

## THE EFFECT OF SOIL PARTICLES AGGREGATION ON ION ADSORPTION

O.G. Usiarow<sup>1</sup>, J. Stawiński<sup>2</sup>, G. Józefaciuk<sup>2</sup>, R. Świeboda<sup>2</sup>

<sup>1</sup>Institute of Agrophysics, Russian Academy of Agricultural Sciences,  
14 Grazhdansky pros., 195220 St. Peterbourg, Russia

<sup>2</sup>Institute of Agrophysics, Polish Academy of Sciences,  
Doświadczalna 4, 20-236 Lublin, Poland

**A b s t r a c t.** The relations governing ions adsorption for overlapped diffuse layers at different surface potentials are shown and they are discussed from point of view of the influence of aggregation on ions adsorption. It is shown that particles aggregation may lead to severe changes of the measured adsorption values what can influence the results of agrochemical and physicochemical soil analysis.

**K e y w o r d s:** aggregation, diffuse double layer, ion adsorption

### INTRODUCTION

The main mechanism of ions adsorption by soils is their accumulation within the electrostatic field of charged surfaces of soil constituents. In general the ions distribution in a diffuse double layer (DL) formed around the charged surface can be described by Boltzman equation:

$$n = n_o \exp(-ez\psi/\theta) \quad (1)$$

where  $\psi$  is the local value of the electric potential within DL,  $e$  is the electron charge,  $z$  is the ion valency,  $\theta$  is the Boltzman constant multiplied by the temperature, and  $n$  and  $n_o$  are concentrations of ions within and out of the DL, respectively.

When defining the ions adsorption in Gibbs terms [5] (as a surface excess of adsorbate per unit surface) one has:

$$\Gamma = n_o \int_V [\exp(-ez\psi/\theta) - 1] dV \quad (2)$$

where the integration is performed by the whole volume of the liquid phase,  $V$ . The adsorption of ions can be calculated when the potential-distance relationship is known. The latter is expressed by the Poisson-Boltzman equation:

$$\nabla^2 \Psi = (-4\pi/\epsilon) \sum_i z_i e n_i \exp(-z_i e\psi/\theta) \quad (3)$$

where  $\epsilon$  is the dielectric constant of the interface,  $\nabla^2$  is the Laplace operator and the summation is for all kinds of ions  $i$ . For binary symmetric electrolyte (i.e. for  $z^+ = -z^- = z$  and  $n^+ = n^- = n_o$  what will be the case for the further considerations) Eq. (3) may be written in the form:

$$\nabla^2 u = \kappa^2 \sinh u \quad (4)$$

where  $\kappa = (8\pi e^2 z^2 n_o / \epsilon \theta)^{1/2}$  is the Debye parameter and  $u = ez\psi/\theta$  is the dimensionless local electric potential. The solution of Eq. (4) at different boundary conditions leads to the calculation of  $u$  for freely expanded as well as overlapped double layers.

The aggregation of particles in suspensions is connected with overlapping of double layers and it significantly changes the potential-distance relationship in the neighbourhood

of particles thus influencing the adsorption of ions. The purpose of the present work is an estimation of the effect of DL overlapping on the adsorption of ions for the model case of flat planar surfaces.

THEORY

For planar surfaces one can find the exact solution of Eq. (4) for both overlapped and freely expanded layers [1]. The first integration gives:

$$du/dx = -2\kappa \sinh(u/2) \tag{5}$$

and for overlapped DL (for this case we later use index *s*):

$$du_s/dx = -\kappa(2\cosh u - 2\cosh u_d)^{1/2} \tag{6}$$

where *x* denotes the distance from the surface and *u<sub>d</sub>* is the value of *u* in the plane of symmetry between two neighbouring surfaces.

Knowing the dependency between the charge of the diffuse double layer,  $\sigma_d$ , and the potential:

$$\sigma_d = -\epsilon\theta/4\pi ez \left. du/dx \right|_{x=0} \tag{7}$$

and the charge of DL and the ions adsorption:

$$\sigma_d = -ez(\Gamma^+ - \Gamma^-) \tag{8}$$

from Eqs (5) and (6) we have:

$$\Gamma^+ - \Gamma^- = -4n_o/\kappa \sinh(u_1/2) \tag{9}$$

and

$$\Gamma_s^+ - \Gamma_s^- = -4n_o/\kappa (\sinh^2(u_1/2) - \sinh^2(u_d/2))^{1/2} \tag{10}$$

where  $u_1 = ez\psi_1/kT$  is the dimensionless potential of the surface. For the case of constant surface potential the change of ions adsorption due to aggregation (overlapping of DL) may be described by the formula:

$$\frac{(\Gamma_s^+ - \Gamma_s^-)^2}{(\Gamma^+ - \Gamma^-)^2} = 1 - \frac{\sinh^2(u_d/2)}{\sinh^2(u_1/2)} \tag{11}$$

As it is seen the decrease of ions adsorption is characterized by the value of *u<sub>d</sub>*, which increases with closing the distance between particles. For  $u_1 \geq u_d \geq 0$  the ratio of adsorption

(LHS of Eq. (11)) may change from 0 to 1. It is worth noting that *u<sub>d</sub>* is a complex function of the distance, the surface potential and the ionic composition of the liquid phase.

After the second integration of Eqs (5) and (6) one has [1]:

$$\text{th}(u/4) = \text{th}(u_1/4) \exp(-\kappa x) \tag{12}$$

and:

$$x = kF(\Phi, k) \tag{13}$$

where *F* is the elliptic integral of the first kind of the argument *k* and amplitude  $\Phi$ :

$$F(\Phi, k) = \int_0^\Phi (d\Phi / (1 - k^2 \sin^2 \Phi))^{1/2} \tag{14}$$

$$\arccos \Phi = \sinh(u_d/2) / \sinh(u/2) \tag{15}$$

$$k = 1 / (\cosh(u_d/2)) \tag{16}$$

For  $x = h/2$ ,  $u_s = u_{1s} = u_1$  and  $\Phi = \Phi_1$  we have:

$$\kappa h = 2k F(\Phi_1, k) \tag{17}$$

The Eq. (11) may be rewritten using the formula relating the force of ion-electrostatic interaction *P<sub>i</sub>* with *u<sub>d</sub>* [3]:

$$P_i = 4\theta n \sinh^2(u_d/2) \tag{18}$$

and for completely overlapped diffuse layers:

$$P_i = P_{i\max} = 4\theta n \sinh^2(u_1/2) \tag{19}$$

Taking the latter into account we have:

$$\frac{(\Gamma_s^+ - \Gamma_s^-)^2}{(\Gamma^+ - \Gamma^-)^2} = 1 - P_i / P_{i\max} \tag{20}$$

Thus a measure of the changes of ions adsorption due to particles coagulation is related to the force of electrostatic repulsion at the coagulation distance *h* and to the maximal value of this force, *P<sub>i</sub>*<sub>max</sub>.

Despite the dependence *P<sub>i</sub>*(*h*) is given in a parametric form, for some cases one can find a direct relationship of  $\Gamma_s^\pm$  against *h*.

For small surface potentials  $u_1 < 1$ , when the Eq. (4) can be linearized and in the case of freely extended DL one has:

$$u = u_1 \exp(-\kappa x) \tag{21}$$

And according to the Eq. (2) when neglecting the second order terms:

$$\Gamma^{\pm} = \pm n_o u_1 / \kappa \quad (22)$$

Analogically for overlapped DL:

$$u_s = u_1 (\exp(-\kappa x) + \exp(-\kappa(h-x))) \quad (23)$$

and:

$$\Gamma_s^{\pm} = \pm n_o u_1 / \kappa (1 - \exp(-\kappa h)) \quad (24)$$

Now combining Eqs (22) and (24):

$$\Gamma_s^{\pm} / \Gamma^{\pm} = 1 - \exp(-\kappa h) \quad (25)$$

The above formula for small surface potentials relates the ions adsorption to the dimensionless distance  $\kappa h$ .

#### DISCUSSION

According to the Eqs (20) and (25) the decrease of ions adsorption in DL may be significant. This effect has to be taken into account while interpreting the results of agrochemical and physico-chemical soil analysis and in particular when the experimental data are taken for different systems.

Eq. (20) states that the aggregation leads to the decrease of both cations and anions adsorption. For small surface potentials,  $u_1$ , when  $\kappa h \gg 1$  (Eq. (25)) the decrease of counter ions adsorption is equal to the decrease of co-ions adsorption. For strong electrostatic interaction the desorption of counter ions has of course to be higher then for co-ions.

The model presented described, however, the situation of flat parallel DL what is rare to be found in reality, but apparently the above relations have to work for the other geometry of DL at least qualitatively. It can be proved using Deriaguin's method [3] of spherical zones for DL thicknesses smaller then the main normal radii of particles.

Figures 1 and 2 illustrate some basic dependences for the ionic adsorption decrease due to DL overlapping. It is interesting to note the sufficiently high precision of  $((\Gamma_s^+ - \Gamma_s^-) / (\Gamma^+ - \Gamma^-))^2$  approximation against distance with Eq. (25) in comparison with the

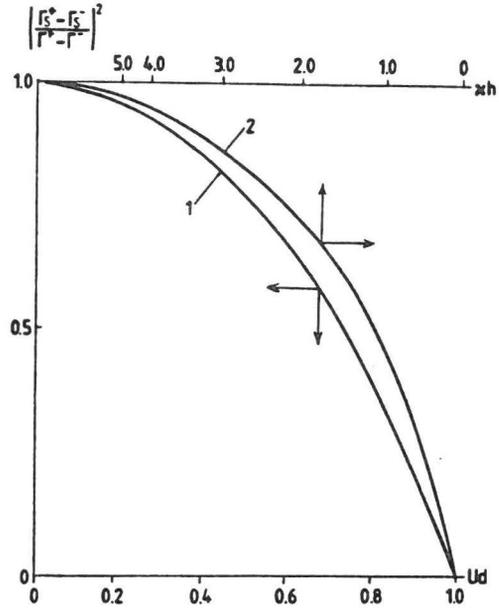


Fig. 1. The relative decrease of ions adsorption with the increase of the electric potential at a half-distance between particles,  $u_d$ , (curve 1) and with the dimensionless distance  $\kappa h$ , (curve 2) for  $u=1$ . Curve 1 calculated numerically from Eqs (11) and (17); curve 2 from Eq. (25).

exact equations. For identical degrees of DL overlapping (i.e. at  $\kappa h = \text{const}$ ) the surface potential has different influence on ions adsorption (Eq. (20)). For high degrees of DL overlapping the values of  $u_1$  have practically no influence on the value of the LHS of Eq. (20), which is equal to 1 at relatively small potentials (Fig. 2, curve 5). At low degree of DL overlapping for low charged surfaces one observes no changes in ions adsorption i.e., the value of Eq. (20) is close to zero (Fig. 2, curve 1). The marked increase of  $((\Gamma_s^+ - \Gamma_s^-) / (\Gamma^+ - \Gamma^-))^2$  for the intermediate values of  $u_1$  occurs. At  $u_1 > 10$  this value tends to reach 1. It is interesting to note that for  $u_1 \rightarrow 0$  the ratio  $((\Gamma_s^+ - \Gamma_s^-) / (\Gamma^+ - \Gamma^-))^2$  depends on the scaled distance  $\kappa h$ . Summarizing: the changes of ions adsorption in colloidal systems are important for all range of surface potential values.

Aggregation of soil particles meets the overlapping of double layers and it occurs

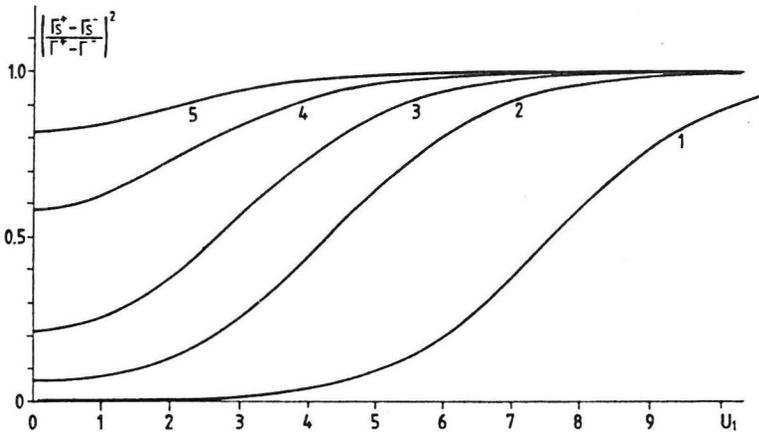


Fig. 2. The relative decrease of ions adsorption with surface potential  $u_1$  for different values of  $\kappa h$ : 1-0.1, 2-0.5, 3-1, 4-2 and 5-3.

when the attraction forces prevail over repulsion forces. The latter are of different nature [3]. Usually one can distinguish two kinds of aggregation: when aggregates are formed in a primary and a secondary energy minima [4]. The secondary aggregation corresponds to the energy minimum  $U_{\min 2}$  what occurs at rather long distance  $h_{\min 2}$  on an potential energy curve when the energetic barrier  $U_{\max}$  is high

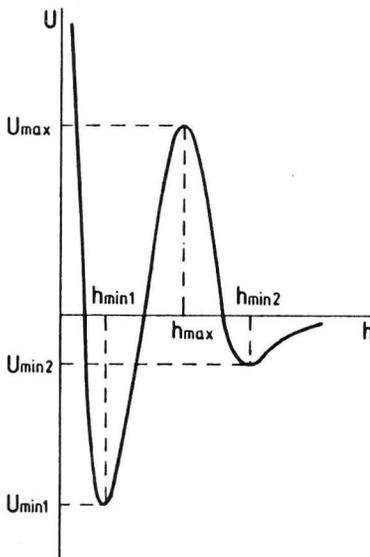


Fig. 3. Schematic diagram of the total potential energy of interaction between dispersed particles against distance relation.

preventing the close contact of particles (Fig. 3). The secondary aggregation forms periodical colloidal structures (PCS) which undergo self-dispersion due to the energy of Brownian movement. PCS occur also in more concentrated suspensions where the repulsion forces are rather high [4]. In relatively diluted suspensions the equilibrium state for secondary aggregation is characterized by average aggregate dimension  $m_{av}$  what reflects the number of particles in aggregate. The value of  $m_{av}$  depends in general on the concentration of dispersed phase and the depth of  $U_{\min 2}$  [6]. The concentration of the equilibrium solution has the great influence on both  $U_{\min 2}$  and  $h_{\min 2}$  so varying the concentration of electrolyte one observes together with the direct ionic exchange effects also the inputs of aggregation. Then to diminish the latter input it seems to be good to measure adsorption in very diluted suspensions. However, it is hardly possible due firstly to a decrease of the amount of adsorbent and secondly to difficulties in estimation of low concentration differences. Additionally it has to be mentioned that secondary aggregation may occur at as low concentrations of colloidal particles as  $10^8 \text{ cm}^{-3}$  [2,3,6].

When either the secondary aggregation or the primary one (for low values of energetic barrier) occurs in a given suspension exclusively,

the degree of aggregation may be experimentally estimated and so the ion adsorption decrease can be evaluated also. The situation is much more complicated when both aggregate types occur simultaneously (at average values of  $U_{\max}$ ) and so the values of  $\kappa h$ , corresponding to the fixation of different particles are markedly different for different aggregates (see Fig. 3). The investigation of such systems is very difficult not only because of high equilibration times but also because of the lack of experimental methods distinguishing the ratio of the primary and the secondary aggregation. This case is met frequently in soil suspensions where solid particles have usually not high electric charge.

It is necessary to note that the above relationships were derived assuming the constant value of surface potential, however it can be proved that the analogical ones hold for constant surface charge [7].

#### CONCLUSIONS

The variations in the measured amount of ions adsorption are estimated by the ratio of the actual to the maximal value of ion-electrostatic forces of interparticle interactions in col-

loidal system.

Aggregation state of colloidal system has a great influence on ions adsorption, what has to be taken into account when measuring the isotherms of ions adsorption in broad range of concentrations.

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