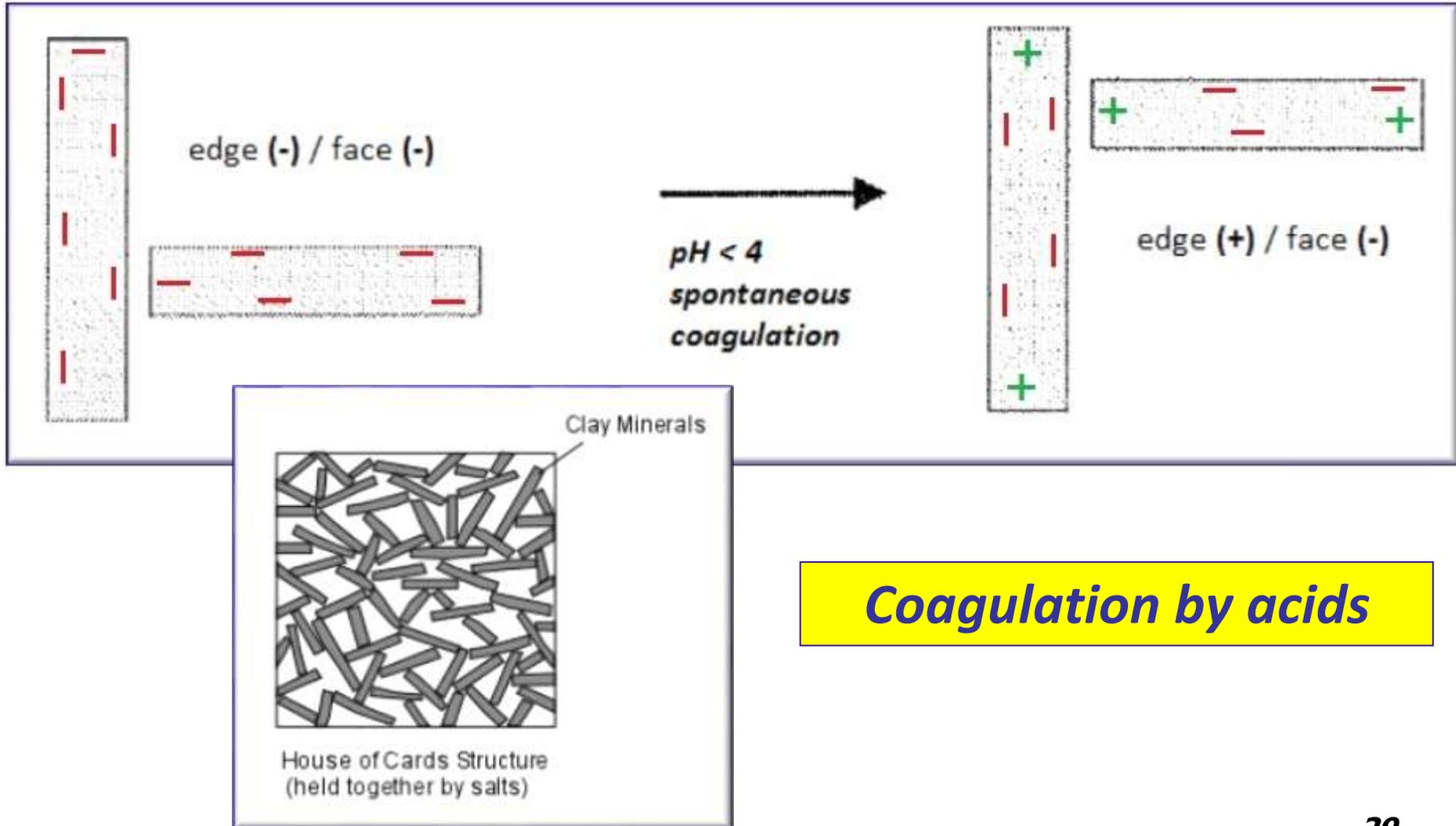


Fig. 5.29. Aggregation of the clay mineral layers with increasing attraction: (a) single layers, (b) band-type aggregates, (c) compact particles. From Permien and Lagaly (1994a).



The edges of the clay mineral particles are positively charged in acidic medium at $\text{pH} < 5$. 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.





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Surface charge heterogeneity of kaolinite in aqueous suspension in comparison with montmorillonite

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Available online 1 September 2006

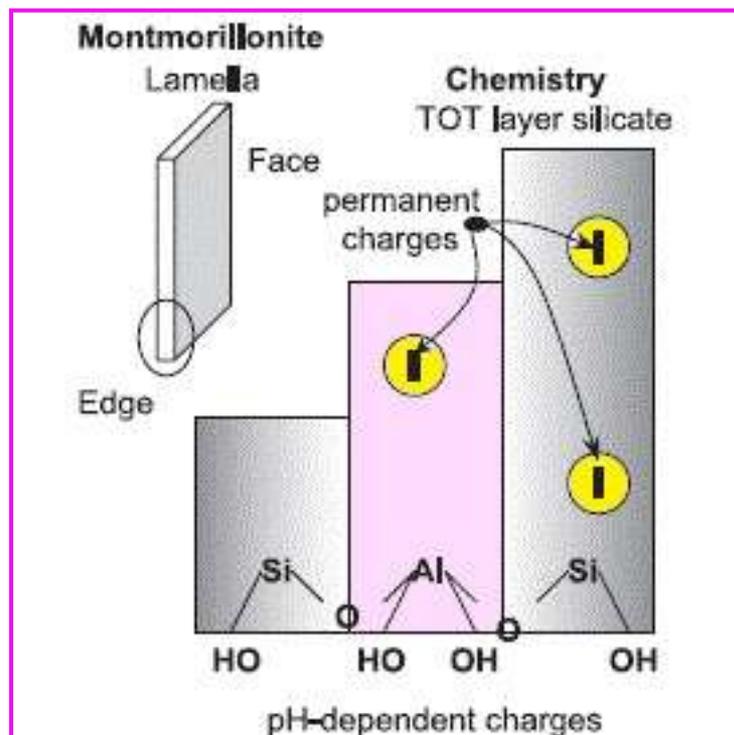


Caulinita e Montmorilonita : Características

Table 1

Size, shape, and charge properties of kaolinite KGa-1 and montmorillonite SWy-2 (data from Wan and Tokunaga, 2002)

Clay mineral	Size nm	Structural charge sites/nm ²	Estimated thickness nm	Edge area % of total
Kaolinite	< ~ 500	~ 0.3	40 to 70	20 to 30
Montmorillonite	> ~ 500	~ 14.9	1	< 1

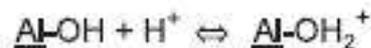


The specific role of pH

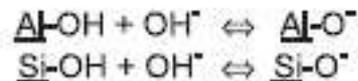
Edge charge development

in chemical reactions on edge sites

Positive



Negative



dispersed in aqueous phase

Electrostatic

patch-wise surface charge heterogeneity

Dominant electric double layer on faces

constant negative surface charge density

$$\sigma_0 = \text{constant and } < 0$$

charge neutralization by a cloud of cations

$$\sigma_0 + \sigma_{d,f} = 0$$

H^+ ions have specific affinity to permanent charges

Hidden electric double layer on edges

constant potential at constant pH

$$\psi_{0,H} = 2.3RT(\text{pH}_{\text{PZC,edge}} - \text{pH})/F$$

H^+ potential determining ions

$$\text{if } \text{pH} < \text{pH}_{\text{PZC,edge}} \quad \psi_{0,H} > 0$$

$$\text{if } \text{pH} > \text{pH}_{\text{PZC,edge}} \quad \psi_{0,H} < 0$$

charge neutralization by a cloud of counter ions

$$\sigma_{0,H} + \sigma_{d,e} = 0$$

Fig. 1. Development of patch-wise surface charge heterogeneity on montmorillonite particles dispersed in aqueous solutions due to crystal lattice imperfections (permanent negative charges on faces) and surface protolytic reactions of edge OH groups (pH-dependent charges on edges). A dominant electric double layer (edl) with constant charge density (σ_0) on the face of lamella while a hidden edl with constant potential at constant pH ($\psi_{0,H}$) on its edge are formed, and both are neutralized by the clouds of counter ions (charge densities of diffuse layers, $\sigma_{d,f}$ and $\sigma_{d,e}$, for faces and edges, respectively).

Particle

permanent charges

T face

Edges

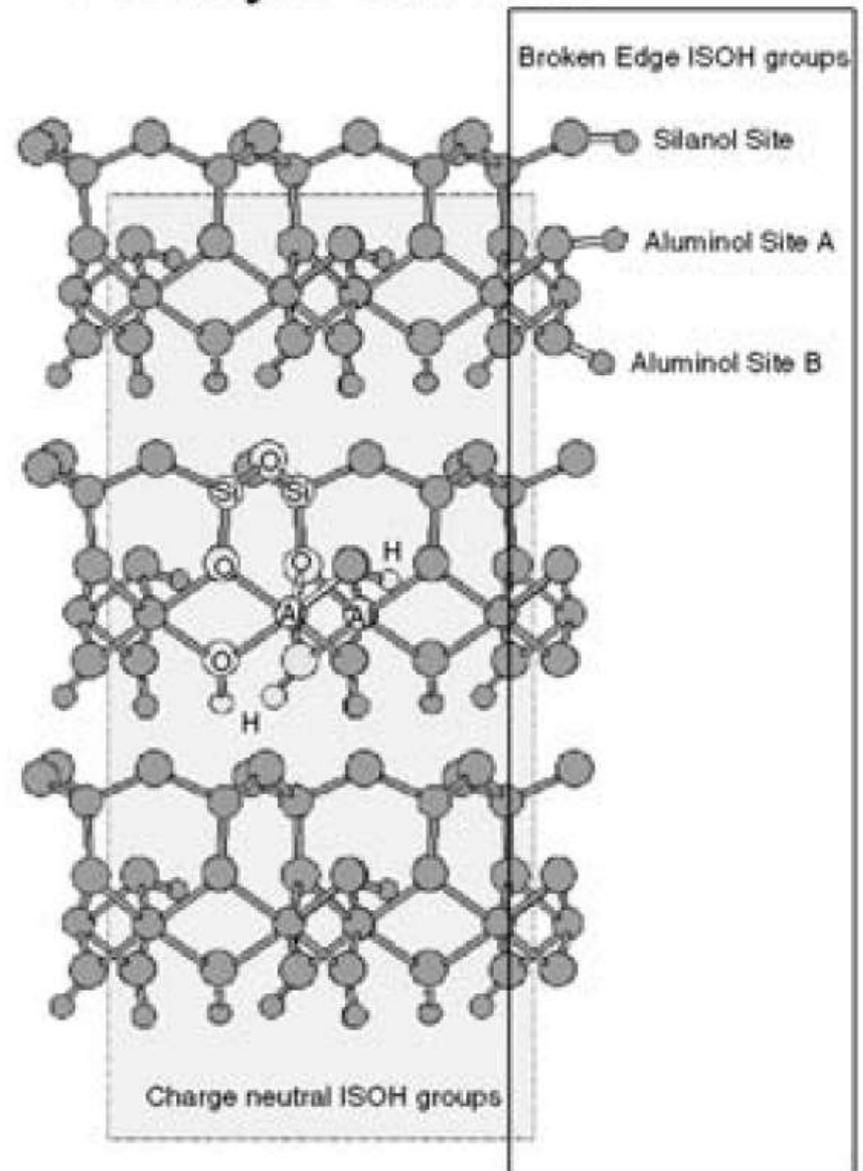
O face

pH-dependent charges

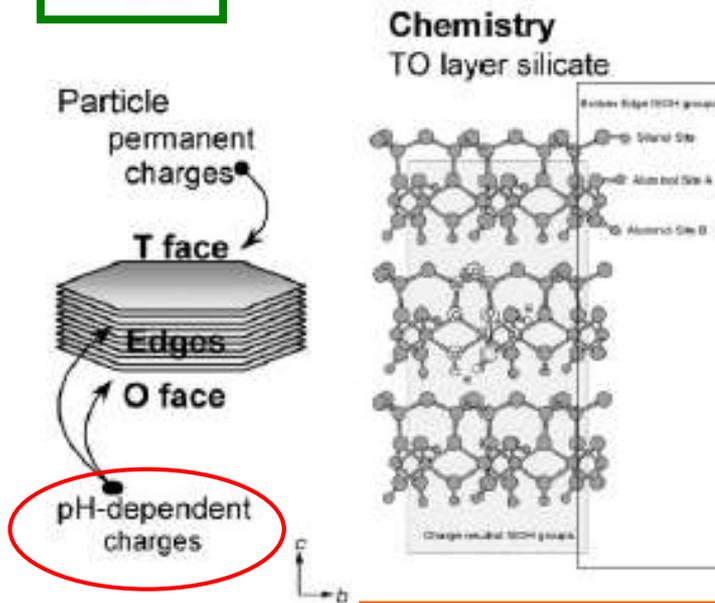


Chemistry

TO layer silicate



Kaolinite



dispersed in aqueous phase

Electrostatic

patch-wise surface charge heterogeneity

Electric double layer on T face

small negative surface charge density
 $\sigma_0 = \text{constant and } < 0$

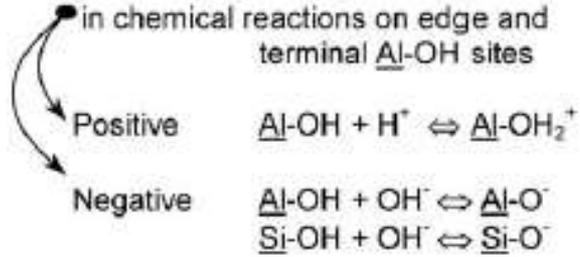
charge neutralization by a cloud of cations
 $\sigma_0 + \sigma_{d,f} = 0$

H^+ ions have specific affinity to permanent charges

Electric double layer on O face and edges

The specific role of pH

O face and edge charge development



constant potential at constant pH

$$\psi_{0,H} = 2.3RT/F(\text{pH}_{\text{PZC,edge}} - \text{pH})$$

H^+ potential determining ions

if $\text{pH} < \text{pH}_{\text{PZC,edge}}$ $\psi_{0,H} > 0$

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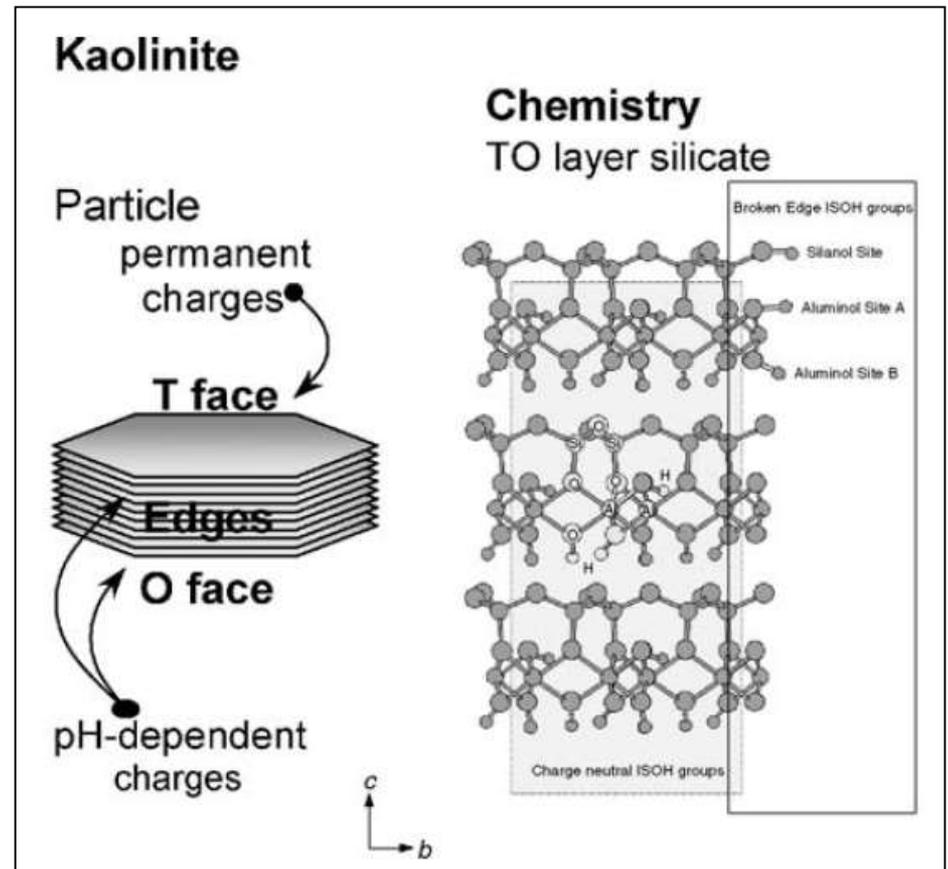
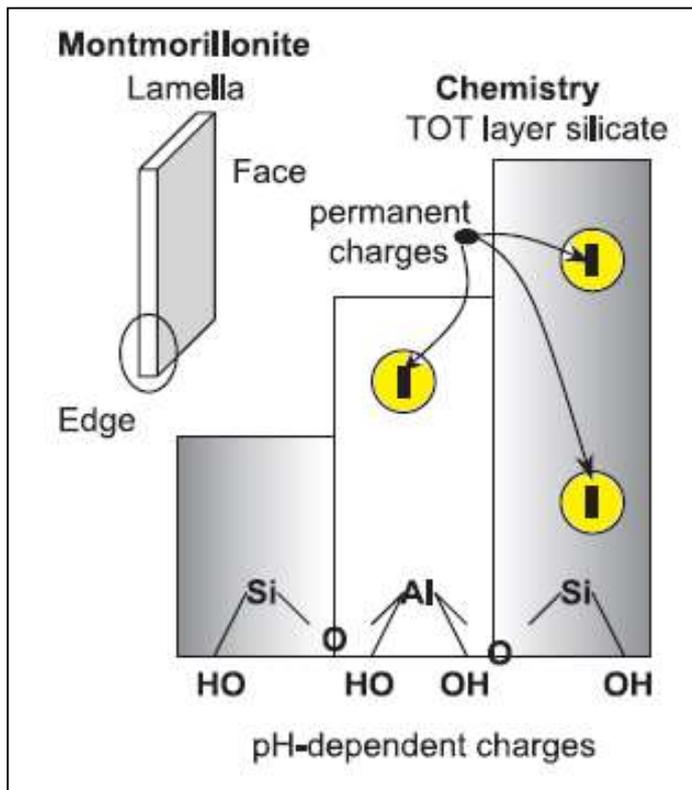
charge neutralization by a cloud of counter ions

$$\sigma_{0,H} + \sigma_{d,e} = 0$$

Fig. 1. Development of patch-wise surface charge heterogeneity on 1:1 type kaolinite (atom arrangement in silica tetrahedral (T) and alumina octahedral (O) layers inserted) particles dispersed in aqueous solutions due to crystal lattice imperfections (permanent negative charges on T faces) and surface protolytic reactions of edge and O face OH groups (pH-dependent charges on edges). An electric double layer (edl) with constant charge density (σ_0) on the T face of particle, while another edl with constant potential at constant pH ($\psi_{0,H}$) on its edges and O face are formed, and both are neutralized by the clouds of counter ions (charge densities of diffuse layers, $\sigma_{d,f}$ and $\sigma_{d,e}$, for T face and edges, respectively).

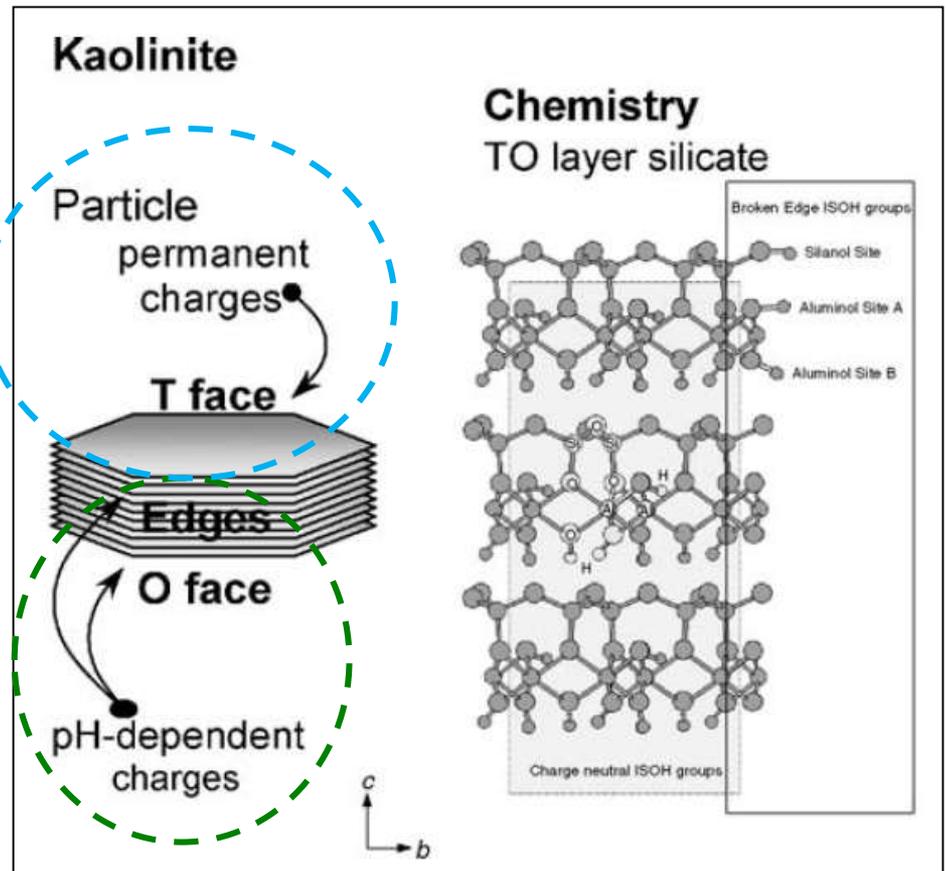
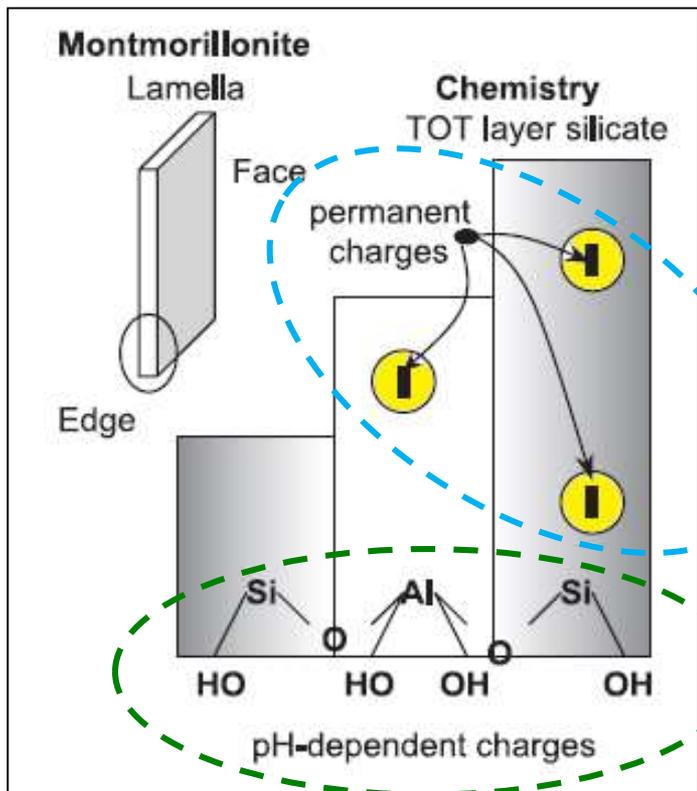


- Clay mineral particles hold both **permanent negative charges** on **faces** and **pH-dependent** (either negative or positive) **charges** developing mainly on **Al–OH active sites at the “broken edges”** and **exposed hydroxyl-terminated planes** in general.
- Since these two types of sites are situated on the given parts of particle surface, different patches exist on the basal planes and edges of clay lamellae, and so **the clay particles are the typical cases of patch-wise surface heterogeneity**.





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Surface Charge Heterogeneity

- *The patch-wise surface heterogeneity is inherent property of clay mineral particles owing to their crystal structure, the basal planes and edges of clay lamellae hold different surface sites in patches.*
- The different patches of particle surface become charged in aqueous suspensions due to the hydration of clay surface itself and rather that of exchangeable cations, and the interfacial acid–base reactions.
- *Surface charge heterogeneity of clay particles may exist in aqueous suspensions.*
- Surface charges are neutralized by a diffuse cloud of ions from electrolyte solutions.
- **Electric double layers (*edl*)** form on each patches; one type with **constant charge density on the faces bearing permanent charges**, and the other type with **constant potential at constant pH** on the parts of surface, **where pH-dependent charges develop, mainly at the edges.**



- Therefore the local electrostatic field formed around particles with different asymmetry in respect of both the aspect ratio and the surface charging of edges and faces is definitely determined by the crystal structure of clay particles.
- The electric fields on the different patches have mutual influence on processes. The electric field on faces due to charge defects in crystal lattice affects not only on ion distribution on basal planes, but also on surface charge formation at edges.

■ The effect of **pH** and indifferent **electrolytes** on the development of surface charge heterogeneity on clay particle is simultaneous, none of them can be interpreted alone.

■ The **pH** of aqueous medium has two kinds of specific role, one is the high affinity of H^+ ions to neutralize the permanent negative charges on faces, and the other is providing chemical species (H^+ and OH^-) to the surface protolytic reactions on broken edges and exposed hydroxyl-terminated planes, in which the pH-dependente double layer forms.



- The fact that ion exchange reaction with H^+ ions always takes place with changing pH, but its extent is significantly influenced by the electrolyte concentration, results in a **characteristic shift in the pH-dependent net proton surface excess** curves measured with **increasing ionic strength**.
 - The effect of **electrolytes** is also doubled, since cations are always involved in the ion exchange process, while both ions of electrolytes obey electrostatic constraints, i.e. take part in formation of diffuse (outer) part of electric double layers on each patch.
-
- With **increasing electrolyte concentration**, on the one hand the ion exchange equilibrium shifts, and on the other hand surface charge neutralization becomes more effective **enhancing the charge formation on pH-dependent sites**, besides the **narrowing of all electric double layers**.



- The existence of **oppositely charged surface parts on particles** is the most interesting question of the surface charge heterogeneity of clays in both theoretical and practical points of view.
- In general, it exists only in aqueous medium under acidic conditions, where Al–OH sites are protonated as proved at pHs below the point of zero charge (PZC) of edge sites (~ 6.5) for montmorillonite.

- Although the oppositely charged patches on clay particles are present in acidic suspensions, **the positive and negative patches may not see, and so do not necessarily attract each other.**

- **Heterocoagulation** becomes perceptible only above a threshold of electrolyte concentration, when electric double layers belonging to different patches remain localized on the faces and edges.
- This **heterocoagulation** threshold is definitely **influenced** by the **geometry** and **layer charge density** of clay particles.



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- The extreme geometry of **montmorillonite lamellae** allows that dominant *edl* extending from the particle faces spills over at low salt concentration, when the thickness of *edl* (Debye length, e.g. ~3 nm at 10 mmol L⁻¹) is larger than that of the thin lamella (~1 nm) and it remains localized on basal plane only at and above 20–30 mmol L⁻¹ NaCl.
- This threshold for the **robust kaolinite particles** is very low, only ~1 mmol L⁻¹ NaCl, where the positively charged edge region of lamellae has emerged, and the onset of heterocoagulation starts probably due to the change in the thickness of *edl* (Debye length ~10 nm in 1 mmol L⁻¹), where it becomes comparable with the thickness of kaolinite lamella (10– 120 nm).

Esmectita – *Electric Double Layer (EDL)*

The role of pH and indifferent electrolytes in the structure of

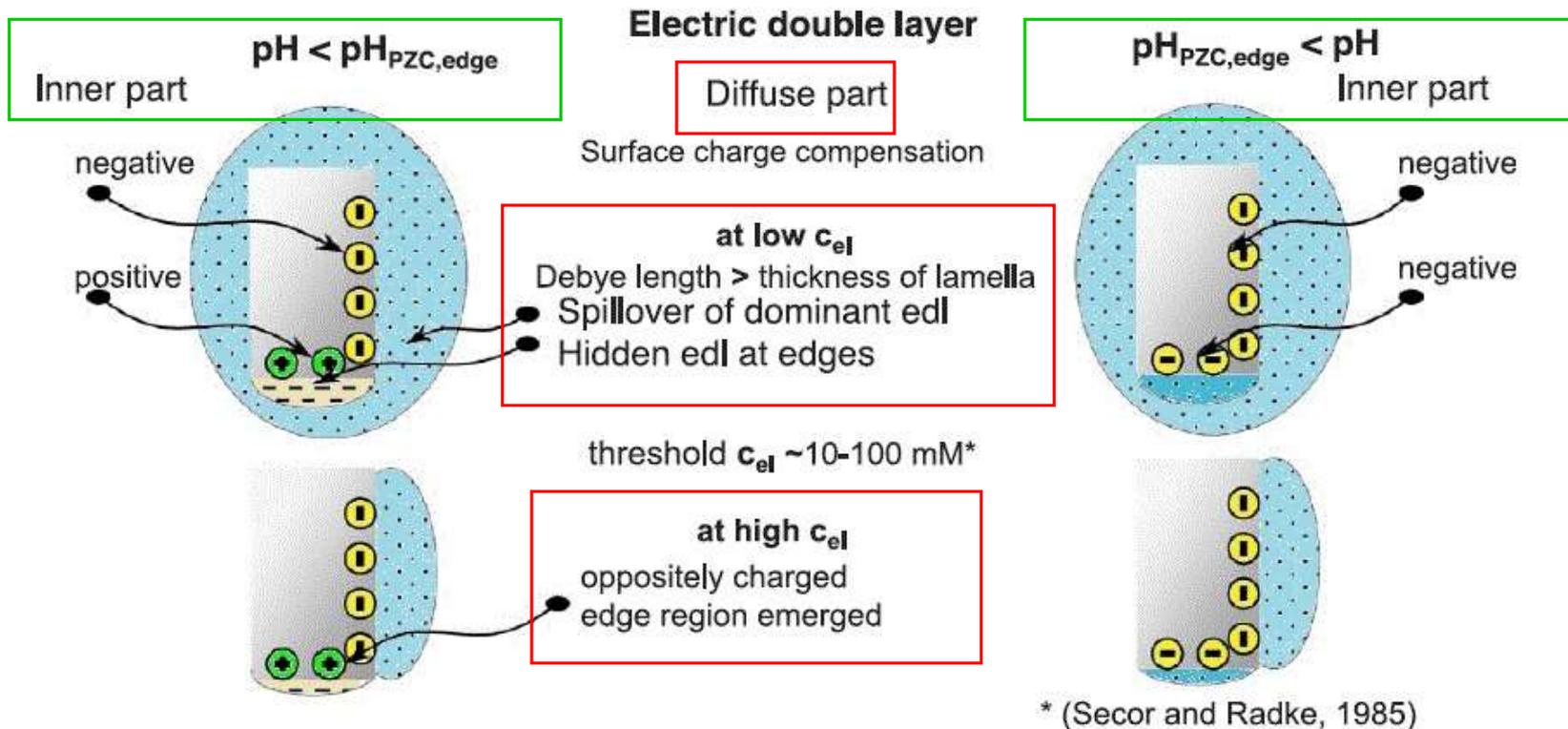


Fig. 2. Schematic representation of the dominant and hidden electric double layers forming around the montmorillonite lamellae under different solution conditions. The effect of indifferent electrolytes on particle charge heterogeneity besides the specific role of pH.



Caulinita – *Electric Double Layer (EDL)*

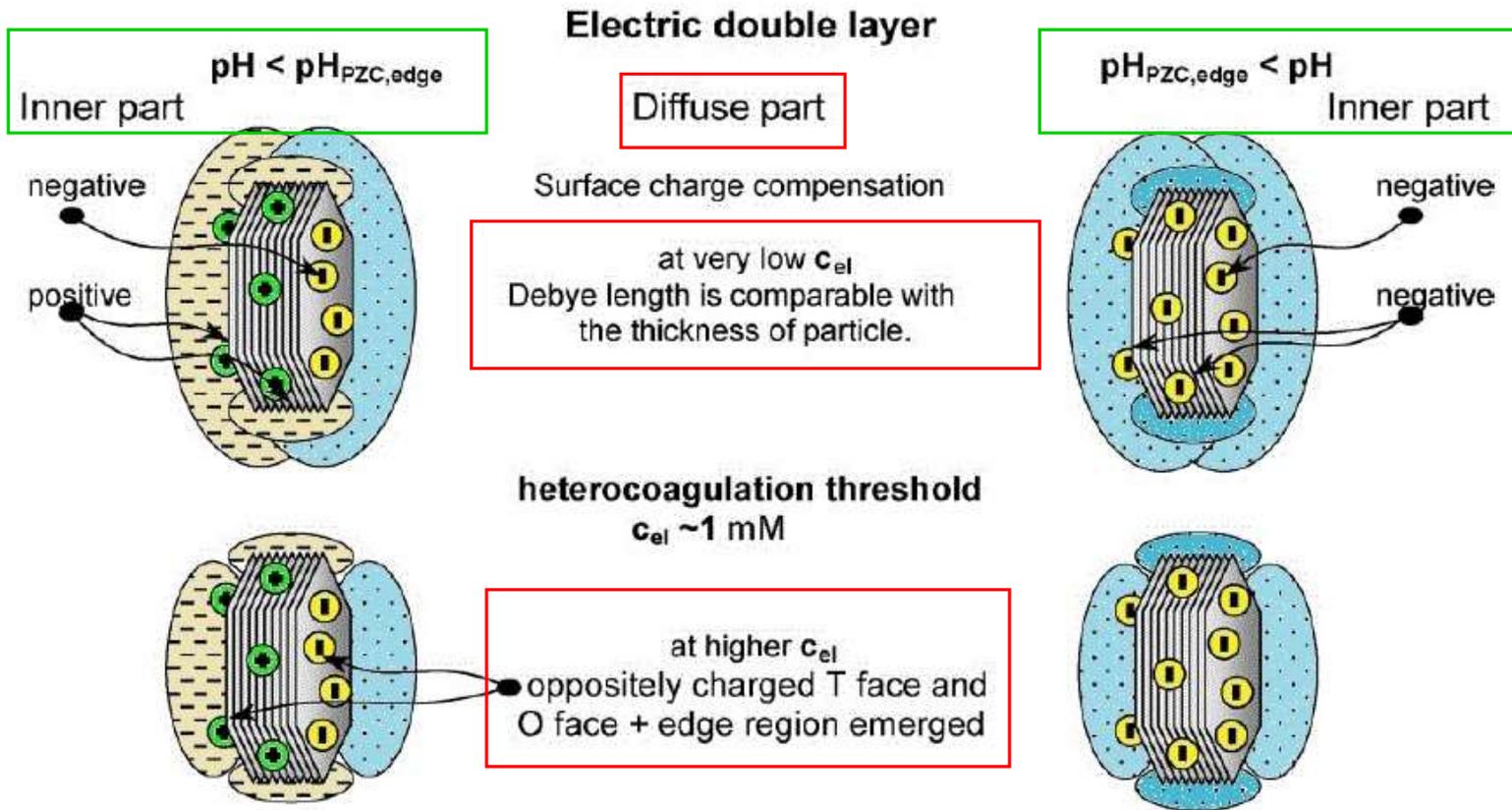


Fig. 2. Schematic representation of the electric double layers forming around the kaolinite particles under different solution conditions. The effect of indifferent electrolytes on particle charge heterogeneity besides the specific role of pH.



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