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Adsorption of surfactants on low-charged layer silicates
Part II: Adsorption of non-ionic surfactants*)**)

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Abstract: Nonionic surfactants were adsorbed on low-charged layer silicates in the interlayers. After drying, the surfactants were arranged in densely packed double layers. However, in suspension considerably higher basal spacings are measured by x-ray diffraction which indicate that large quantities of non-ionic surfactants are adsorbed. With the aid of calorimetry, enthalpies of displacement were recorded which suggest strong interactions of the non-ionic surfactants with smectites. In analogy to tests on hydrophilic SiO_2, the adsorption of smectites is found to depend on the degree of ethoxylation of the non-ionic surfactant. The adsorption declines with increasing EO content.

Key words: Surfactants – silicates – adsorption – calorimetry – x-ray diffraction

1. Introduction

In recent years non-ionic surfactants have gained worldwide importance. In the Federal Republic of Germany alone, due to the variety of application possibilities, the application quantity of non-ionic surfactants has increased from 83 200t in 1978, to 142 800t in 1985 [1].

Since an advantageous application of non-ionic surfactants is frequently based on the exploitation of interactions with interfaces, it seems to be useful to examine these interactions in detail. While ionic surfactants can be adsorbed on interfaces through ion exchange, the adsorption of non-ionic surfactants follows another mechanism.

Hydrogen bonds and van der Waals forces between polar ranges of adsorbate and substrate influence the non-ionic surfactant adsorption [2]. Which of the forces prevails depends both on the constitution of the non-ionic surfactant and of the substrate. The adsorption behavior of alkylphenol ethoxylates from aqueous solutions has been the subject of numerous works [3]. Hsiao and Dunning [4] examined the adsorption of octylphenol ethoxylate and nonylphenol ethoxylate on sand and found that the adsorption depends on the EO chain length. The adsorption isotherms belong to the Langmuir type. Seng and Sell [5] examined the adsorption of alkylphenol ethoxylates with different chain length on Aerosil with hydrophilic and hydrophobic surface. They discovered that for hydrophilic SiO_2 the adsorption clearly depends on the EO chain length while in the case of hydrophobic SiO_2 the dependence of adsorption on the EO chain length is less distinct.

In the case of hydrophilic SiO_2 surfaces, the surfactant molecules with hydrogen bonds are bonded via the EO part of the surfactant at the interface, in the case of hydrophobic SiO_2 surfaces via the nonpolar nonylphenol part of the surfactant molecule. The adsorption mechanism of

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**) This paper is part of W. Röhl's doctorial dissertation at the Heinrich-Heine University, Düsseldorf non-ionic surfactant on Volclay bentonite was described by Schott [6] using the example of dodecanol ethoxylate with 14 EO. Between the layers the surfactant molecules are arranged parallel to the surface. These results corresponded with the model developed by Lagaly and Weiss [7] for the arrangement of long chain molecules in the interlayer spaces of low-charged 2:1 clay minerals. Platikanov et al. [8] examined the adsorption of fatty alcohol ethoxylates on montmorillonite treated with quaternary alkyl ammonium compounds. The different constitution of the interlayer surfaces accounts for the difference in the results of [6] and [8].

The present work aims to show how differences in the layer silicate structure affect the non-ionic surfactant adsroption. Since with these surfactants the adsorption on hydrophilic surfaces only depends on the number of EO units [5], the alkyl chain length was not varied.

For the first time, apart from adsorption isotherms calorimetric measurements were used for the characterization of the adsorption of non-ionic surfactants on the layer silicates. In conformity with works of Partyka and Rouquerol [9] who examined the enthalpy of displacement of surfactants on sand with the aid of microcalorimetry, the adsorption tests on layer silicates were complemented with calorimetric measurements; here, the investigations by Dekany et al. [10] became of interest.

2. Materials and methods

2.1. Materials

Clay minerals: For the tests sodium bentonite from Wyoming, USA, calcium bentonite from Bavaria (Mine Linde) and a synthetically produced sodium hectorite (Laporte) were utilized. The layer silicates were not pretreated.

Non-ionic surfactants: Because of the interest of technical application non-ionic surfactants with technical purity were used. EO distributions are specified in Table 1. In addition to nonylphenol ethoxylates (NP) with 6, 8, 12, 15 EO a dinonylphenol ethoxylate with 17 EO (DNM 17) was used.

2.2. Methods

Adsorption: For the tests, surfactant solutions of different concentration were added to 100 mg layer silicate, stirred for 1 h to adjust the equilibrium and then centrifuged for more than 20 min with 6000 l/min. The adsorption equilibrium was already reached after approx. 30 min. The initial surfactant concentrations were higher than the critical micelle concentration. After decanting, the residual surfactant concentration in the supernatant solution was determined and the adsorbed surfactant quantity was calculated.

The solid material was examined both in situ and by x-ray powder diffraction in an air-dried state. In order to separate Na^+-hectorite from the aqueous solution after adsorption of NP 12, NP 15 and DNP 17, approx. 10 mg Na_2SO_4 had to be added. Bentonites did not require an addition of electrolytes.

Determination of the non-ionic surfactant concentration: Since the studied non-ionic surfactants have conjugated double bonds, their concentration was determined spectrophotometrically (UV spectrophotometers, Hitachi). Measurements were taken in the extinction maximum of 222–224 nm.

Table 1. Characteristic data of nonionic surfactants*)

	NP6	NP8	NP12	NP15	DNP17
Molecular weight (MW)	484	572	748	880	1094
Active Substance content (%)	97.5	97.5	97.5	97.5	97.5
CMC (mol/l)	1.5×10^{-5}	4×10^{-5}	7.5×10^{-5}	5×10^{-5}	1.5×10^{-4}
Average EO degree	6	8	12	15	17

*) Supplied by Hüls, Marl
Water content: lower 0.5 %; pH of 1 % solution: 8

X-ray powder diffractometry: The basal spacing of the dried layer silicates was determined by means of an x-ray diffractometer (Siemens, D 500) with computer-aided data evaluation (Diffrac 500). Measurements were taken in the angle range $2\Theta = 1\text{–}12°$ (Cu-K^{α}-radiation, Ni-filter, automatic aperture and scattered ray baffle, rotating tray). The measurements in suspension occurred by means of the x-ray diffractometer (Seifert, type XRD 3000) under Mylar foils.

Zeta potential: Zeta potential measurements were carried out by means of a microelectrophoresis-apparatus (Pen-Kem, "Laser Lee Meter", model 501). The zeta potential values were calculated according to the Smoluchowski approximation.

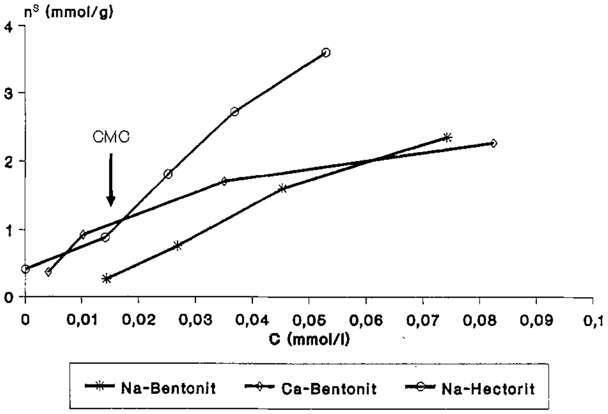


Fig. 1. Adsorption of NP6 on Na^+-hectorite, Na^+-bentonite, and Ca^{2+}-bentonite from aqueous solution at 25 °C, pH = 8

Calorimetry: A titration calorimeter by Tronac was used to measure the enthalpy of displacement during adsorption (model 1250). The isothermal measuring principle [11] is especially suitable for the examination of adsorption processes during which several reactions run parallel. With the titration method the surfactant solution is added to the aqueous layer silicate suspension by means of titration over a period of 6 min. The quantity of heat released is measured as a function of time.

3. Results and discussion

Nonionic surfactants adsorb in large quantities on low-charged layer silicates (Fig. 1). As in the case of cationic surfactants [12] there is also an adsorption in the silicate interlayer space which leads to an increase in basal spacing. For the adsorption of NP6 on Na^+-hectorite, Na^+-bentonite, and Ca^{2+}-bentonite no plateau values of the isotherms are attained for surfactant equilibrium concentrations up to 0.08 mmol/1.

A correlation can be established between this high adsorption capacity of smectites and the strong swelling power of these lowcharged layer silicates. Large surfaces result with which the surfactants can interact. The interlayer spaces of hectorite can be more easily accessed than those of bentonite. This is manifested by the strong ascent of the isotherm and a higher quantity of adsorbed Na^+-hectorite (Fig. 1) in spite of comparable theoretical interlayer surface areas for hectorite and bentonite (760–830 m^2/g).

Furthermore, this fact is confirmed both by higher heats of wetting of Na^+-hectorite ($\Delta_w H = -49$ J/g) as compared to Na^+-bentonite ($\Delta_w H = -15$ J/g) and the greater mean increase in basal spacing during the adsorption of the surfactants on hectorite. Proceeding from a basal spacing of the dry layer silicate sample of 0.94 nm [13], the basal spacing in the case of the NP6 adsorption on hectorite is 7.5 nm (measured in suspension); in the case of adsorption on Ca^{2+}- or Na^+-bentonite it is only 5.8 nm.

For the examined layer silicates Fig. 2a, b, c represent the influence of the increasing EO content on adsorption. The adsorption of nonylphenol ethoxylates on layer silicates declines with an increasing degree of ethoxylation. These results correspond with tests on the adsorption of nonylphenol ethoxylates on hydrophilic SiO_2 [4]. The decrease from NP6 to NP12 is more distinct than that from NP12 to DNP17. The lower adsorption of longer chain surfactant molecules can be explained by the fact that the EO groups are linked to the hydrophilic surface via hydrogen bonds. According to an increasing number of EO groups less adsorption places are available for flat-adsorbed molecules.

Own tests have revealed that the sedimentation volume of layer silicates in water declines with an increasing degree of ethoxylation of the non-ionic surfactant.

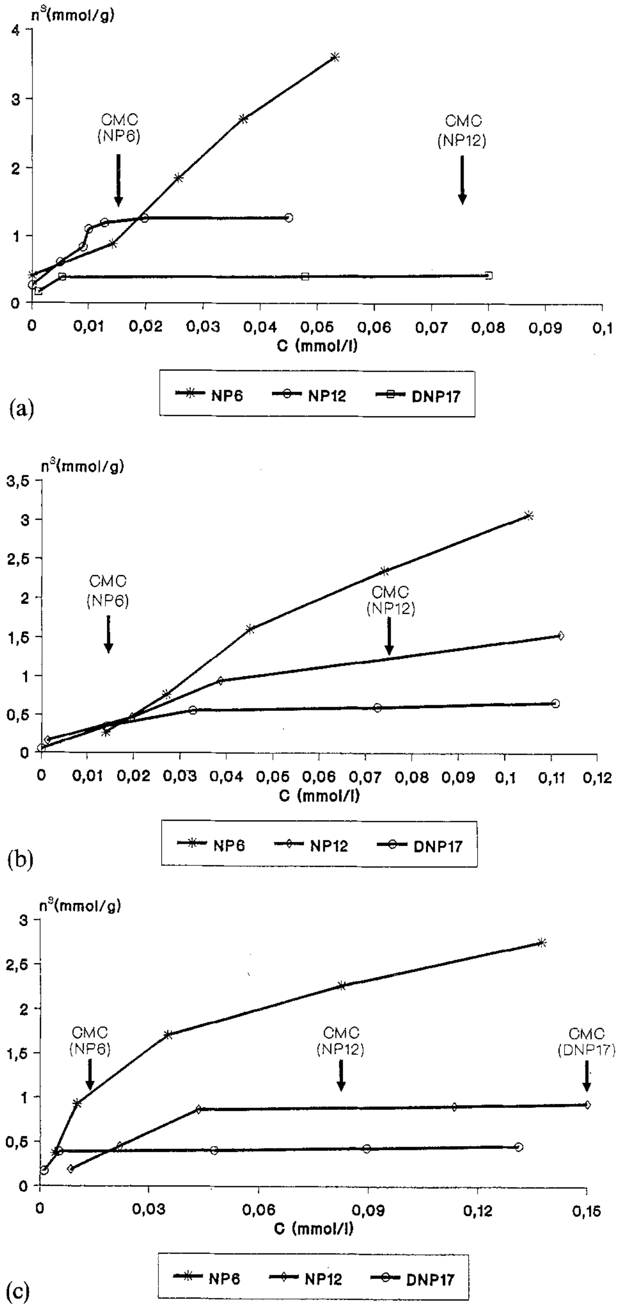


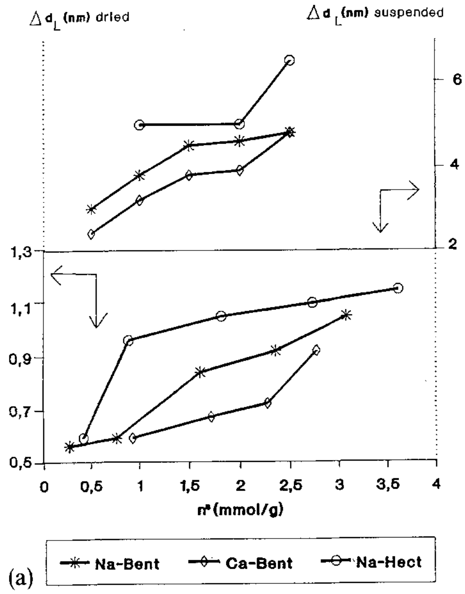
Fig. 2. Adsorption of nonylphenol ethoxylate with different degrees of ethoxylation at 25 °C, pH = 8 a) on Na$^+$-hectorite, b) on Na$^+$-bentonite, c) on Ca^{2+}-bentonite

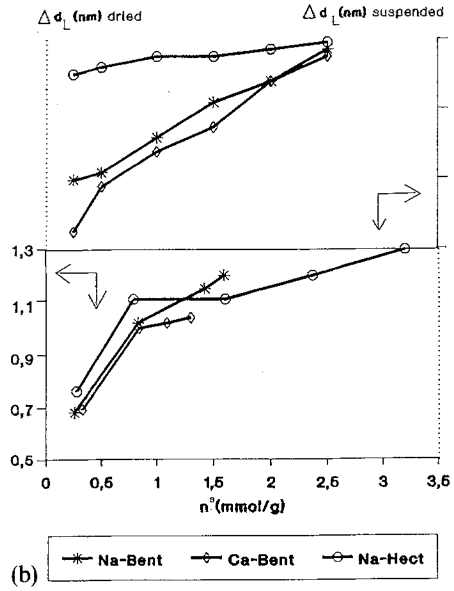
These results are congruent with the results obtained by Dekany et al. [10, 13, 14] in other dispersing agents. An increasing adsorption on the external layer silicate surface presumably leads to a stabilization in the suspension and prevents the formation of a larger sediment volume. Zeta potential measurements show that with an increasing adsorption of non-ionic surfactant molecules the zeta potential decreases because of a screening of the surface charge. For Na$^+$-hectorite the zeta potential changes from − 51 mV without surfactant addition to − 27 mV after NP6 adsorption in the saturation range. Analogous zeta potential decreases were measured for NP8, NP12, NP15, and DNP17. Because of steric hindrance, the possibility of penetration of the layer silicate interlayer spaces is limited.

For NP6, x-ray diffraction measurements in the dried state yielded a basal spacing of 2.1 nm in Na$^+$-hectorite and Na$^+$-montmorillonite. In a suspended state, medium basal spacings up to 7.5 nm were determined in Na$^+$-hectorite after non-ionic surfactant adsorption and up to 5.8 nm in Na$^+$-montmorillonite (Fig. 3). The reference point for this increase in basal spacing is the basal spacing of a dry layer silicate sample without adsorbed surfactant molecules in the interlayer space: $d_L = 0.94$ nm [13]. According to the model developed by Lagaly and Weiss [7], an increase in basal spacing of 0.4 nm for low-charged smectites corresponds to a monolayer structure of molecules arranged parallel to the silicate layers. Increases in basal spacing of 0.8 nm suggest a double layer arrangement of flat lying molecules. Increases in basal spacing of 1.2 nm represent densely packed double layers in which the molecular chains are no longer arranged completely flat on the interface. Parts of the molecular chains overlap so that the increase in basal spacing corresponds to three overlapping molecular chains. In aqueous suspensions, the surfactant molecules are arranged perpendicularly and diagonally respectively to the interface.

Figure 3a shows that for Na$^+$-hectorite, due to the better swelling capacity, increases in basal spacing of 1.2 nm (measured in dried state) are already achieved with lower adsorbed surfactant quantities while for Na$^+$-montmorillonite analogous increases in basal spacing can only be achieved with clearly higher quantities of adsorbed non-ionic surfactant.

The increase in basal spacing in the suspended state suggests that for hectorite the NP6 molecules (estimated molecular length in an extended state approx. 4.0 nm) are largely perpendicular to the intermediate surface of the layer silicate; the clearly lower increase in basal spacing of Na$^+$-montmorillonite only allows the diagonal arrangement of the non-ionic surfactant so that more space is required for the surfactant molecule. Figures 3b and 3c illustrated the increases in basal spacing after adsorption of NP8 and NP12 respectively, measured in suspension and a dried state, in relation to the adsorbed quantity. In analogy to Fig. 3a, NP8 and NP12 show comparable increases in basal spacing in suspension. In the following the adsorption capacity is calculated from the volume change in the interlayers of the layer silicates [13–16].





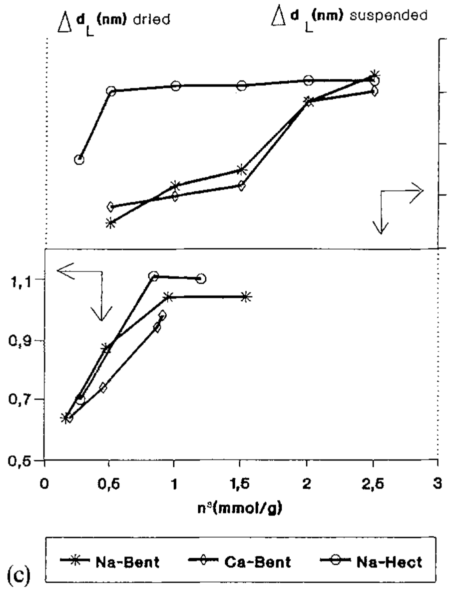


Fig. 3. Interlayer expansion Δd_L of Na$^+$-hectorite, Na$^+$-bentonite, and Ca^{2+}-bentonite as a function of the adsorbed quantity of surfactant in dried state and in suspension (reference value: thickness of silicate layer = 0.94nm [13]) a) surfactant: NP6, b) surfactant: NP8, c) surfactant: NP12

$$V_{\text{int}} = 0.232(d_L - d_L^{\text{dry}}) \quad (\text{nm}^3/(\text{Si, Al})_4\text{O}_{10})\,.$$

In the case of adsorption of NP6 on Na$^+$-hectorite, for example a basal spacing of 7.5 nm is measured in suspension. With $d_L^{\text{dry}} = 0.94$ nm [13] and a value of 360 g/mol for the molecular weight of a (Si, Al)$_4$O$_{10}$ elementary cell [14] an increase in the volume of 2.55 cm^3/g results. On the other hand, only a basal spacing of 5.8 nm is measured for Na$^+$-montmorillonite, corresponding to an increase in the volume of 1.89 cm^3/g.

In Table 2 the corresponding values for Ca^{2+}-bentonite and two longer chain surfactants (NP8 and NP12) are specified. From the values for the increase in the volume which were obtained from the increases in basal spacing, it can be calculated which percentage of this volume is filled with surfactant molecules. For this purpose, the volume of the maximally adsorbed surfactant quantity $n^s_{\max}$ must be calculated. A surfactant density of 1 g/cm^3 is presumed. (The molecular weights of the corresponding surfactants are listed in Table 1).

Table 2. Adsorption of nonionic surfactants on smectites

		Na-Hectorit	Na-Bentonit	Ca-Bentonit
$n^{s}_{\max}$ [mmol $\times$ g^{-1}] 1)	NP6	3.60	3.00	2.80
	NP8	3.20	1.50	1.20
	NP12	1.30	1.30	0.93
$V^{s}_{\max}$ [cm^{3} $\times$ g^{-1}] 2)	NP6	1.74	1.45	1.36
	NP8	1.83	0.86	0.69
	NP12	0.97	0.97	0.70
d_{L} [nm] 1)	NP6	7.5	5.8	5.8
	NP8	7.9	7.7	7.5
	NP12	8.2	8.3	8.0
Δd_{L} [nm] 3)	NP6	6.56	4.86	4.86
	NP8	6.96	6.76	6.56
	NP12	7.26	7.36	7.06
$\Delta V_{(\mathrm{int.\,in\,Susp})}$.[cm^{3} $\times$ g^{-1}] 4)	NP6	2.55	1.89	1.89
	NP8	2.70	2.62	2.55
	NP12	2.82	2.86	2.74
$V^{s}_{\max}/V_{\mathrm{int}} \times 100$[%] 5)	NP6	68	77	72
	NP8	68	33	27
	NP12	35	34	25
$\Delta h_{\max}$ [kJ $\times$ mol^{-1}] 6)	NP6	– 8.30	– 3.30	– 3.00
	NP8	–	– 4.90	– 5.10
	NP12	–	– 7.80	– 7.90

1) $n^{s}_{\max}$ and d_{L} = experimental
2) $V^{s}_{max} = n^{s}_{\max} \times V_{\mathrm{M}}$
3) $\Delta d_{\mathrm{L}} = d_{\mathrm{L}} - d^{\mathrm{dry}}_{\mathrm{L}}$ (with $d^{\mathrm{dry}}_{\mathrm{L}} = 0.94$ nm)
4) $\Delta V_{\mathrm{int}} = 0.233 \times (d_{\mathrm{L}} - d^{\mathrm{dry}}_{\mathrm{L}})$
5) $V^{s}_{\max}/V_{\mathrm{int}} \times 100$ = fraction of incorporated nonionic surfactant
6) $\Delta h_{\max} = \Delta H_{\max}/n^{s}_{\max}$

The juxtaposed results reveal that 68–77’ of interlayer space of smectites are filled with NP6, whereas approx. 23–32’ of interlayer space are filled with water molecules. With increasing molecular length, but also with increasing hydrophilicity of the non-ionic surfactants, the proportion of the interstitial non-ionic surfactant quantity clearly decreases.

The calorimetric measurements (Fig. 4) clearly show that the exothermic specific enthalpy values for NP6 on Na^{+}-hectorite are clearly stronger than those on bentonites. This must be attributed to the higher quantity of NP6 adsorbed on hectorite as compared to adsorption on bentonite (Fig. 1). The strong ascent of the enthalpy isotherm in the case of adsorption of NP6 on Na^{+}-hectorite indicates that the NP6 inclusion in the hectorite interlayers is determined by stronger forces of interaction than in the case of bentonites.

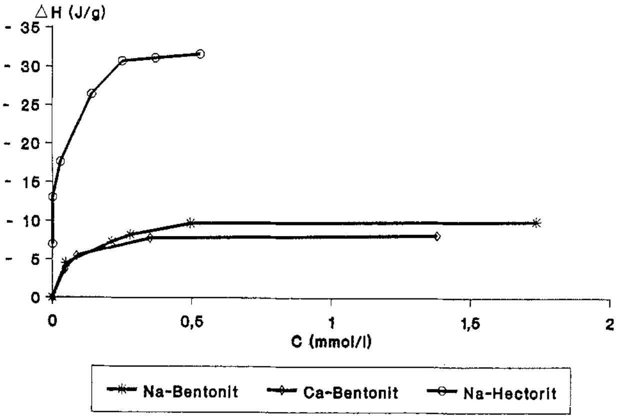


Fig. 4. Enthalpy of displacement as a function of NP6-equilibrium concentration (25 °C, pH = 8)

A comparison between the enthalpy isotherm and the increase in basal spacing (Fig. 5a, b, c) reveals that the enthalpy and basal spacing measured at the dried sample show a comparable

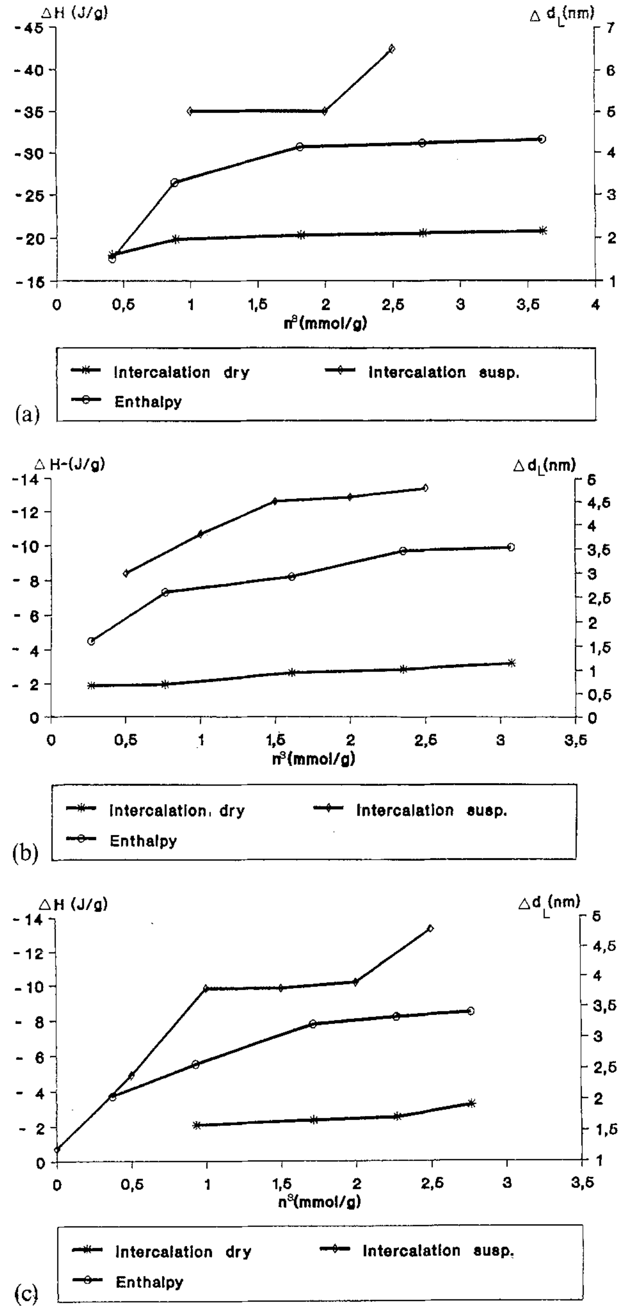


Fig. 5. Enthalpy of displacement and interlayer expansion as a function of NP6-adsorption a) on Na^+-hectorite, b) on Na^+-bentonite, c) on Ca^{2+}-bentonite

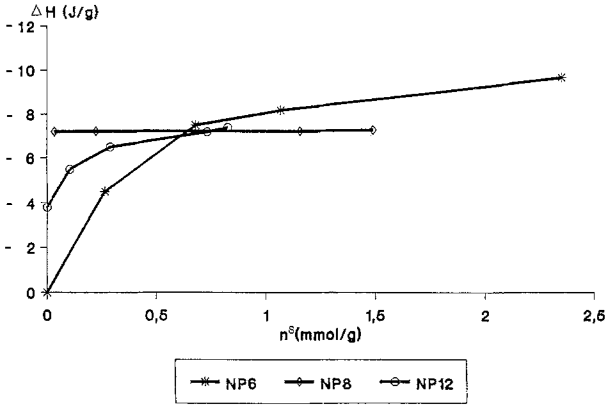


Fig. 6. Enthalpy of displacement ΔH of nonylphenyl ethoxylate with 6, 8, 12, EO as a function of adsorption of surfactant on Na^+-bentonite

dependence on the adsorbed quantity. An adsorption of the non-ionic surfactants, mainly in the interlayers, is confirmed.

Figure 6 illustrates the influence of the ethoxylation degree on the enthalpy of displacement. In spite of increasing EO contents, the enthalpy of displacement only declines insignificantly. This must presumably be attributed to the fact that the adsorption in the interlayer spaces occurs only with low energy exchange, caused by weak physical forces of interaction.

Summary

Nonionic surfactants adsorb on smectites in the interlayer spaces; after drying they form densely packed double layers. Considerably higher basal spacings are measured in suspension which suggests a perpendicular or diagonal arrangement of the adsorbed non-ionic surfactant molecules to the interface. While the increase in basal spacing of Na^+-montmorillonite and Na^+-hectorite after non-ionic surfactant adsorption in a dried state always leads to densely packed double layer arrangements, the increases in basal spacing in the suspended state clearly differ. The surfactant quantities that adsorb on Na^+-hectorite are clearly higher than those absorbed on Na^+- or Ca^{2+}-bentonite respectively. A better dispersibility and disaggregation of hectorite in aqueous suspensions accounts for this phenomenon. For the non-ionic surfactant adsorption in the interlayers, enthalpies of displacement are measured which suggest strong interactions with Na^+-hectorite. The enthalpies of displacement measured for bentonites are clearly lower than those measured for Na^+-hectorite. This must be due to lower swelling capacity, the disaggregation capacity and peptization which must be attributed among other factors to its higher layer charge. With the aid of enthalpy of displacement determined by means of microcalorimetry, it could be shown that the adsorption of non-ionic surfactants is caused by physical interaction forces. In analogy to the adsorption at hydrophilic SiO_2 the adsorption on layer silicates also declines with an increasing degree of ethoxylation; this can be explained by the fact that the interactions non-ionic surfactant/interface occur predominantly via the EO part of the molecule. The degree of adsorption and the increase in basal spacing is determined by the substrate. Basal spacings determined by x-ray diffraction in suspended state show a clear increase in basal spacings for Na^+-hectorite and Na^+-bentonite while the layer enlargement remains limited in the case of Ca^{2+}-bentonite, which is due to an incomplete and presumably delayed exchange.

List of symbols

n^s	adsorbed amount of surfactants (mmol/g)
n^s_{max}	maximal adsorbed amount of surfactants
d_L	basal spacing (nm)
Δd_L	interlayer separation because of adsorption
V_M	molar volume of surfactant
V^s_{max}	volume of adsorbed surfactants (cm^3/g)
ΔV_{int}	volume between the silicate layers (interlayer volume) (cm^3/g)
ΔH	enthalpy of displacement (J/g)
Δh_{max}	max. molar enthalpy of displacement (kJ/mol)

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