Predictive ion-electrostatic model of disjoining pressure of synthetic gel structures in coarse-dispersed soil substrates

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Abstract. The mechanism of disjoining pressure controlling the swelling and water absorption of gel structures for soil conditioning is discussed. Its quantitative description is based on the fundamental ion-electrostatic model of soil water sorption isotherms containing the phase variable of gel swelling degree and specific surface area index of the soil substrate. The model adequately reproduces the s-shape of soil water sorption isotherms in a wide range of water activity from 0.05 to 0.999 depending on the working doses of hydrogels in the range of 0.05-0.3 mass%. Reinforcement of gel structures with amphiphilic dispersed particles increases the effect of disjoining pressure and water absorption.

1. Introduction

Synthetic gel structures are actively used in modern agronomy and landscaping to optimize water-retention and ion-exchange capacity of soils, their erosion resistance, as well as to fix trace elements and plant protection products in the rhizosphere [1-9]. The actual task of soil physics is a scientifically based forecast of the action of certain doses of hydrogels on the technological properties and characteristics of soils. Studies [10–12] indicate the possibility of spatial organization of polydisperse soil systems in the form of gel structures of a colloidal matrix (humus, mineral colloids) between the surfaces of soil particles of larger size (the solid-phase skeleton). Electron microscopy of the colloidal-dispersed soil complex with magnification of 25000-100000 times confirms this possibility and reveals two types of gel structures, reinforced and non-reinforced with dispersed particles [12]. These soil-gel structures must have an additional disjoining pressure by Deryagin [13] due to the presence of new interfaces of solid and liquid phases. Quantitative description of disjoining pressure in natural soils is based on the fundamental ion-electrostatic model [14, 15]. The goal of this study was to adapt this model to synthetic gel structures in coarse-dispersed soil substrates.

2. Objects and methods

Synthetic gel structures were formed in the sandy soil substrates (medium-grained and fine-grained quartz sands) on the basis of strongly swelling polymer hydrogels (SSPHs) represented by the "Aquasorb" European trademark, radiation-cross-linked polyacrylamide (PAA), synthesized at the Institute of Chemical Physics of the Russian Academy of Sciences [5], and innovative products of the Ural chemical factory, according to our patented technologies of filling of the polymer matrix [16, 17].
These products include VUM-ITH hydrophilic gel synthesized from the base co-polymer of acrylamide and ammonium acrylate filled by solid biocatalytic wastes and filterperlit as well as VM-P hydrogel synthesized from the base co-polymer of acrylamide and sodium acrylate and containing as a filler amphiphilic finely dispersed peat and ionic silver. The VM-P hydrogel could presumably form gel structures of the reinforced type due to the fine-dispersed filler.

Figure 1. Scheme of swelling polydisperse system with gel structures and disjoining pressure (the author’s generalization of concepts [10–12]).

Figure 2. Impact of SSPHs concentration (C) on dispersion (S) and total surface energy (Es) of solid phase in soil substrate.

Figure 3. Simulation of the influence of SSPHs concentration on water sorption isotherms (on example VM-P hydrogel).

Pre-swollen hydrogels containing about 100 kgH₂O/kg, were mixed with a sandy substrate in perforated from the bottom cylindrical 2x4 cm plastic tubes for centrifugation. Obtained mineral-gel compositions were capillary saturated in centrifuge tubes by distilled water to the state of maximal swelling. Working doses (concentrations) of SSPHs varied in the range of 0.05-0.3% per mass of the solid phase of the mineral substrate.

Water sorption isotherms in mineral-gel compositions were obtained by the method of equilibrium centrifugation [14] and termodesorption [18]. The Regression Wizard algorithm of the S-Plot-12
computer program was used to estimate the parameters of disjoining pressure model in gel structures from experimental data.

3. Results and discussion

The scheme of structural spatial organization of polydisperse systems with polymer gel structures of reinforced and non-reinforced types between the surfaces of mineral soil particles and additional disjoining pressure in accordance with the concepts of [10–12] is shown at figure 1. In [14, 15, 19] we put forward a fundamental ion-electrostatic model of disjoining pressure for quantitative description of water sorption isotherms in soils and sediments with colloidal-dispersed complex in the following biexponential form:

\[ rh = \exp \left[ \frac{M}{RT} a \cdot \exp \left( -\frac{W}{S_0 \lambda} \right) \right] = \exp \left[ \frac{M}{RT} a \cdot \exp \left( -bW \right) \right], \tag{1} \]

where \( rh \) is relative air humidity or soil water activity [dimensionless], \( R=8.314 \text{ J/(mol·K)} \) is universal gas constant, \( T [\text{K}] \) is the absolute temperature, \( M = 0.018 \text{ kg/mol} \) is the molar mass of water, \( W [\text{kg/kg}] \) is soil water mass content, \( b [\text{kg/kg}] \) is the physically based parameter controlled by the dispersion and the electric double layer properties, \( a [\text{J/kg}] \) is the physically based parameter reflecting the surface shape and potential (charge), \( S [\text{m}^2/\text{kg}] \) is the variable effective specific surface of the interphase boundary, \( \rho[\text{kg/m}^3] \) is the water density, \( \lambda [\text{m}] \) is the effective Debye electric double layer thickness. In a standard stable state with a minimum absorbed water film thickness (\( h_0 = 2\lambda_0 \)), the effective specific surface area (\( S_{WRC} \)) is defined by equation [19]:

\[ S_{WRC} = \frac{1}{2\rho r}, \tag{2} \]

where \( r = 1.38 \cdot 10^{-10} \text{ m} \) is a crystallochemical radius of water molecule. The ratio \( a/b \), according to [19] is the integral surface energy of the disperse system (\( E_s, [\text{J/kg}] \)) per unit mass of the solid phase.

Figure 2 shows the linear dependence of the specific surface area and the integral surface energy of mineral-gel compositions on the concentration of SSPHs obtained for 30 samples in 3 replications. Using these dependencies, we adapted the fundamental model (1) for prediction of disjoining pressure in gel structures at a known (planned) dose of SSPHS:

\[ rh = \exp \left[ \frac{M(mC + E_s^0)}{RT(kC + S_0)} b_0 S_0 \cdot \exp \left( -\frac{b_0 S_0}{(k + S_0/C)} W \right) \right] = \exp \left[ \frac{M(mC + E_s^0)}{RT(kC + S_0)} b_0 S_0 \cdot \exp \left( -\frac{b_0 S_0}{(k + S_0/C)} W / C \right) \right], \tag{3} \]

where \( mC + E_s^0 \) is a linear function of the integral surface energy growth under the influence of a given concentration of SSPHS (\( C \% \)) relative to the initial surface energy of the mineral soil substrate \( E_s^0 \) (for the studied gel compositions in the range \( C = 0.05-0.3\%, m = 21097\%^{-1}, E_s^0 = 1699.5 \text{ J/kg} \)); \( kC + S_0 \) is a linear function of dispersion growth under the influence of a given concentration of SSPHS relative to the initial dispersion of the mineral soil substrate \( S_0 \) (for the studied gel compositions in the range \( C = 0.05-0.3\%, k = 167.2 \text{ kg}^{-1}, S_0 = 9.2 \text{ m}^2/\text{g} \)); \( W/C [\text{dimensionless}] \) is the degree of swelling of the hydrogel; \( b_0=1/(\lambda S_0 \rho) [\text{kg/kg}] \) is the physically based parameter controlled by the dispersion and the electric double layer properties for the soil mineral substrate. Substituting the value \( b_0=1/(\lambda S_0 \rho) \) in (3) gives the expression for the argument of the exponential function in the form:

\[ \frac{W / C}{\lambda (pk + \rho S_0/C)}, \tag{4} \]

where the denominator can be interpreted as an increment of the effective Debye thickness of the double electric layer during the formation of the gel structure, and the value \( C/(S_0 \rho) \) as the effective thickness of the gel film distributed over the surface of the mineral substrate.

Calculation of water sorption isotherms by gel compositions depending on their concentration (degree of swelling) according to the new model (1) gave a satisfactory convergence with real data within confidence intervals at the significance level \( p = 0.01 \) with standard approximation errors \( s = 0.02-0.06 \). An example of such a forecast for the VM-P hydrogel with maximum water absorption is
shown at figure 3. Note that unlike the known fundamental and empirical models for soil water sorption isotherms [20], model (3) for the first time adequately described very problematic for known models of sorption isotherms area with water activity within $0.98 < \text{rh} \leq 0.999$, where the isotherm curve sharply rushes up. Generally, the obtained results allow making approximate engineering calculations of optimal doses of synthetic soil conditioners for the formation of the required water-holding capacity in mineral coarse textured substrates for soil-landscape design projects without time-consuming hydrophysical experiments.

4. Conclusion
Water absorption and swelling of synthetic gel structures is associated with the effect of an additional disjoining water pressure in polydisperse systems. Its quantitative description is based on the fundamental ion-electrostatic model that uses variable degree of swelling of hydrogels and dispersion (specific surface area) of the mineral soil substrate. The model predicts satisfactorily the basic hydrophysical characteristics of water retention of gel compositions with mineral soil substrates in the form of soil water sorption isotherms under the influence of a given dose (concentration) of SSPHs in a wide range of water activity (equilibrium air humidity) up to $\text{rh}=0.999$.

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