
SOIL PHYSICS

Dependence of the Osmotic Pressure and Electrical Conductivity of Soil Solutions on the Soil Water Content

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Abstract—The osmotic pressure and electrical conductivity were determined with the use of instrumental methods (centrifuging, conductometry, and cryoscopy) in equilibrium soil solutions as the functions of moisture (the mass ratio between solid and liquid phases) for the soils of different geneses and textures. These functions proved to have a nonlinear character with one extremum. A theoretical substantiation to this phenomenon is suggested. It is based on the concept of competing interphase interactions in soil and develops the classical ideas by A.A. Rode. Upon the low soil water content, surface (molecular and ion-electrostatic) forces of the solid phase bind water molecules and prevent them from hydrating ions and dissolving electrolyte salts in the soil solution; as a result, electrical conductivity and osmotic pressure values approach zero in this case. With an increase in the water content, water molecules escape gradually from the energy field of surface forces, and their activity (chemical potential) and dissolving capacity also increase. This results in the expected growth of the electrical conductivity and osmotic pressure of the equilibrium solution extracted from the soil. The maximum values of the studied parameters are observed at the water content approximately equal to the maximum molecular water capacity (or to the boundary zone, within which capillary gravitational forces influencing the soil liquid phase become prevailing over the surface interphase interaction forces). The further increase in the soil water content lowers the electrical conductivity and osmotic pressure of equilibrium solution because of dilution of the fixed mass of electrolyte salts. For quantitative description of the revealed functional dependence, we suggest an empirical mathematical model in the form of modified equation of lognormal distribution.

Keywords: soil solution, solid and liquid phases, interphase interactions, concentration, activity, thermodynamic potential, dispersion, modeling

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INTRODUCTION

Interaction between the solution and the solid phase in soils controls the composition and concentration of the former via a diverse set of chemical, physical, physicochemical and biological processes operating in a soil as an open, polycomponent, polydisperse bio-abiotic system. The humus-clayey, or more precisely, colloidal-disperse complex of soil (CDC) plays the leading part in this interaction, as it represents the most active portion of the soil solid phase with the high potential surface energy [15, 29]. Despite the evident influence of surface interphase interactions on soil solutions, soil science is mainly focused on the study of substantive composition and chemical reactions, including ion-exchange processes, actually apart from the solid-phase components and upon strong dilution with distilled water, i.e., in such proportions with dry soil, which are not met in nature in consolidated porous media [8, 15, 21,

30, 42]. Few studies deal with the analysis of actual soil solutions by extracting them with gravitational or vacuum lysimeters, membrane presses or centrifuges, by replacement with other liquids, or using in situ measurements, i.e., conductometry, potentiometry, and ion-selective electrodes [4–7, 10, 12, 14, 16–18, 20, 24, 26, 36, 37, 39, 41, 47, 49]. These studies often reveal the dependence between the effective concentration (activity), electrical conductivity (EC), osmotic pressure and other properties of soil solution and the soil water content, or, in essence, the solid : liquid soil phases ratio [1, 6, 9, 10, 16, 17, 19, 23, 26, 39]. However, information on the kind of this dependence is ambiguous.

A number of researchers point to the rising electrolyte concentration, EC, and osmotic pressure in the pore solution upon a decrease in the water content or thermodynamic potential (capillary-sorption pressure) of soil moisture [12, 14–16, 18, 24, 40]. This increase is

usually observed upon the use of gravitational or vacuum lysimeters (capillary-sorption pressure ranging from 0 to -1 atm), i.e., upon the transition from gravitational to capillary moisture; it is related to the fractionation of soil solution by the pores of different sizes or, in essence, to the phenomenon of hydrodynamic dispersion, upon which large open pores contain the solution of lower concentration as compared to fine or closed pores, in which the proximity of solid-phase source and a longer time of equilibrium solution state favor its enrichment with ions [12, 14, 34]. In our opinion, this is not the only, and possibly, not the principal explanation, as it artificially represents the soils as a set of incoherent capillaries of different sizes, each filled with electrolyte of its own concentration. The alternative lies in the routine law of dilution/concentration of soil solution upon an increase/decrease of the water content, which was first formulated by Campbell for the osmotic pressure (potential) [40]:

$$P_{os} = P_{os}^0 W_s W, \quad (1)$$

where P_{os} , P_{os}^0 (kPa) is the osmotic pressure of soil solution at the water content W (wt %) and in the saturation condition W_s (%) (the total water capacity), when all pores are filled with the liquid phase, respectively. Linear ratios $P_{os}^0 = 36EC^0$, where EC^0 (dSm/m) is the EC of soil solution upon the total water capacity; $P_{os}^0 = C_0 RT$, where C_0 (mol/L) is the concentration of osmotically active substances upon soil saturation with water; R (J/(mol K)) is the universal gas constant; and T (K) is the absolute temperature, which are valid for dilute solutions, link indices of osmotic pressure, effective concentration, and EC and attest to the universal character of Eq. (1) for all of them [3, 40]. On soil desiccation (concentration of solution), Eq. (1) will be evidently valid up to a certain critical moisture, upon which the solubility equilibrium is achieved for the predominating ion components, after which the concentration and osmotic pressure will stabilize in the above-sediment solution. This fits completely the theoretical ideas about the solid–liquid phase interaction in soil discussed in [15] assuming only the hyperbolic instead of linear dependence (inverse instead of direct proportionality) between concentration and moisture according to Eq. (1). The idea about dilution/concentration on increasing/decreasing moisture as a factor of symbiotic dynamics of concentration and osmotic pressure in soil solution was also suggested in [9].

However, there is a no less number of works in soil science pointing to the opposite relationship between the studied indices and soil moisture, i.e., to their decrease rather than increase upon soil drying. Above all, these are the classical data obtained by Trofimov, Dumanskyi, Dolgov and a number of other researchers generalized in the fundamental work by Rode [23]. These data attest to the presence of a certain category

of water bound by surface forces (insolubilizing volume or saltless film), which is almost devoid of dissolved salts, and, therefore, manifests negligibly low values of EC and osmotic pressure, which are typical of deionized water. A decrease in the concentration of ions and EC in solutions that are pressed, centrifuged, or displaced by the nonpolar liquid in fine-dispersed clay minerals, silts, and sediments starting from a certain water content was described in the classical work by Kryukov [17]. Electrical conductivity of the soil proper as a three-phase system also most often manifests the decreasing trend upon the decreasing moisture, which forms the basis for conductometric methods of moisture assessment in soils, sediments, and other porous fine-grained materials [6, 19, 20, 34, 39, 43].

Finally, very scarce works point to the possible existence of a complicated nonlinear dependence between the studied properties of soil solution and the mass portion of water as a function with an extremum (maximum) [1, 9, 10, 26]. In our previous work, we identified such a relationship for the EC in equilibrium solutions in soddy-podzolic soils, successively extracted by centrifuging in a wide range of capillary-sorption pressure of the soil water (0–1000 kPa, $pF = 4$).

The present research is aimed at the theoretical substantiation and experimental study of such relationships not only for EC but also for osmotic pressure in the equilibrium solutions of soils differing in their genesis and grain-size distribution; we also attempt to describe them quantitatively using the universal mathematical model.

OBJECTS AND METHODS

The soil samples differing in their genesis, particle-size distribution, salinization degree, and structural state were the objects of experimental research. Soddy-podzolic sandy loamy, silt loamy, and clay loamy soils of different cultivation degrees (Ap horizon) (Eutric Albic Reisols (Loamic, Aric, Cutanic, Ochric)) from Moscow oblast (the Chashnikovo test plot of Moscow State University); gray forest silt loamy soil (A1 horizon) (Eutric Retisol (Loamic, Cutanic, Humic)) from Tula oblast; leached silt loamy chernozem (Ap horizon) (Luvic Chernic Phaeozem (Loamic; Aric, Pachic)) from Lipetsk oblast; alluvial soddy sandy loamy soil (A1 horizon) (Eutric Fluvisol (Arenic, Humic)) from Amur oblast; peat bog lowland soil (T horizon) (Eutric Hemic Histosol) from Tver oblast (the Western Dvina test plot belonging to the Institute of Forest Science of the Russian Academy of Sciences); and arid soils from the Astrakhan lowland—brown semiarid soil (Calcaric Endosalic Cambisol (Loamic, Ochric)), A1 horizon, sandy loam, $EC_{1:1} = 3.7$ dS/m, BC horizon, $EC_{1:1} = 18.7$ dS/m; meadow-chernozemic solonchak (Mollic Stagnic Solonchak (Loamic, Humic)), B_{Ca} horizon, heavy loam (clay), $EC_{1:1} = 11.7$ dS/m, BC horizon, silt loam,

$EC_{1:1} = 30.0$ dS/m—were examined. The $EC_{1:1}$ index is the soil water EC in dilution 1 : 1 (dry soil : water) pointing to the degree of soil salinization in the range from nonsaline (<4 dS/m) to strongly saline (16–33 dS/m) soils. Gradation data according to [3] were developed for the EC of water extracts from a water-saturated paste; they were used as tentative. Actually, due to dilution effect, the salinization degree may be somewhat higher for soils with the total water capacity lower than 100% of the water mass portion. However, the surface conductivity of the paste partially compensates for this increase. For most of the studied soils, experiments were performed with loose samples sieved through a 1 mm screen; for soddy-podzolic soils, with undisturbed cylindrical monolith samples of 3 cm in height and 3 cm in diameter.

The equilibrium soil solutions were obtained, and soil water retention curves (WRCs) were found using the original author's method of equilibrium centrifuging on CUM and CLN-16 (Russia) centrifuges with angular rotors and the maximal speed up to 8000–12000 rpm [25, 45]. Samples were placed in bottom-perforated metal or plastic holders and installed in 100-mL centrifuge test tubes on rests for collecting the soil solution separated by centrifuging. After each centrifuging stage at a certain rotation velocity, the soil samples were weighed on an analytical balance ACCULAB-620 (USA) with the accuracy up to 0.001 g, and the separated solution was tested for EC using DIST-WP4 (HANNA Instruments) conductometer with an accuracy 0.01 dS/m. A special electrode nozzle was used for measurements in tiny volume of liquid. An aliquot of centrifuged liquid (1 mL) was sampled with a medicine syringe with a thin needle and transferred to a mini cuvette of the same volume to perform conductometric measurements. Such a small constant volume was used to standardize the measurement conditions, since at the last centrifuging stages, the soil solution output was small and rarely exceeded 2 mL. Initially, soil samples were saturated for 24 h with distilled water with the EC close to zero (or, more precisely, undetectable with a conductometer of the given accuracy class) to reach the total water capacity. Using the data on changes in the sample mass at each centrifuging stage and the centrifuge rotation velocity, we calculated the equilibrium water content and the capillary-sorption potential of soil water according to [45]. All analyses were performed in four replicates.

The osmotic pressure (potential) of soil solution was calculated as the algebraic difference between the total water potential and the capillary-sorption water potential at the same water content of the samples in agreement with the theory of additivity of thermodynamic potentials of soil water [9, 31, 40]. To assess the total potential, we used the cryoscopic method in our modification [27] with an automated registration of freezing curves by programmed hydrothermal sensors DS1923 (USA). The WRC and the water content—total water potential relationship were approximated

using the van Genuchten and Campbell models, as well as the fundamental ion-electrostatic model of disjoining pressure (the modified Derjaguin equation) [25, 33, 34].

To approximate the experimental data with nonlinear mathematical models, we used Sigma Plot 2001 program with the incorporated algorithm of nonlinear regression Regression Wizard [2]. Along with the model parameter values, the program estimated automatically their variation in the form of relevant standard deviations, the statistical significance (difference from zero), as well as the major statistical indices, i.e., the reliability value (R^2) and standard approximation error (s).

RESULTS AND DISCUSSION

Figure 1 shows the experimental data on the absolute values of capillary-sorption (WRC), total, and osmotic potentials of soil water depending on its mass portion (water content) in soils of different textures and salinities from the Astrakhan Lowland. The total water potential curves were approximated by the Campbell function [40] (curve 1) and the WRC (according to van Genuchten) function [34] (curve 2) and by the disjoining pressure model [25, 33] (curve 3). The osmotic potential (pressure) curve was built according to the difference between the total and capillary-sorption potentials calculated for the fixed moisture values using the mentioned functions. Thus obtained dependence $P_{os}(W)$ shows a complex shape of extremum (maximum) function in the area of low and medium water content (10–20%). This variation depends on the dispersion and salinization degree of the samples. At first, with the decreasing moisture, the osmotic pressure grows rather gently and gradually. After the extremum having been achieved, it sharply decreases within a narrow range (4–7(10)%) of moisture. The described shape of this curve $P_{os}(W)$ is most distinctly pronounced in the inserts to Fig. 1, in which the semilogarithmic scale of pressure (potential) on the vertical axis is changed to an ordinary scale.

In this case, the routine van Genuchten model is used for the WRC description [34]. Despite a close (in general) correlation with experimental data ($R^2 = 0.98–0.99$, $s = 0.3–1.2\%$), the model may predict erroneously in the area of noncapillary soil moisture bound by surface forces in approaching the so-called residual moisture parameter (Θ_r) in the van Genuchten function, which is often taken as the maximal air-dry moisture or “insolubilizing volume (IV)” [34]. The mathematical van Genuchten function becomes indefinite in this point. The parameter (Θ_r) proper was reproduced with a big error upon data approximation (the relative error ranging from 13 to 60%) with the significance level below permissible values $p = 0.15–0.17$; for the strongly saline sample from the BC hori-

zon of solonchak (Fig. 1d), this parameter did not differ from zero.

Therefore, to our mind, $P_{os}(W)$ calculation appears to be more accurate upon the approximation of a part of the WRC by the fundamental ion-electrostatic model of disjoining pressure [25, 33], which gives us a straight line in semilogarithmic coordinates in the area of film and adsorbed moisture. This line crosses the total potential curve at a lower moisture as compared to the van Genuchten model, the latter infinitely sharply rising upward in the water content area close to Θ_r , which contradicts the physical essence of capillary-sorption pressure of soil moisture [33]. The alternative model suggests a more accurate description in the considered area ($0.997 \leq R^2 \leq 0.999$) as compared to the van Genuchten function in case of a twofold reduction in the number of parameters (two instead of four) and their statistical reliability at the significance level $p < 0.001$. Figure 2 shows the result of improved estimation of $P_{os}(W)$ obtained from the difference between the total potential and the capillary-sorption pressure estimated using the ion-electrostatic model. The general type of relationship is the same; however, the position of the extremum point and the moisture of the close to zero osmotic pressure move left along the water content axis, i.e., their values decrease.

The results obtained by us in this study, as well as the analogous assessment of $P_{os}(W)$ described in previous paper [9] appear to be indirect estimates, because for a small number of experimental points, the total water potential and the WRC largely depend on the models used for their approximation and interpolation. This fact undoubtedly makes thus obtained results less valuable in scientific respect and gives way to criticism. Thus, Sudnitsyn [31] provides numerous experimental data proving total discrepancy between WRCs and the total thermodynamic potential in the area of medium and low moisture, which gives him reasons to criticize the conclusion about P_{os} tending to zero upon soil drying and their determination via joining the parts obtained by the sorption (total potential) and tensiometric (capillary pressure) methods as suggested in [9]. Later, it was concluded that the applicability of calculations according to Voronin only for nonsaline soils with a relatively small osmotic component of the total thermodynamic (chemical) potential of soil water [34]. However, in our opinion, this idea radically contradicts both the fundamental essence of the Voronin method and the experimental data [9] it is based on, because these data, as well as our results (Fig. 1, 2) obtained for various samples, including strongly saline soils attest to the same dependence $P_{os}(W)$ tending to zero in the area of the low moisture water content. What is the matter? Most likely, the reason is in the methods of sample preparation (soil moistening) and water removal. In paper [31], the tensiometric section might have been obtained from the samples of one kind, whereas the total potential (psy-

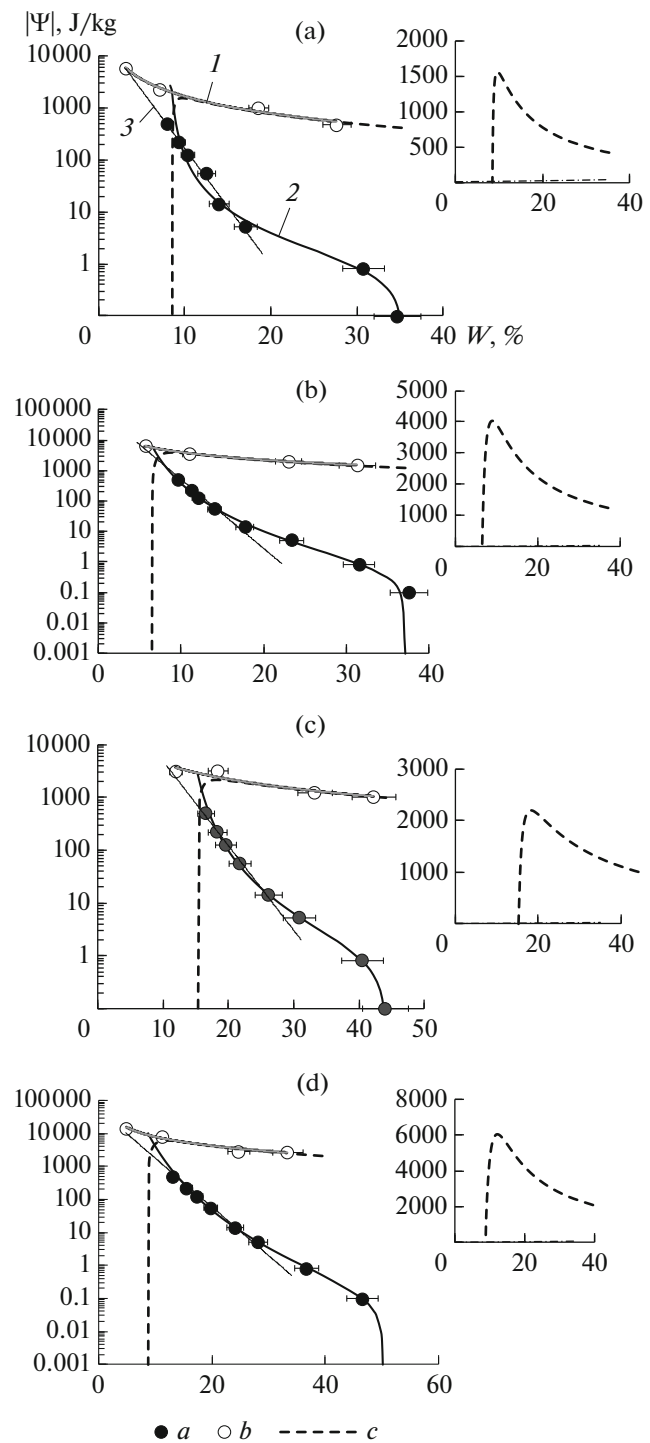


Fig. 1. Dependences of absolute values of the (a) capillary-sorption and (b) total water potentials and (c) osmotic pressure in the liquid phase on the mass percent of water in soil: (1, 2, 3) data approximation by hydrophysical models; insert graphs show $P_{os}(W)$ function transformed to an ordinary scale. Soils: (a and b) brown semidesert soil, A1 and BC horizons, respectively; (c and d) solonchak, B_{Ca} and BC horizons, respectively. See the text for remaining designations and explanations.

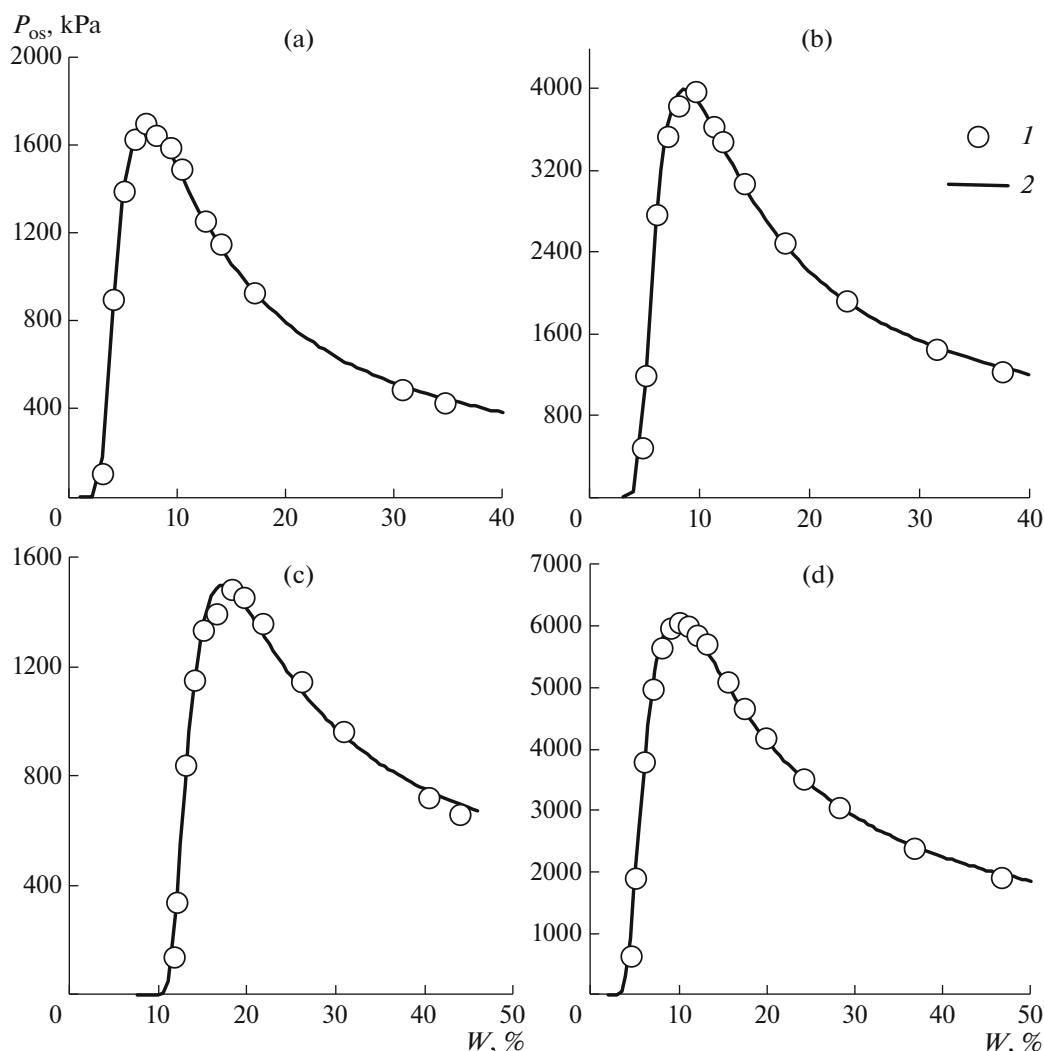


Fig. 2. Dependence of the osmotic pressure of soil water on the soil water content and its simulation. Soils: (a, b, c, and d) see Fig. 1; (1) calculated and experimental data (calculation of the difference between the total and capillary-sorption water potentials), (2) model (2).

chrometry and cryoscopy) was measured on the samples of another kind prepared either by adding the calculated amount of water to the air-dry soil or by air drying (or thermostat drying) of the samples initially wetted to the total water capacity. In this case, the data discrepancy is expected, since salts are partially removed with water solution upon tensiometry (pressing or centrifuging) and remain in the soil upon the determination of the total water potential by cryoscopy and psychrometry to create an additional air-dry solid phase on sample drying. This increases the water retention significantly in the area of low moisture, which was proved experimentally [28]. If to measure the total and capillary sorption potentials simultaneously using the same samples, no discrepancies arise, and the $P_{os}(W)$ curve estimated from their difference regularly tends to zero upon soil drying in the area of low values of the soil water content.

The direct estimation of EC of solution extracted from soil may serve as an independent evidence. The EC value is related to the concentration of electrolytes and osmotic pressure, which convinces us in versatility of nonlinear dependences of P_{os} on the water content (Fig. 3). This parameter also shows the initial rise of EC in the measured equilibrium centrifuged solution in the course of decreasing soil water content; further, after the maximum is passed, in the area of medium and low water content (about 35–30% of total water capacity, or one-third of the possible water content in consolidated soil). It manifests a rather sharp decrease down to conventionally zero values (undetectable by the HI DIST-WP4 device used this study). This does not mean that EC reaches an absolute zero, as even the water completely devoid of dissolved salts is capable of conducting electric current. However, the zero instrument reading with 0.01 dS/m resolution proves that

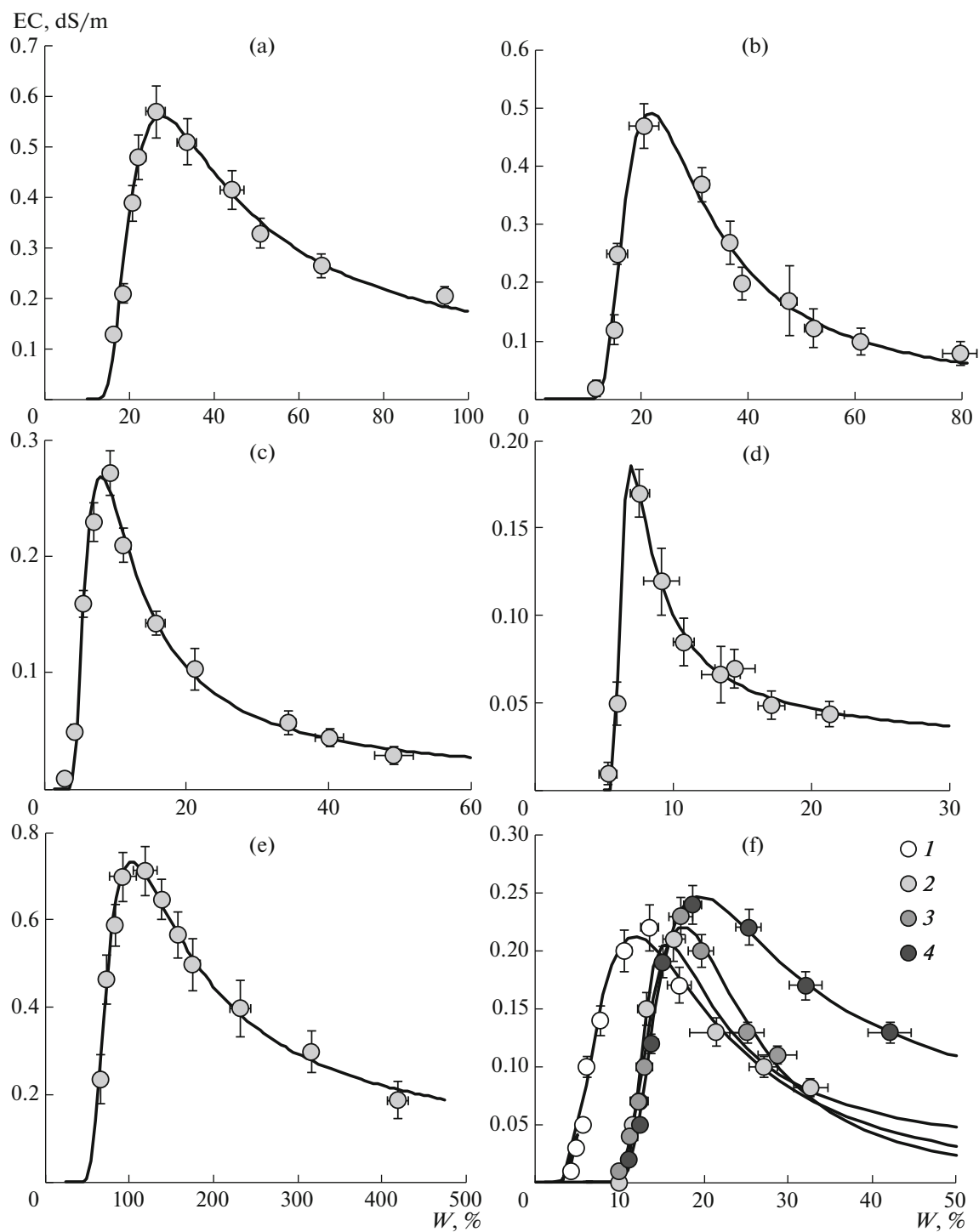


Fig. 3. Dependence of the EC of equilibrium soil solutions on the soil water content. Soils: (a) chernozem; (b) gray forest; (c) and (f) soddy-podzolic; (d) alluvial soddy; (e) peat bog; (f) textures of soddy-podzolic soils: (1) sandy loam, (2) and (3) silty loam, and (4) clay loam. Round symbols designate experimental data, lines stand for model (2).

this water does not differ from distilled water in the content of salts (ions). This experimental fact confirms the result of previous indirect assessment of osmotic pressure tending to zero in soil solutions in the area of low soil water content. It also agrees completely

with the direct measurement of parameters of equilibrium soil solutions extracted from fine-dispersed systems by pressing, centrifuging, or displacement by other liquids; in particular, it is in line with a tendency to a decrease in the concentration of electrolytes (the

total content of ions) upon the decreasing water content starting from some critical water content in such systems [10, 17].

A comparison of our experimental results with published data [1, 9, 10, 17, 26] allows us to conclude on the universal character of the dependence of active concentration, osmotic pressure, and EC in equilibrium soil solutions on the soil water content. This dependence takes the form of nonlinear function with the extremum as shown in Figs. 1–3. Let us turn to the theoretical explanation of such a relationship and to its mathematical simulation. Historically, the first attempt to give a fundamental interpretation of $P_{os}(W)$ dependence was made in [9] proceeding from two effects, i.e., the soil solution concentration in the area of relatively high water content and the “insolubilizing volume” at the low water content close to the maximum hygroscopic moisture [9]. Being unaware of this work earlier, we proposed a similar in essence explanation based on the concept of competing interphase interactions in soil physical systems [25, 26]. Let us consider it in detail and let us try to substantiate it proceeding from the available experimental data.

Let some initial equilibrium concentration of electrolytes and the relevant osmotic pressure and EC exist under the condition of saturation or oversaturation (paste, suspension). If this water occurs in the free state, i.e., outside the field of soil surface forces, and shows an ordinary solvency, the decreasing content of this kind of water in soil should result in a gradual growth of active concentration, EC, and osmotic pressure in the equilibrium solution according to the Campbell law (1). Approximation of the ascending sections of the curves $P_{os}(W)$ and $EC(W)$ by the exponential model $y = aW^{-b}$, where y is the analyzed parameter of soil solution, and a and b are empirical constants, appears to be a good evidence in favor of concentration/dilution mechanism rather than the alternative hypotheses of dynamics of the studied soil solution characteristics (e.g., the hypotheses of solution “fractionation” by pores or hydrodynamic dispersion). The model manifests high determination coefficients ($R^2 = 0.98–0.99$) for the statistically reliable parameters at the significance level $p < 0.01$, with the b parameter varying from 0.77 (soddy-podzolic clay loamy soil) to 1.44 (gray forest silt loamy soil); it does not differ statistically significantly from 1 at $p = 0.05$ (which is usually applied in soil science) irrespectively of the analyzed property (either osmotic pressure P_{os} or electrical conductivity EC). This fact indicates that the suggested model is actually equivalent to Eq. (1).

The rise in active concentration should continue up to reaching the solubility equilibrium for the ion predominating in the soil solution, after which the active concentration (the osmotic pressure and EC) might be stabilized at some maximal levels. If it had been so, we would have derived unambiguous curves of the rise in these parameters with decreasing soil water content,

or, at least, their rise up to the maximum, after which no changes should take place. However, in fact, the experiments point to the permanent opposite trend of decreasing concentration, osmotic pressure, and EC in the equilibrium solutions starting from some critical water content upon the soil drying. This trend may be explained by the fact that the residual water falls into the field of surface forces of the fine-dispersed solid phase, including apparently the precipitated salts that have reached the solubility equilibrium on concentrating; in this case, the competition for water molecules begins between the soil surface and the solution ions. An alternative hypothesis arising from the nonlinearity of EC function and decreasing its values at high (3–10 M) concentrations of electrolytes [38] is, on one hand, unlikely for most of soils (except for solonchaks); and, on the other hand, it may be reduced to our explanation, if to take precipitating salts for the analogue of the soil solid phase. Finally, when the energy of molecular interactions between the solvent (water) and the solid phase exceeds their energy of interaction with free ions of the liquid phase, the bound water may evidently lose its dissolving capacity for salts [23]. All direct measurements of the liquid extracted from soil [17, 23, 26] (Fig. 3), as well as indirect assessments [9] (Figs. 1 and 2) permit us to conclude that this water contains virtually no salts and does not represent a concentrated solution with the low EC as stated in [38].

In the classical dispute [23] on the mechanisms of water-retention capacity of soils (surface hydration or cation hydration), this effect, in turn, markedly points to the fact that the interaction energy between the ions of double electric layer (DEL) and the surface of colloidal-disperse complex (CDC) of soil is higher than the energy of their hydration. Therefore, the CDC surface contributes most of all to the water-retention capacity of soils, with the diffusive layer of DEL being its peculiar continuation (bifurcation) in the disperse medium (Fig. 4). This scheme shows the bonds between DEL ions and adsorbed counter-ions on the surface (and, probably, counter ions of the sediment precipitated upon concentration of salts in the soil solution) as “springs” that may stretch as affected by heat motion without breaking unlike ions in the free solution outside DEL. In this scheme, DEL cations represent in essence the same surface charges, only at some distance from the surface. They spend the bulk of free energy for the strong electrical (Coulomb) interaction with the surface. The more energy, the closer to the surface (this is shown in darkening tone in Fig. 4). Only the residual energy is spent for the interaction with the polar water molecules (hydration). Therefore, being removed (pressed by the membrane press at the pressure of thousands kPa, or centrifuged), the soil water contains almost no dissolved electrolytes, and the soil does not acquire any electrical charge, as it would have been if DEL cations had been bound to water (hydrated) stronger than to the surface.

Hence, we regard the attempts to calculate quantitatively the input of exchange cations to the water retention according to the cation exchange capacity and the degree of cation hydration [31, 32] as senseless, because DEL cations and adsorbed exchangeable ions in disperse systems do not possess that amount of hydration energy and that degree of ionization as determined for free solutions, which was correctly stated by Rode [23]. Outside the diffusive layer of DEL (conventionally, because the exponential decrease in the concentration of ions in the diffusive layer suggests that there are no distinct boundaries in this system) ions of the free pore solution are completely hydrated (blank symbols in Fig. 4). However, they do not contribute to the increase in the water-retention capacity of the soil solid phase (capillary-sorption pressure) and only add to the osmotic component in the total water potential. Finally, the phenomena of recharging colloids, as well as the points of charge inversion and “zero potential” that can be reached not only in chemical and physicochemical experiments [15, 30, 42], but also in nature, mean the absolute loss of water-retention capacity in case the soil water would have been bound only by exchangeable ions, which is not actually observed.

The above-discussed scheme explains the experimental results and points to the complicated processes of solid–liquid interaction in soils, in particular, to the mobile boundaries between the soil water (solution) categories distinguished according to the force of bonding with the solid-phase matrix [25, 26]. Classical ideas giving the priority role to dispersion and structure of solid-phase soil components should be apparently improved because the capacity of soil particles to bind water, and, hence, the boundary of firmly bound water category (“insolubilizing volume”) are controlled also by the composition and concentration of the liquid phase (i.e., by parameters of the soil solution proper) along with the mentioned factors. Therefore, for the same particle-size distribution (texture) of soil, the IV value turns out to be higher for saline soils or upon using the concentrated solutions instead of fresh water. The same is also true for changing solution composition, i.e., when single-charged cations are replaced by bi- or tri-charged cations. These, allegedly insignificant (from the viewpoint of capillary model of water retention that predominates in soil science) changes lead (according to the alternative ion-electrostatic model) to shrinking DEL and, respectively, to reducing water volume bound by surface forces (film and adsorbed water). The dotted line in Fig. 4 marking the conventional boundary of this category of bound water will move left in this case, closer to the surface of colloidal-disperse complex.

The results obtained in the work in the form of universal functional dependence between soil solution characteristics and moisture are important for all major divisions of soil science. For soil physics, these are the patterns of thermodynamic potentials as

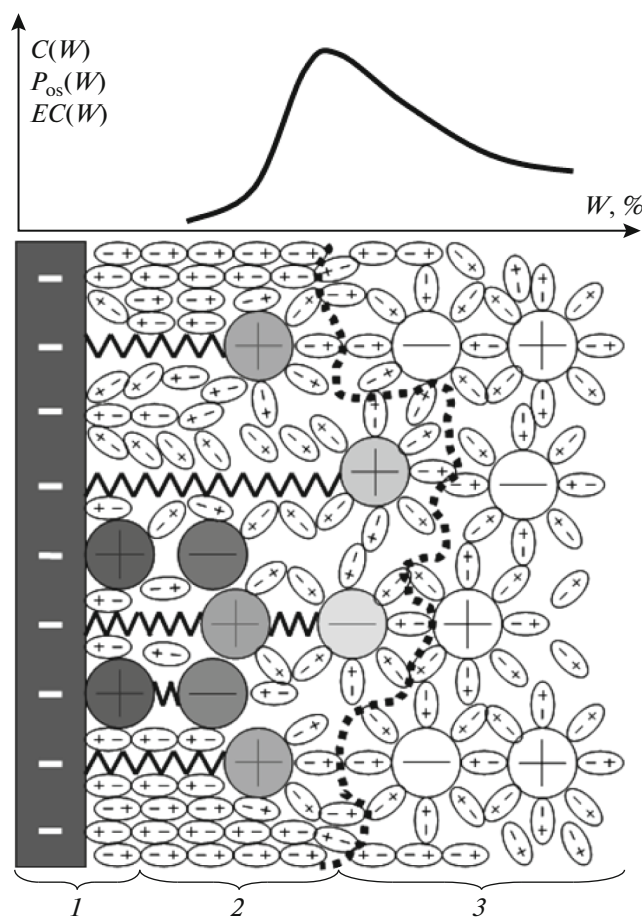


Fig. 4. Surface-energy mechanism of the formation of water-retention capacity and concentration of solution in soil: (1) a flat surface of solid negatively charged particle of the colloidal disperse complex and the adsorption layer; (2) diffusive layer of DEL with branched conventional boundary of acting surface forces (dotted line), to which the maximum on the curves of concentration (C), osmotic pressure (P_{os}), and electrical conductivity (EC) as dependent on the water content is allocated (top of the figure); and (3) free soil solution; see the text for other designations and explanations.

dependent on the soil water content, the idea about the mobile boundaries between different kinds (categories) of soil water, and simple techniques of their quantitative estimation according to the experimental curves $EC(W)$ or other moisture functions (active concentration, osmotic pressure). There are grounds to consider the extremum (maximum) moisture in these curves to be equal to the maximum molecular water capacity (MMWC) of soil or to the conventional boundary of active impact of surface forces (molecular and ion electrostatic) from the solid-phase matrix on the soil solution [26]. In its turn, water with conventionally zero EC (concentration or pressure) in the equilibrium soil solution corresponds to insolubilizing volume value, or to the maximum adsorption water capacity according to Voronin [34], which character-

izes firmly bound water [26]. In this case, the simple, quick, accurate, and cheap method [26] of assessing the indicated soil-hydrological constants from $EC(W)$ curves along with the determination of capillary-sorption potential and osmotic pressure of soil water almost through the entire natural diapason of moisture variation may be used successfully instead of well-known labor-consuming techniques, which are often devoid of fundamental substantiation, e.g., the estimation of MMWC according to Lebedev, Kolyasev, or Dolgov-Matskevich, or the estimation of insolubilizing volume using standard osmotic solutions and soil pastes [18, 22, 23, 34]. The proposed approach estimates the actual thermodynamic balance and the limits of surface forces operation in the disperse three-phase system with the inherent composition and concentration of soil solution. In case of using some universal solutions with standard concentrations of electrolytes, the insolubilizing volume (maximum water adsorption capacity) values will differ from the actually observed values due to inevitable competition between water retention by fine-dispersed particles and new osmotically active components of the liquid phase in accordance with the scheme shown in Fig. 4.

In chemistry and physical chemistry of soils, knowing the dependence of the active concentration and related properties of soil solutions in dependence on the water content permits more precise prediction of ion exchange, sorption, and other chemical reactions in soil, as well as other processes, for which the equilibrium thermodynamic constants are known. Determination of equilibrium constants in laboratory appears to be allowable for strong dilutions (which are atypical for soils); however, to predict the processes that go actually in consolidated three-phase chemical systems (reactors) with variable moisture, one should replace actual active concentrations by the chemical equations with these constants, whereas the former may vary 3–10 times due to the concentrating/diluting effect only for the same amount of electrolytes as is seen in Figs. 1–3. Concentration variation on the descending branch from MMWC to IV can reach several dozen times. Meanwhile, as far as we know, these effects being the direct consequence of the complex nonlinear relationship between the active concentration of solubles and moisture are not taken into consideration in the present-day computer models of energy and mass exchange in distributed reactive porous media [34].

For agrochemistry and soil biology, the significance of this dependence consists of the possibility to determine more precisely and optimize the conditions of mineral nutrition of plants, as well as the boundaries of soil microbiota functioning. For instance, the root consumption at the soil moisture close to MMWC may be apparently no less productive than for the higher content of moisture, since the increment in nutrition concentration in the liquid phase in the form of soluble salts compensates for the mitigating flow of

liquid proper. The technique of introducing the mineral nutrition elements and plant protectants to the rhizosphere in the form of hydrogel compositions [46] is also fundamentally substantiated. For gels, the dependence between the active concentration of ions and the moisture is pronounced in a wide rather than narrow (MMWC) zone that shows almost permanent maximal concentrations lowering at rising moisture only with the gradual transition of gel to sol (physical dilution) [17]. Unlike capillary-porous bodies, gels represent two-phase systems always saturated with water, which fills the entire possible volume, which probably ensures the maximal contact and mass exchange with the solid phase and the known stability in the composition and content of equilibrium solution upon shrinkage and swelling.

Consideration of the results obtained in the agrochemical assessment of salinization shows that soil drying to the MMWC upon the formal absence of salinization ($EC_{1:1} < 4$ dS/m) may lead, according to the observed regularities in $EC(W)$ and $P_{os}(W)$ curves, to EC up to 12 dS/m and higher in the equilibrium solution, i.e., to the values typical of solonchaks exerting substantial suppression of vegetation [13]. At the same time, the permanent presence of a certain amount (dependent on the colloidal complex dispersion and the ionic strength of free solution) of nearly distilled water appears to be no less important positive ecological factor. For the higher plants with the root potential rarely exceeding 15–20 atm (1500–200 J/kg) this water will be virtually unavailable despite the fact that it may reach 20–30% and more of the total amount of water, e.g., in clayey Vertisols of Tunisia [25]. For soil microflora with the absolute water potential up to 3–90 kJ/kg at spore germination and higher (actinomycetes), this medium (even solonchaks) will be quite suitable for life and reproduction according to [13]. The above-discussed list (far from being exhaustive) of possible application of the universal dependence of the soil solution characteristics from moisture obtained in our study testifies to its importance for the soil science. The use of this relationship is simplified significantly, if it is quantitatively formalized by an adequate mathematical model. Therefore, the final part of our study will be aimed at deriving such a model.

Thermodynamic moisture potential, as well as chemical potential of a component of soil solution are the fundamental logarithmic functions of the activities. Formally, for the normal (Gauss–Laplace) distribution of potentials in the multicomponent thermodynamic system, we may speak about the lognormal distribution of active concentrations (mass or mol shares) of all its components. In fact, in the recent decades, soil science has presented a number of successful physicochemical models of structural-functional properties and processes that follow lognormal distribution [11, 34, 35, 44, 48]. The modified law of lognormal distribution [11] as applied to the quantitative descrip-

Table 1. Results of $Pos(W)$ and $EC(W)$ data approximation by model (2) and their statistical processing

Sample	Model (2) parameters and statistics					
	a	b	MMWC	IV	R^2	s
Osmotic pressure (Fig. 2)						
a	1772 ± 19	0.34 ± 0.02	6.99 ± 0.10	0.63 ± 0.10	0.996	38.1
b	3997 ± 47	0.44 ± 0.02	8.60 ± 0.11	1.81 ± 0.14	0.995	91.5
v	1501 ± 27	0.59 ± 0.04	17.24 ± 0.25	7.39 ± 0.43	0.988	54.7
d	6126 ± 46	0.39 ± 0.02	9.79 ± 0.10	1.14 ± 0.11	0.997	111.1
Electrical conductivity (Fig. 3)						
a	0.56 ± 0.02	0.43 ± 0.06	21.64 ± 0.73	6.65 ± 1.31	0.974	0.03
b	0.49 ± 0.03	0.32 ± 0.06	21.70 ± 0.72	4.94 ± 1.59	0.966	0.03
c	0.27 ± 0.04	0.36 ± 0.08	7.95 ± 0.93	1.49 ± 0.65	0.953	0.05
d	0.19 ± 0.02	0.61 ± 0.04	6.93 ± 0.19	4.87 ± 0.27	0.988	0.01
e	0.73 ± 0.01	0.43 ± 0.03	103.69 ± 1.71	22.53 ± 3.07	0.989	0.02
f-1	0.21 ± 0.01	0.17 ± 0.09	11.78 ± 0.66	0.19 ± 0.07	0.981	0.01
f-2	0.21 ± 0.01	0.49 ± 0.10	15.62 ± 0.53	7.22 ± 1.28	0.967	0.02
f-3	0.22 ± 0.01	0.25 ± 0.09	17.42 ± 0.54	3.09 ± 1.81	0.988	0.01
f-4	0.25 ± 0.01	0.47 ± 0.06	19.39 ± 0.37	5.72 ± 0.75	0.994	0.01

For sample designations, see Figure captions to Figs. 2 and 3.

tion of relationship between the concentration properties of solution and the soil water content results in the following model:

$$F = a \exp \left[- \left(\frac{\ln \left(\frac{W + b}{\text{MMWC} + b} \right)}{b \ln \left(\frac{W}{\text{IV}} \right)} \right)^2 \right]. \quad (2)$$

Here, F stands for the simulated function of $EC(W)$ and $P_{os}(W)$ represented as the probability density of mass share (active concentration) of electrolytes in the soil with variable moisture; a is the maximal value of this function in the extremum point at $W = \text{MMWC}$; and b is the empirical parameter controlling the width of the distribution peak. Numerator in the under exponential function shows the mathematical expectation of average in the surrounding of b median (the geometric mean) with the central value of MMWC (the distribution peak coordinate along the water content axis); denominator stands for variance with the limit minimal value $W = \text{IV}$. Function (2) is evidently defined at semi-infinite section $\text{IV} < W < \infty$, which fits the lognormally distributed value [11] and the physical essence of soil moisture as any solid/liquid mass ratio on dilution/concentration; in doing so, the standardized probability density $f = F/a$ changes from zero to one, i.e., remains a finite value not exceeding 1 according to its physical sense.

The results of data approximation by model (2) are shown as curves (Figs. 2 and 3) with model and statistical parameters listed in the Table 1. Both the visual analysis of the graphs and the statistical data attest to

the adequacy of the proposed model to experimental data for all soil samples and studied parameters $EC(W)$ and $P_{os}(W)$. The values of approximation reliability R^2 varied from 0.974 to 0.999 for standard errors $s = 0.008$ – 0.056 dS/m for EC and $s = 38$ – 111 kPa for osmotic pressure, which is substantially lower than the errors of experimental estimation (conductometry) and calculation of these values. Index $100s/a$ standing for the relative standard approximation error for most of cases does not exceed 3–5%. If relative values normalized according to their maximums (EC/EC^{\max} and P_{os}/P_{os}^{\max}) are used, parameter a does not differ statistically significantly from 1. Therefore, the initial four-parameter function (2) is reduced to a three-parameter function, with one of the three remaining parameters (MMWC) being set apriori as the maximum abscissa for the studied experimental curves. Mathematically, this reduces the data approximation problem to the search for two remaining parameters (IV and b) and to the specification of the a priori set MMWC value. This makes it possible to find promptly an optimal solution for the description of a very complex nonlinear dependence (Figs. 2 and 3) by, in essence, two-parameter equation for the area $\text{IV} < W$.

Thus, in this study we managed not only to come up with one kind of curves describing the functional relationship between the soil solution parameters and the soil water contents in two radically different experiments and to substantiate it fundamentally but also to propose an adequate mathematical model of the obtained universal function.

CONCLUSIONS

(1) Soil solution is characterized by a universal functional relationship between active concentration, osmotic pressure, and EC values versus mass percent of water in soil in the form of a nonlinear function with an extremum (a peak).

(2) This function shape may be explained by the manifestation of competitive interactions between water molecules and solid phase and ions in the solution at the low water content along with the effects of concentration/dilution soil solution in the area of medium and high water content.

(3) The maximum on the curves (conventionally, the maximum molecular water capacity) fits the upper boundary of surface forces influence on soil solution and its maximum active concentration; the minimal values of concentration, osmotic pressure, and EC (experimentally indistinguishable from zero) are observed in water firmly bound by surface forces (a conventional condition of insolubilizing water volume).

(4) To describe the obtained relationship, we suggest the mathematical model in the form of a modified function of lognormal distribution of the studied parameters of solution presented as the probability density of their mass content (active concentration) in the soil with variable water content.

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REFERENCES

1. A. A. Ananyan, "Water crystallization in freezing and frozen rocks," in *Modern Concepts about Related Water in Minerals* (Academy of Sciences of USSR, Moscow, 1963), pp. 59–63.
2. I. S. Belyuchenko, A. V. Smagin, L. B. Popok, and L. E. Popok, *Data Analysis and Mathematical Modeling in Ecology and Nature Management* (Kuban State Agricultural Univ., Krasnodar, 2015) [in Russian].
3. E. Bresler, B. Mc Neal, and D. L. Carter, *Saline and Sodic Soils: Principles—Dynamics—Modeling* (Springer-Verlag, Berlin, 1982; Gidrometeoizdat, Leningrad, 1987) [in Russian].
4. T. L. Bystritskaya, V. V. Volkova, and V. V. Snakin, *Soil Solutions of Chernozems and Gray Forest Soils* (Nauka, Moscow, 1981) [in Russian].
5. T. L. Bystritskaya, E. Kovach-Lang, and V. V. Snakin, "Soil solutions as the parts of the cycle of chemical elements in the forest-steppe zone of Hungaria," *Ekol. Kooperatsiya*, No. 3, 58–63 (1984).
6. A. F. Vadyunina, E. V. Shein, A. V. Kirichenko, V. M. Goncharov, and L. P. Kopikova, "Electrical conductivity of saturated and unsaturated soil and pore solutions," *Vestn. Mosk. Univ., Ser. 17: Pochvoved.*, No. 2, 42–49 (1984).
7. E. F. Vedrova and V. M. Korsunov, "Composition of lysimetric waters in soddy-podzolic soils of Western Siberia," *Pochvovedenie*, No. 6, 49–54 (1985).
8. L. A. Vorob'eva, *Chemical Analysis of Soils* (Moscow State Univ., Moscow, 1998) [in Russian].
9. A. D. Voronin and V. D. Skalaban, "Relationships between full, capillary-sorption, and osmotic potentials of water in soil," *Pochvovedenie*, No. 12, 121–125 (1978).
10. N. I. Gorbunov and I. G. Tsyurupa, "Heterogenic concentration of a solution isolated from clay minerals and soils," *Pochvovedenie*, No. 33, 166–171 (1947).
11. E. A. Dmitriev, *Mathematical Statistics in Soil Science* (Moscow State Univ., Moscow, 1995) [in Russian].
12. R. I. Zaitseva, N. G. Minashina, and I. I. Sudnitsyn, "Concentration of sodium chloride solutions in pores of various size," *Eurasian Soil Sci.* **30**, 284–289 (1997).
13. D. G. Zvyagintsev, G. M. Zenova, E. A. Doroshenko, A. A. Gryadunova, T. A. Gracheva, and I. I. Sudnitsyn, "Actinomycete growth in conditions of low moisture," *Biol. Bull.* **34**, 242–247 (2007).
14. E. I. Karavanova and E. A. Timofeeva, "Chemical composition of solutions in macro- and micropores in the upper horizons of soils in the Central Forest State Biosphere Reserve," *Eurasian Soil Sci.* **42**, 1357–1363 (2009).
15. E. I. Karavanova and S. Ya. Trofimov, *Liquid Phase of Soils* (Universitetskaya Kniga, Moscow, 2009) [in Russian].
16. E. I. Karavanova, E. A. Timofeeva, and A. V. Smagin, "Water retention curves and chemical compositions of soil solutions from some soils of the Central Forest State Nature Biosphere Reserve," *Moscow Univ. Soil Sci. Bull.* **62**, 190–195 (2007).
17. P. A. Kryukov, *Solutions in Rocks, Soils, and Clays* (Nauka, Novosibirsk, 1971) [in Russian].
18. N. G. Minashina, "Concentration and composition of salts in the solution of a gypsum-containing soil as dependent on the soil water content," *Eurasian Soil Sci.* **38**, 718–726 (2005).
19. S. V. Nerpin and A. F. Chudnovskii, *Soil Physics* (Nauka, Moscow, 1967) [in Russian].
20. A. I. Pozdnyakov, *Field Electrophysics of Soils* (Nauka, Moscow, 2001) [in Russian].
21. A. A. Ponizovskii, D. L. Pinskii, and L. A. Vorob'eva, *Chemical Processes and Equilibria in Soils* (Moscow State Univ., Moscow, 1986) [in Russian].
22. O. G. Rastvorova, *Physics of Soils: Practical Manual* (Leningrad State Univ., Leningrad, 1983) [in Russian].
23. A. A. Rode, *Soil Moisture* (Academy of Sciences of USSR, Moscow, 1952) [in Russian].
24. *Bound Water in Disperse Systems* (Moscow State Univ., Moscow, 1977) [in Russian].
25. A. V. Smagin, "Theory and methods of evaluating the physical status of soils," *Eurasian Soil Sci.* **36**, 301–312 (2003).
26. A. V. Smagin, "Soil-hydrological constants: physical meaning and quantification based on equilibrium cen-

- trifugation,” Dokl. Ekol. Pochvoved. **1** (1), 31–56 (2006).
27. A. V. Smagin, N. B. Sadovnikova, M. V. Glagolev, and A. V. Kirichenko, “New instrumental methods and portable electronic devices for the ecological monitoring of soils and adjacent media,” Ekol. Vestn. Sev. Kavk. **2** (1), 5–17 (2006).
 28. A. V. Smagin and N. B. Sadovnikova, “Physical mechanisms of water retention and dispersion dynamics in soils, rocks, and colloid-dispersed materials,” Ekol. Vestn. Sev. Kavk. **13** (4), 4–20 (2017).
 29. T. A. Sokolova, “Clay soil material as a block of “memory” about soil cover formation,” Pochvovedenie, No. 5, 582–590 (1995).
 30. T. A. Sokolova and S. Ya. Trofimov, *Sorption Properties of Soils. Adsorption. Cation Exchange* (Universitetskaya Kniga, Moscow, 2009) [in Russian].
 31. I. I. Sudnitsyn, *Movement of Soil Moisture and Water Consumption by the Plants* (Moscow State Univ., Moscow, 1979) [in Russian].
 32. I. I. Sudnitsyn, A. P. Shvarov, and E. A. Koreneva, “Integral energy of soil hydration,” Estestv. Tekh. Nauki, No. 10, 85–87 (2011).
 33. I. I. Sudnitsyn, A. V. Smagin, and A. P. Shvarov, “The theory of Maxwell–Boltzmann–Helmholtz–Gouy about the double electric layer in disperse systems and its application to soil science (on the 100th anniversary of the paper published by Gouy),” Eurasian Soil Sci. **45**, 452–457 (2012).
 34. *Theories and Methods of Soil Physics* (Grifi K, Moscow, 2007) [in Russian].
 35. V. V. Terleev, W. Mirschel, V. L. Badenko, I. Yu. Guseva, and P. D. Gurin, “Physical-statistical interpretation of the parameters of the soil water retention function,” Agrofizika, No. 4, 1–8 (2012).
 36. E. I. Shilova and K. G. Kreier, “Carbon dioxide of soil solution and its role in pedogenesis,” Pochvovedenie, No. 7, 65–72 (1957).
 37. T. E. Shitikova, “Composition of lysimetric waters of soddy-podzolic soils, Pochvovedenie, No. 4, 27–38 (1986).
 38. V. V. Shcherbakov and Yu. M. Artemkina, “Electromagnetic properties of solutions,” in *Proceedings of the All-Russia Forum of Young Scientists “A Step to the Future”* (APFN Scientific Technical Association, Moscow, 2012), pp. 20–28.
 39. E. C. Brevik, Th. E. Fenton, and A. Lazari, “Soil electrical conductivity as a function of soil water content and implications for soil mapping,” *Precis. Agric.* **7** (6), 393–404 (2006). doi 10.1007/s11119-006-9021-x
 40. G. S. Campbell, *Soil Physics with BASIC* (Elsevier, Amsterdam, 1985).
 41. R. Giesler, U. S. Lundstrom, and H. Grip, “Comparison of soil chemistry assessment using zero-tension lysimeters or centrifugation,” *Eur. J. Soil Sci.* **47** (3), 395–405 (1996).
 42. M. E. Essington, *Soil and Water Chemistry: An Integrative Approach* (CRC Press, Boca Raton, 2004).
 43. B. R. Hanson and K. Kaita, “Response of electromagnetic conductivity meter to soil salinity and soil-water content,” *J. Irrig. Drain. Div., Am. Soc. Civ. Eng.* **123**, 141–143 (1997).
 44. K. Kosugi, “Lognormal distribution model for unsaturated soil hydraulic properties,” *Water Resour. Res.* **32**, 2697–2703 (1996).
 45. A. V. Smagin, “Column-centrifugation method for determining water retention curves of soils and disperse sediments,” *Eurasian Soil Sci.* **45**, 416–422 (2012). doi 10.1134/S1064229312040126
 46. A. V. Smagin, “Thermodynamic evaluation of the impact of strongly swelling polymer hydrogels with ionic silver on the water retention capacity of sandy substrate,” *IOP Conf. Ser.: Earth Environ. Sci.* **52** (012087), 1–7 (2017). doi 10.1088/1755-1315/52/1/012087
 47. V. V. Snakin, E. Kovasc-Lang, and T. L. Bystritskaya, “Methodological aspects of in situ ionometry in grassland ecosystems,” *Abstr. Bot.* **10**, 87–95 (1986).
 48. V. Terleev, R. Ginvesky, V. Lazarev, A. Nikonorov, I. Togo, A. Topaj, K. Moiseev, E. Abakumov, A. Melnichuk, and I. Dunaeva, “Predicting the scanning branches of hysteretic soil-water retention capacity with use the method of mathematical modeling,” *IOP Conf. Ser.: Earth Environ. Sci.* **90** (012105), (2017). doi 10.1088/1755-1315/90/1/012105
 49. D. Zabowski and F. C. Ugolini, “Lysimeter and centrifuge soil solutions: seasonal differences between methods,” *Soil Sci. Soc. Am. J.* **54**, 1130–1135 (1990).

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