Adsorptive and Colloidal Properties of Soil Fractions.

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Introduction

The properties of soils have tremendous impact on various aspects of human life and environment. Some of those properties have purely economical character, though in the result of agricultural use may also have adverse influence on environment. However, from the more general point of view, soils may be seen as a system protecting us against spreading of local pollution thanks to their adsorptive character. At the same time, the long-term retention of pollutants by soils and other similar systems (river sediments etc.) may result in their release and transfer to air, waters as well as foodstuffs. Such a release may have a slow character, however in some situations may happen quite suddenly - depending on the external factors (floods or rains, acidity, temperature, presence of other substances like salts, character of adsorbed chemicals etc.).

Experimental

Soil samples

In this study several types of local soils (Lublin region, Poland; originally collected in 1994 and 1996 [1-4] far from inhabited, industrial or agriculturally active areas; not farmed for over 30 years) are studied (see Table 1). The soils, dried and screened on a 1mm sieve, were then divided into fractions by Kohn's sedimentation method [5]. The most interesting soil fractions from the point of view of this study are those with high pore volume and/or high surface area - especially fractions of pararendzina soil G6.

Table 1. Granulometric composition and physicochemical properties of the soil samples.

Soil [1-4]	Code	Bulk density [g/cm^3]	Particle size [mm]	Mass fraction x_f	S_{BET} (S_{soil}, S_f) [m^2/g]	Fractional BET surface area, x_{fs}	Pore volume, V_p [cm^3/g]	Micropore volume [cm^3/g]	Mean pore size [Å]
Black earth soil	**G1**	**1.03**		**1.0**	**1.00**		**0.0022**	**0**	**88**
	G1f1*		*0.5-0.2*	*0.479*	*0.31*	*0.139*	*0.0003*	*0*	*50*
	G1f2		0.2-0.1	0.375	1.7	0.596	0.0032	0	76
	G1f3		0.02-0.01	0.138	1.9	0.244	0.0042	0	89
	G1f4*		*<0.002*	*0.008*	*2.7*	*0.021*	*0.0070*	*0*	*103*
Peat soil	**G2**	**0.52**		**1.0**	**1.97**		**0.0023**	**0**	**46**
	G2f1		0.2-0.1	0.414	2.4	0.441	0.0022	0	38
	G2f2*		*0.02-0.01*	*0.017*	*2.1*	*0.015*	*0.0033*	*0*	*63*
	G2f3		<0.002	0.569	2.1	0.543	0.002	0	39
Lessive soil	**G3**	**1.35**		**1.0**	**17.2**		**0.0215**	**0.00069**	**50**
	G3f1		0.2-0.1	0.997	15.2	0.989	0.0198	0.00056	52
	G3f2*		*<0.002*	*0.003*	*54.6*	*0.011*	*0.0764*	*0.0023*	*56*

Soil	Sample		size						BET
Brown soil	**G4**			**1.0**	**8.6**		**0.0136**	**0**	**64**
	G4f1		0.2-0.1	0.809	5.8	0.742	0.0108	0	75
	G4f2		0.02-0.01	0.183	7.4	0.214	0.0139	0	75
	G4f3*		*<0.002*	*0.008*	*33.5*	*0.044*	*0.0576*	*0*	*69*
Sandy podsolised soil*	***G5****	***1.86***		***1.0***	***0.71***		***0.0010***	***0***	***57***
	G5f1*		*0.5-0.2*	*0.995*	*0.49*	*0.909*	*0.0008*	*0*	*68*
	G5f2*		*0.005-0.002*	*0.005*	*14.6*	*0.091*	*0.0378*	*0*	*104*
Para-rendzina soil	**G6**	**1.17**		**1.0**	**58.0**		**0.132**	**0.0020**	**91**
	G6f1*	*sandy*	*0.5-0.2*	*0.264*	*0.58*	*0.002*	*0.001*	*0*	*100*
	G6f2	margle	1.5-1.0	0.283	111.0	0.466	0.277	0.0024	72
	G6f3*		*0.02-0.01*	*0.094*	*50.0*	*0.070*	*0.118*	*0.0013*	*94*
	G6f4		0.01-0.005	0.113	50.1	0.084	0.118	0.0019	94
	G6f5		<0.002	0.246	103.8	0.377	0.237	0.0036	91

(The soil samples written with italic and marked with asterisk* were not used in adsorption experiment.)

Granulometric composition and surface structure

The properties of obtained fractions were studied by various methods. Standard BET surfaces as well pore volumes and sizes were calculated from the data of nitrogen adsorption at the temperature of liquid nitrogen (78K). From the point of view of surface properties the relative importance of particular soil fraction may be expressed by its "fractional surface area", x_{fs} , showing what is a share of fraction's surface in the overall soil surface area:

$$x_{fs,i} = \frac{x_{f,i} S_{f,i}}{\sum_i x_{f,i} S_{f,i}} \approx \frac{x_{f,i} S_{f,i}}{S_{soil}} \qquad (1)$$

where i - soil fraction index, $x_{f,i}$ - mass fraction, $S_{f,i}$ - specific surface area, S_{soil} - specific surface are of original soil.

Due to some losses as well as surface/pore restructuring in the sedimentation process, the sum of fractional surface areas may differ slightly from the specific surface of original soil (see Table 1).

Acidity of soil samples

Adsorption on solids depends strongly on acid/base properties of the system, i.e. both adsorbate as well adsorbent. Changes of solution pH usually affect various sorption processes (adsorption, ionic exchange, precipitation) very strongly, however most natural soils have vary large buffer capacity as well as natural pH usually within pH range 5-8.

Soil acid/base properties were investigated in (a) pure water suspension (10g of soil in 25 cm^3 of CO_2-free H_2O; measurement after 30 min.) and in (b) salt solution (10g of soil in 25 cm^3 of 1 mol/dm^3 KCl solution; measurement after 18 hrs.). The pH values of soil fractions were found to be within 5.5 to 8 with small differences between fractions of particular soils (See Table 2).

Table 2. pH of soil fractions.

Soil	Fraction	pH in H_2O	pH in KCl solution
Black earth soil	G1f1	8.02	7.72
	G1f2	7.38	6.72
	G1f3	7.06	6.71

	G1f4	7.34	6.31
Peat soil	G2f1	6.91	6.31
	G2f2	6.50	5.90
	G2f3	6.12	5.78
Lessive soil	G3f1	6.89	5.59
	G3f2	6.80	5.50
Brown soil	G4f1	7.02	6.29
	G4f2	7.13	6.54
	G4f3	7.08	5.99
Sandy podsolised soil*	*G5f1*	*6.98*	*7.02*
	G5f2	*7.01*	*6.95*
Pararendzina soil	G6f1	8.03	7.40
	G6f2	7.23	8.04
	G6f3	7.15	7.20
	G6f4	6.93	7.04
	G6f5	6.86	6.89

not used in titration or adsorption experiments

This fact may be explained by the method of separation (sedimentation) not allowing for removal of chemical impurities from soil fractions. The pH measured in water (after 30 min., 10g of soil in 25 cm^3 of CO_2-free H_2O) was higher by 0.1 to 0.5 pH units than pH measured in salt solution (after 18 hrs., 10g of soil in 25 cm^3 of 1 mol/dm^3 KCl solution).

Electrokinetic potential

The measurements of ζ (zeta) potential (ZetaSizer 3000, Malvern Instruments, USA) confirmed this observation. It was found that the dependencies of ζ on pH were almost identical for all soil fractions that contained mostly crystalline silica (quartz). However, quartz-poor fractions had ζ-potentials by 1/3 smaller in magnitude (Fig.1). The comparison of isoelectric point, pH_{iep} = 2.5 - 3 (extrapolated values) with soil acidities, leads to the conclusion that such soil components like $CaCO_3$ and CaO do affect soil pH, however they do not affect strongly the pH_{iep} values resulting mainly from the presence of acidic groups [6]. It must be mentioned, that prior to the experiments, all fractions were homogenized mechanically in dry state and further dispersed by ultrasonication in solution.
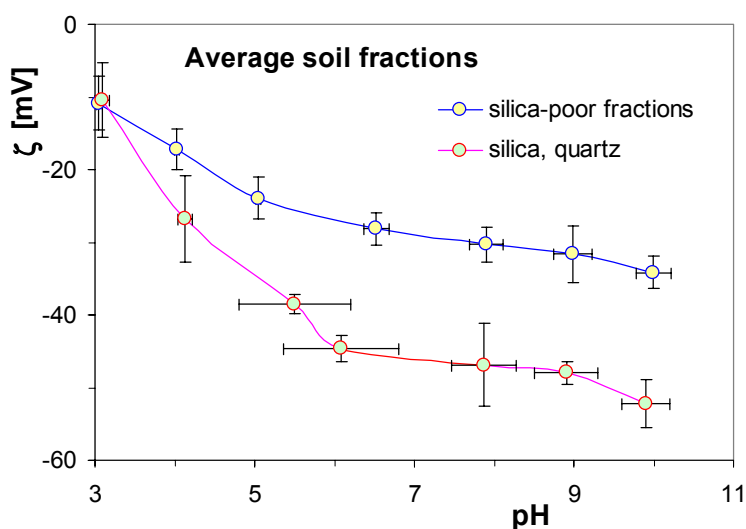

Fig. 1. Averaged ζ-potential of all silica-rich (red) and silica-poor (blue) soil fractions.

Potentiometric titration and specific surface charge in electrolyte solution.

        3 soil fractions (G1f2, G3f1 and G4f2) were selected for potentiometric titration experiments. An automatic PC-driven titrator (Dosimat 665, Metrohm, Switzerland) with a precise pH-meter (pHm240, Radiometer, Copenhagen) were used. Titrations were performed for 2 different masses (0.2g and 1.0g) in 50 cm^3 of 0.1 mol/dm^3 NaCl solution with initial pH established by addition of 0.2 or 1 cm^3 or 0.1 mol/dm^3 HCl and 0.1 mol/dm^3 NaOH was used as titrant. In figures 2, 3 and 4 the titration curves are presented together with electrolyte titration curves. Specific surface charge, Q_s, point of zero charge, pH_{pzc}, and solubility were then determined from this data (see below). The pH_{pzc} values (7.0, 7.6 and 7.5 respectively) were in agreement with earlier measured equilibrium pH values (see Table 2).
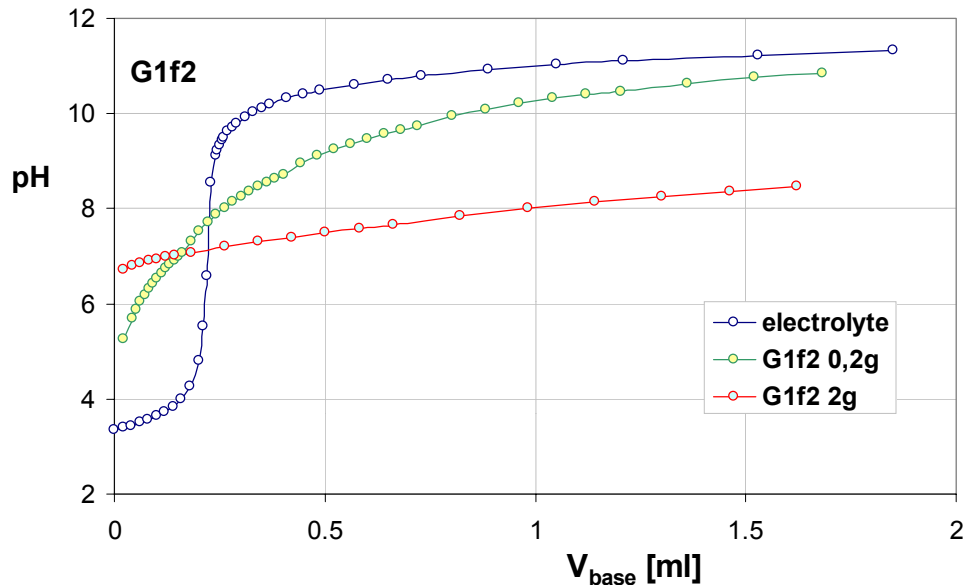
Fig. 2. Potentiometric titration of soil fraction G1f2.
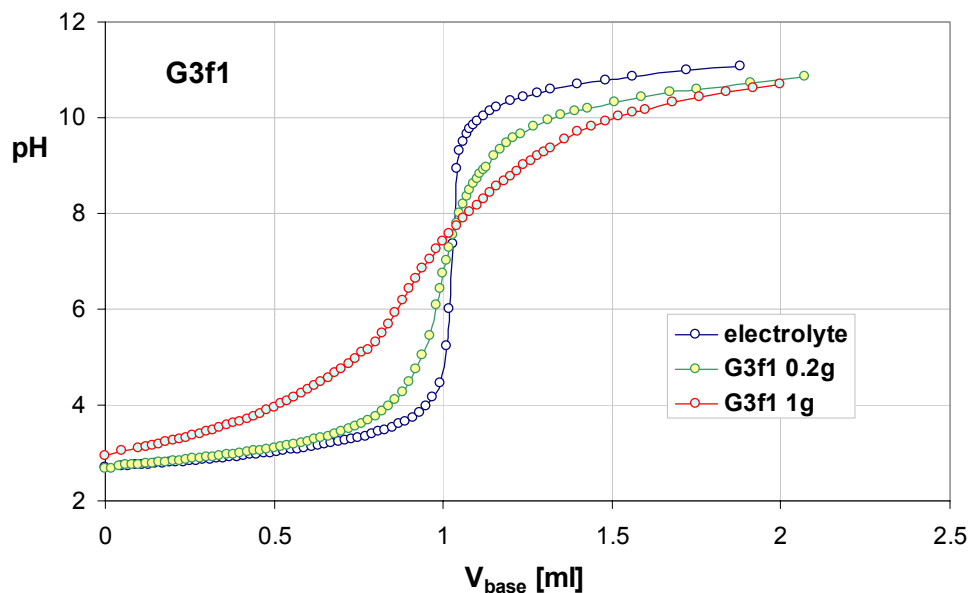
Fig. 3. Potentiometric titration of soil fraction G3f1.
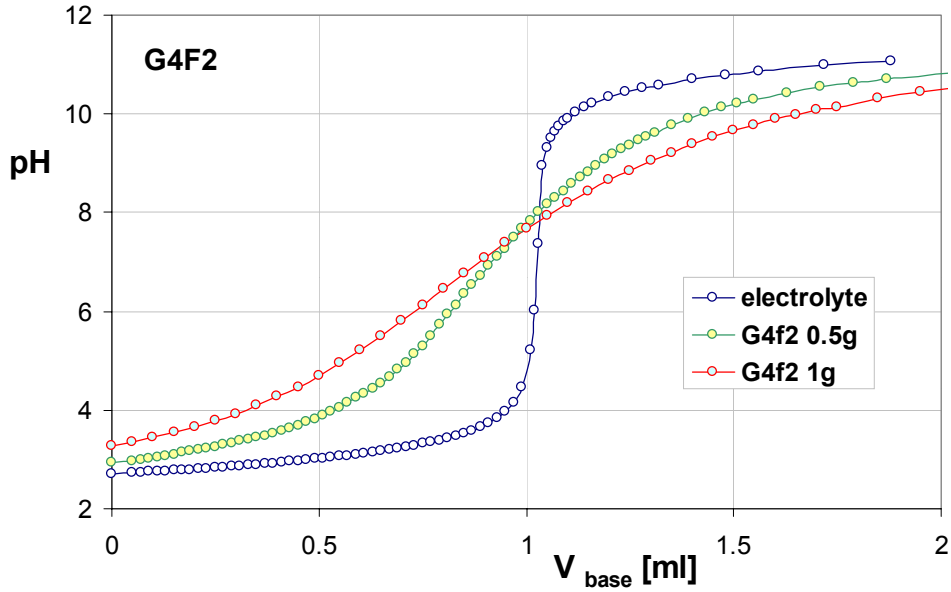
Fig. 4. Potentiometric titration of soil fraction G4f2.

The acid/base consumption curves may be interpreted by assuming that part of the base consumption (more or less when compared with electrolyte curve) results from the creation of surface electric charge (adsorption of ions, dissociation of surface groups) the rest is due to the dissolution and/or precipitation. For the constant pH and variable sample mass, the first should be proportional to the surface area, the second should be more or less constant if solution is at equilibrium (i.e. is saturated with partially soluble major sample components or minor contaminant).
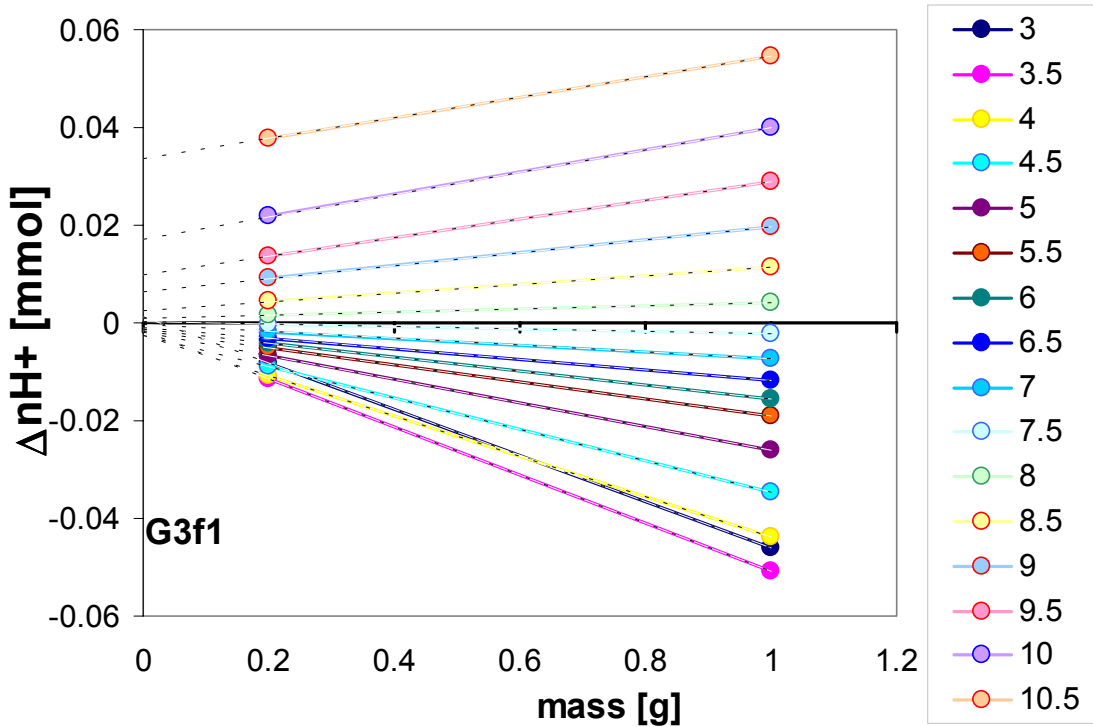
Fig. 5. Analysis of potentiometric titration data for soil fraction G3f1 (Fig. 3) according to the Eqn. 3. Slope of the lines (numbers are constant pH values) is proportional to the surface charge density, the y-intercept is related to solid dissolution.

$$\Delta n_{H^+(base)} = \Delta n^*_{H^+(base)} - \frac{Q_s \cdot m \cdot S_{BET}}{F} \qquad (3)$$

where Q_s is specific surface charge, m - sample mass, F - Faraday constant, $\Delta n_{H^+(base)}$ is the difference in base consumption [mol] between sample supension and electrolyte, whereas $\Delta n^*_{H^+(base)}$ is the constant for depending on solution pH related to sample dissolution (see above).

The example of such a plot for soil fraction G3f1 and several pH values is shown in Fig. 5.

The raw data of titration (Figs. 2-4) were analysed by means of equation (3) (cf. 5) and results are presented in Figures (6-8).

For G1f2 and G4f2 strong dissolution of soil and alkalization of solution for low pH values was found, however for G3f1 very intense dissolution for pH > 8 was observed. Both observed processes explain high buffer capacity of soils.
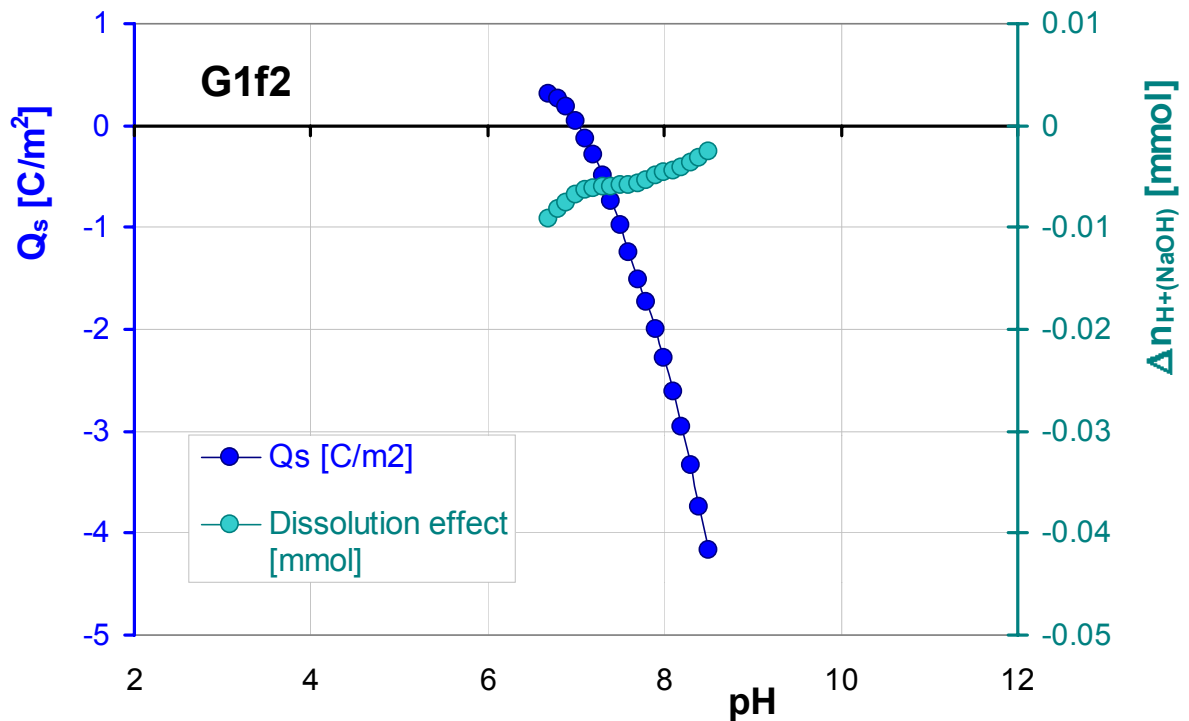
Fig. 6. Surface charge density Q_s and sample dissolution effect for soil fraction G1f2.
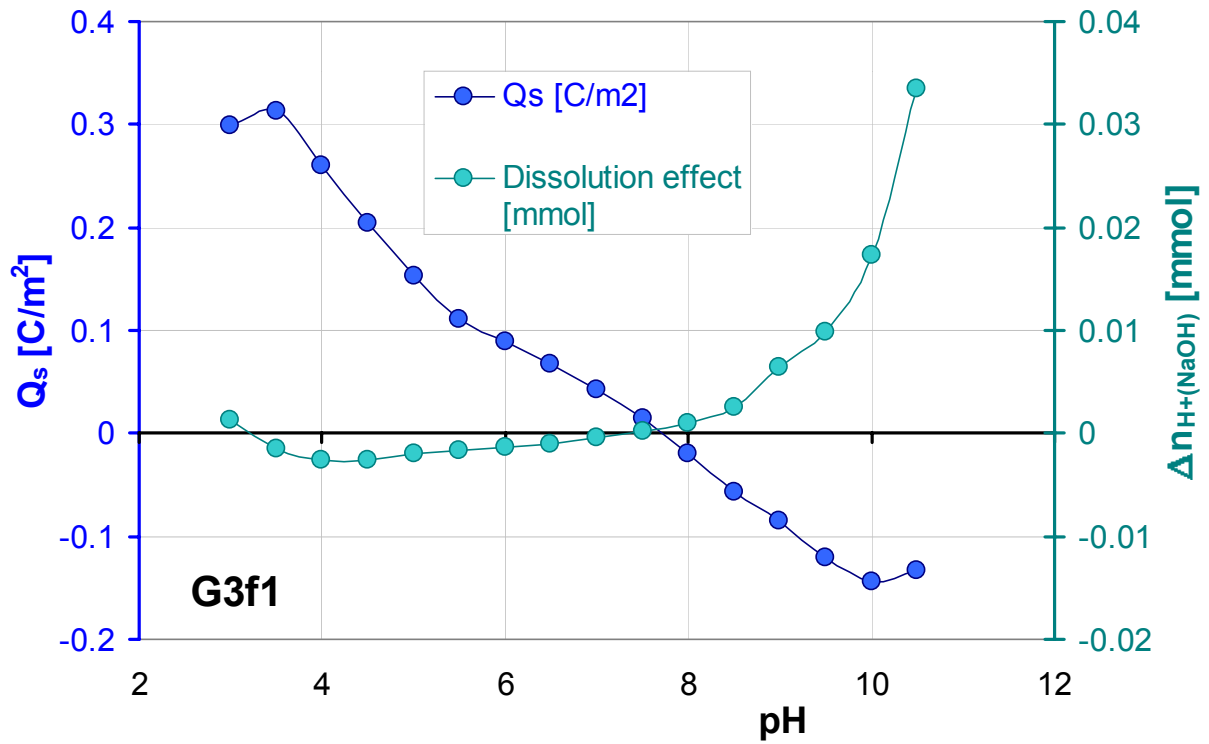
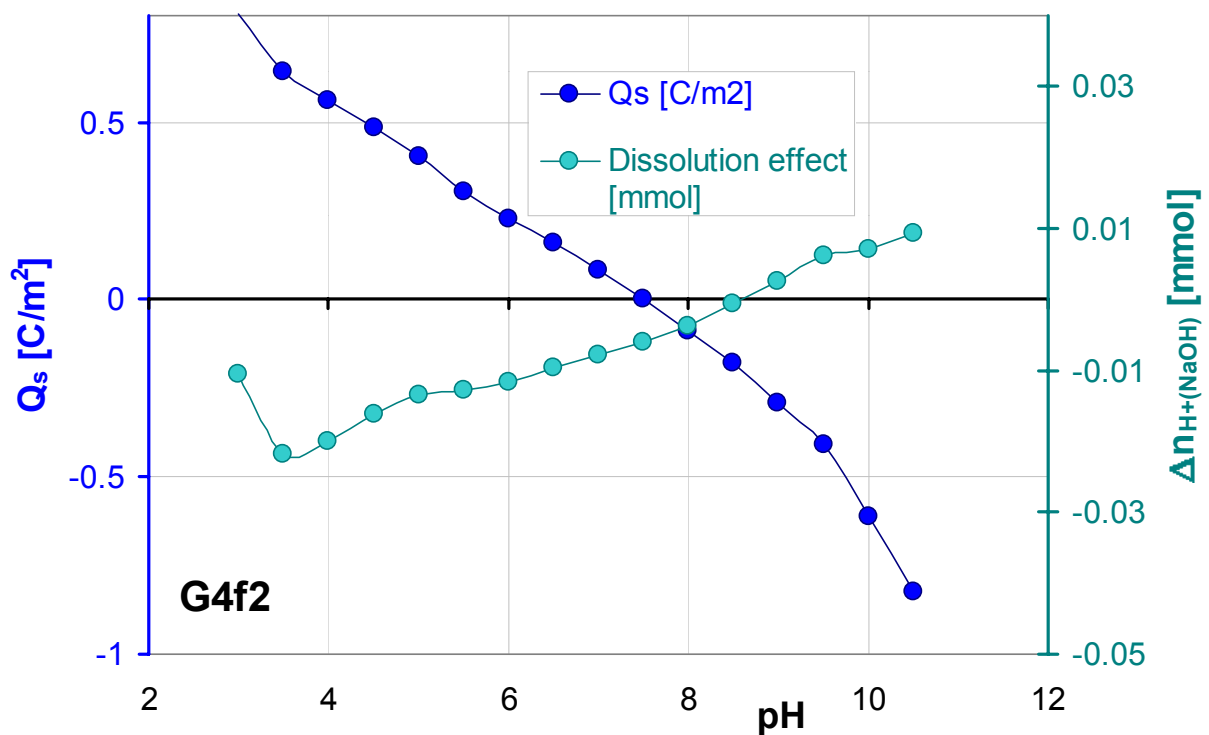Fig. 7. Surface charge density Q_s and sample dissolution effect for soil fraction G3f1.

Fig. 8. Surface charge density Q_s and sample dissolution effect for soil fraction G4f2.

Parallel determination of specific surface charge by potentiometric titration and adsorption of lauric acid by radiotracer method

A single soil fraction sample G6f2 (characterized by a high surface area ~110 m^2/g) was used in adsorption experiment with lauric acid (LA). 50 cm^3 of well stirred acidified suspension of 0.2g of G6f2 was titrated with NaOH in the presence of lauric acid. LA was added as sodium laureate, SL, and contained some radiotracer ^{14}C-SL. Initial concentrations in solution were in the range 8·10^{-6} - 10^{-3} mol/dm^3 - well below CMC for SL (~20 mmol/dm^3). 15-20 samples of suspension (3 × 0.1 cm^3 each) were collected and centrifuged during titration. Equilibrium concentration of LA in solution was determined through β-activity of samples (Beckman LS5000TD counter). Total LA sorption was calculated from mass balance. Obtained data were presented in the linear Langmuir plot *a* vs *a/c* (Fig. 9).

The character of obtained isotherms obviously does not corresponds to Langmuir model (ideal bulk and surface phases) [6]. Comparison of such behavior with several theoretical isotherms presented in co-ordinates Langmuir linear plot (Fig. 10) shows clear similarity to FG and Kiselev models (large points simulate sparse experimental data and broken lines show resulting fitted "theoretical" lines). Especially Kiselev model seems to be well fitting the experimental system properties (LA and SL form micelles by association).

By fitting the data it was found that obtained sorption isotherm data (for fixed pH values) could well be explained by the Kiselev adsorption isotherm (Eq. 2) (physical adsorption of association prone molecules):

$$a = a_m \frac{Kc \cdot [1 + K_n(a/a_m)]}{1 + Kc \cdot [1 + K_n(a/a_m)]} \tag{2}$$

where: *a*, a_m - equilibrium adsorption and adsorption (monolayer) capacity, *K* -adsorption equilibrium constant, K_n - association constant and *c* - equilibrium concentration.
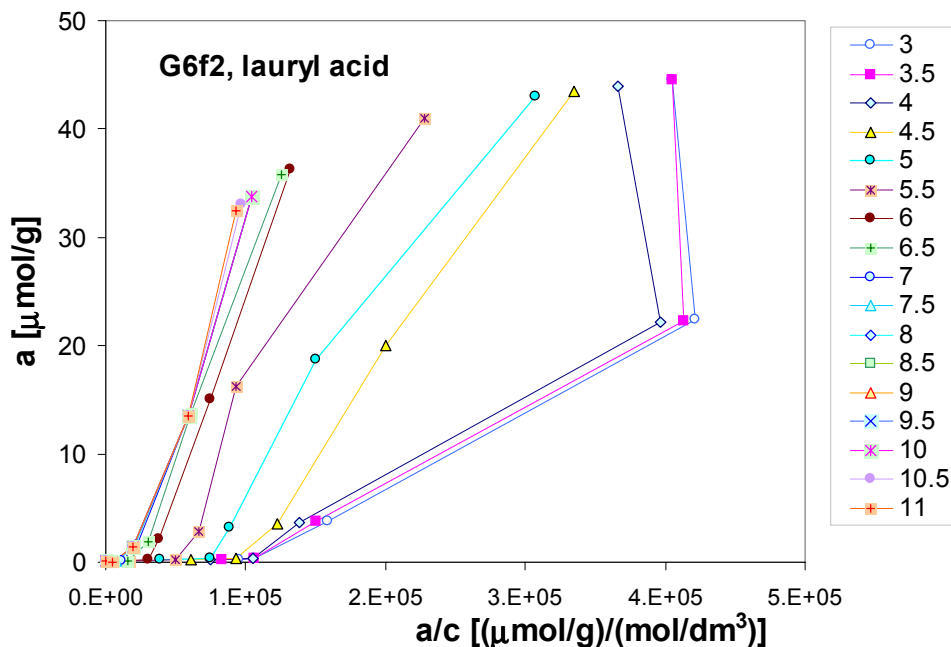

Fig.9. Sorption of lauric acid (LA) on soil fraction G6f2 in linear Langmuir co-ordinates.
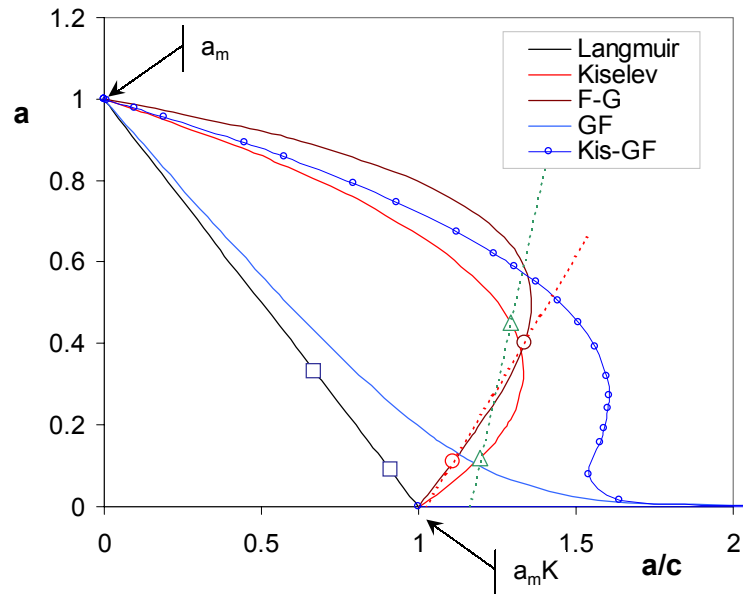
Fig. 10. Comparison of model isotherms [6]: Langmuir (L, ideal adsorbed and bulk phases), Fowler-Guggenheim (FG, non-specific lateral interactions in adsorbed phase), Kiselev (Kis, associative interactions in adsorbed phase), Generalized Freundlich (GF, energetic heterogeneity in surface phase), Kiselev-GF (Kis-GF - lateral interactions and surface heterogeneity). Isotherms are presented in linear co-ordinates of Langmuir model.
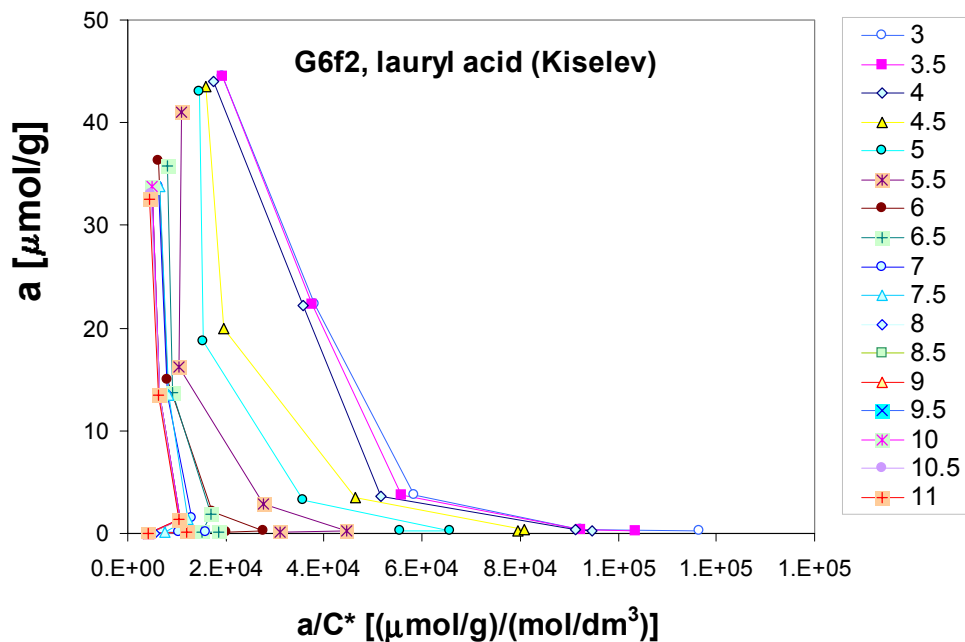

Fig. 11. The sorption of lauric acid (LA) on soil fraction G6f2 in linear Kiselev co-ordinates a vs. a/C^* where $C^* = c \cdot [1 + K_n(a/a_m)]$ (cf. 9 and 10).

Fitted K_n values were in the range 10-50 (optimum 20) with some influences from surface heterogeneity for low concentrations. The data are presented in the linear Kiselev co-ordinates a vs. a/C^* where $C^* = c \cdot [1 + K_n(a/a_m)]$ (Fig. 11). In the case of perfect agreement with the model straight lines should be obtained. The dependencies obtained are close to linearity for medium and high adsorption values, however they also have quite distinct sections corresponding to week heterogeneity effects for very low concentrations. Isotherms closer to

the adsorption axis represent weaker adsorption (compare a_mK in Fig. 10). It means that with the increase of pH adsorption equilibrium constant K is decreasing. This change is especially sharp close to the $pH≈pK_a$ value of LA. For pH > 7-8 the laureate anions are practically the only form of lauric acid present in solution. Thus soil charging should have strong impact on LA adsorption.

In Fig. 12 the specific surface charge curves (calculated formally without correction for soil dissolution or reaction with lauric acid) for various initial concentrations of lauric acid as well for titration of LA solution without soil are compared.
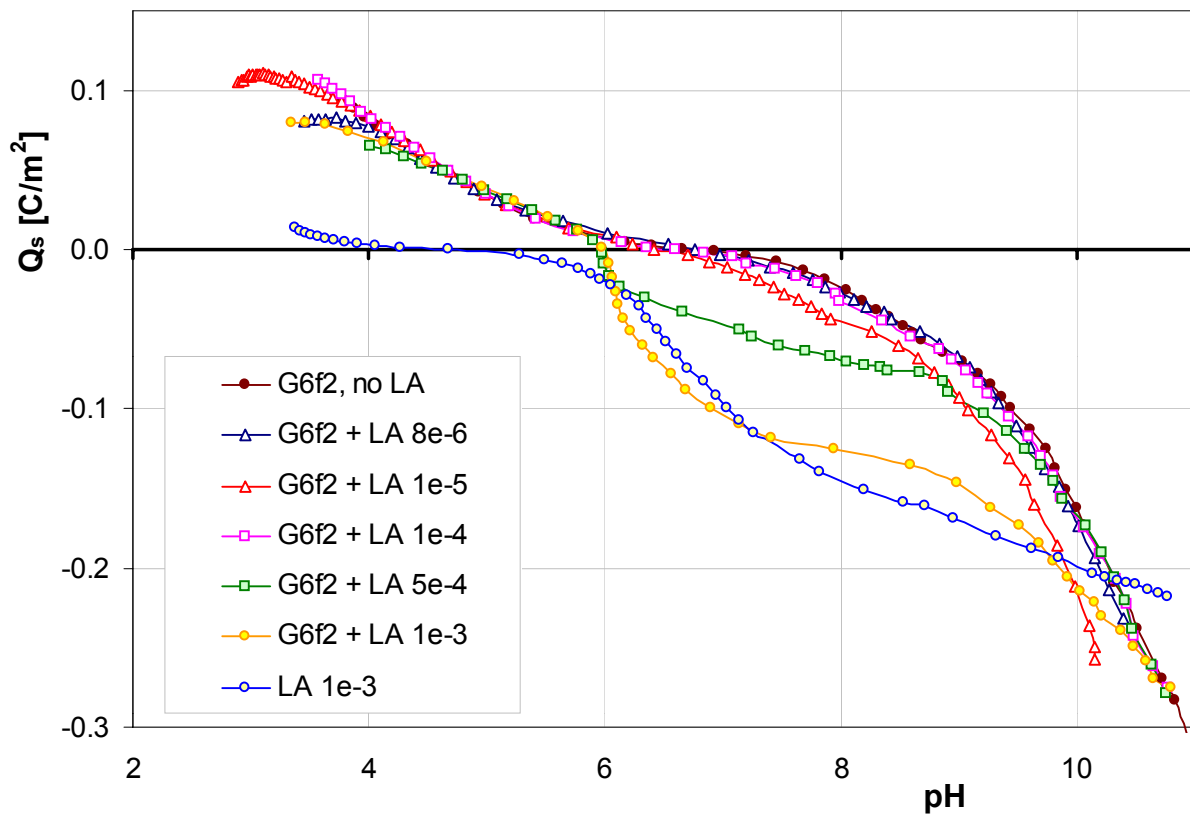

Fig. 12. The formal surface charge densities for soil fraction G6f2 in the presence of various solutions of lauric acid, lauric acid without soil.

The analysis of data presented in Fig. 12 suggests that for initial concentrations of LA below 10^{-4} mol/dm^3 all curves agree quite well (with some discrepancy for 10^{-5} mol/dm^3). Then for higher concentrations and 6 < pH < 10 the soil titration curves become similar to the titration curves of pure lauric acid. In order to explain this phenomenon, the data from Fig. 12 were recalculated into differential ones and compared to titration of pure LA (Fig. 13). Those curves show: (a) the difference between titration of soil with given concentration of LA minus titration of pure soil, (b) the difference between titration of soil with given concentration of LA minus titration of pure LA.

For pH values below 6, titration in the presence or without lauric acid gives the same results. In the range of pH 6-8 the influence of LA on surface charge is an apparent effect (*b*-curves; diamonds in Fig. 13) and is related to the reaction of LA with base and not the change of soil state. However for higher pH the surface charge of soil evidently is decreasing in magnitude, however it couldn't be determined what part of this "formal charge" constituted soil dissolution effect. It is confirmed by the further analysis (*a*-curves; squares in Fig. 13), where the at pH = 8 a strong extremum in base consumption (formal charge) is observed. However,

the magnitude of this additional base consumption is falling rapidly with pH what most probably reflects the decrease of soil charge resulting from strong adsorption of laureate anions.
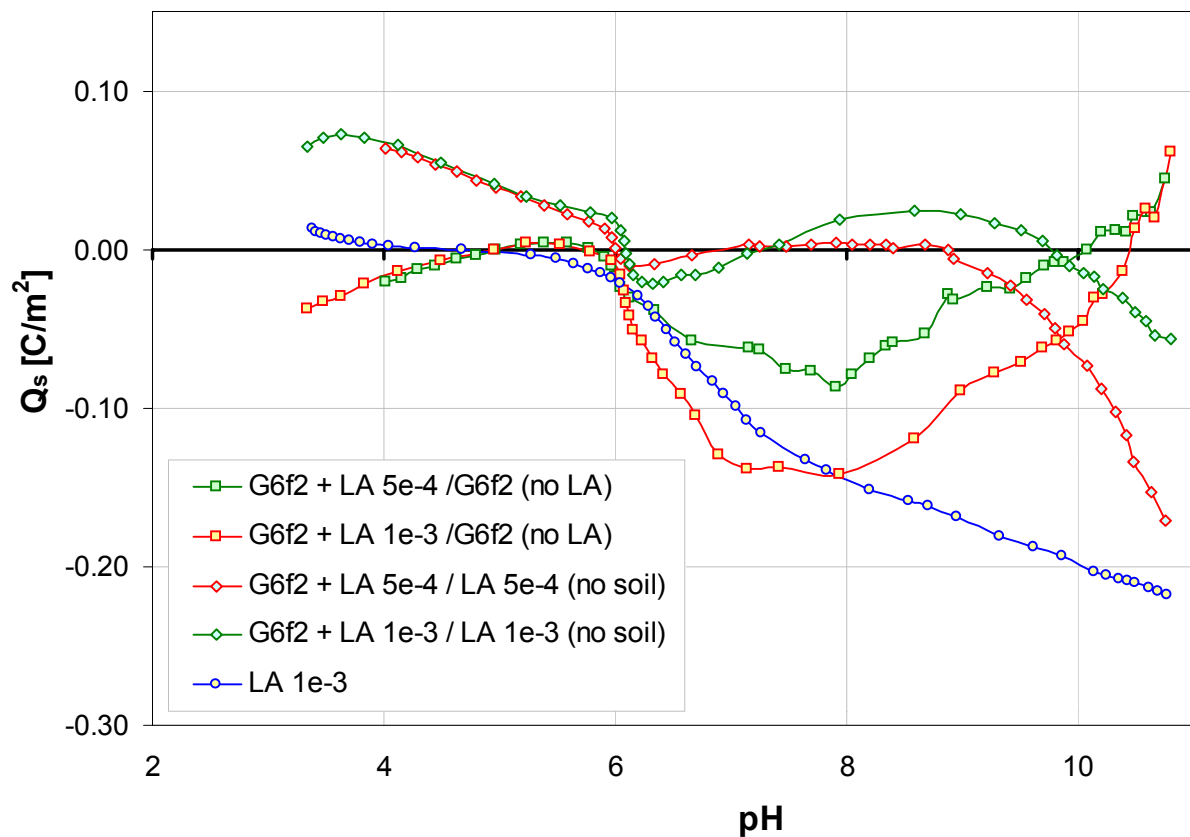

Fig. 13. Differential formal charge curves (*a*-curves: squares; *b*-curves: diamonds; see text).

Conclusions

All soils investigated consisted of two distinctly different fractions – silica-rich and silica-poor ones. Analysis of adsorption data shows importance of lateral interactions of associative character. The predominant influence of pH on adsorption of lauric acid is determined.

1. IAEA Measurement of Radionuclides in Food and the Environment. A Guidebook, (Technical Reports, ser, No. 295, IAEA, Vienna) 1989, p.5.
2. S. Chibowski, J. Zygmunt and Z. Klimowicz, .Polish J. Environ. Studies 6 (1997) 57.
3. S. Chibowski, J. Zygmunt and Z. Klimowicz; J. Radioanal. Nuclear Chem., 231 (1998) 57; 242 (1999) 278.
4. B. Dobrzański, S. Uziak, Z. Klimowicz, J.Melke in: Badanie gleb w laboratorium i w polu, (UMCS, 1992).
5. J. Lyklema, Colloid Interface Sci, 99 (1984)
6. A. Deryło-Marczewska and M. Jaroniec, in: Surface and Colloid Science, Matijević E., (ed.), Plenum Press: New York 1987, vol. 14, p. 301.