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Solid Earth Discussions

Interactive comment on "Ion's association in soil and vadose zone of Azov-Black sea region" *by* A. A. Batukaev et al.

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On behalf of my co-authors, thanks a lot for your positive and constructive comments and suggestions on our manuscript.

The article is devoted to the important issue of equilibria in water solution, which is necessary for a proper understanding of the evolution of soils, mass transfer in the unsaturated zone. The authors contributed to the interpretation of these processes in terms of the classical theory of electrolytes. The proposed model is a definite development of the theory of electrolytes for heterogeneous geosystems, the properties of which are very difficult to interpret.

According to the article, there are comments:

Comment 1. In the theory of electrolytes, there is a concept of ion's activity. One of the adopted chemical symbols for ion's activity is γ. The authors in their models into the equation (19) introduced the activity coefficient, but represent it as γe. What is difference of γe from the standard designation symbol γ, and whether there is some difference between the standard form and the form of the activity coefficient of the ion, the authors stated. This is subject to eliminate.

Answer We thank the reviewer for an opportunity to comment our model in more details. According the reviewer's comment, to the section "Discussion" of the article's final version is added the following text:

An activity coefficient is a factor used in thermodynamics to account for deviations from ideal behaviour in a mixture of chemical substances. Activity coefficients may be determined experimentally, can be calculated theoretically using the Debye–Hückel equation and other models.The γe factor in (19) is not a result of direct determination or direct calculation, but an integral product of several stages of modeling taking into account laws of solution's chemical thermodynamics and corresponding equations. For this reason, we propose the activity coefficient with an additional index "e" in respect to the family name of AP Endovitsky who offered the algorithm.

Comment 2. In the physical model for extraction the soil solution, the authors used a substrate of soil and sand, which is considered an analog of the studied original soil. The presence of sand dramatically increases the hydraulic conductivity of an artificial system that distinguishes it from natural brown soil. In addition, simulating the humidity in an artificial system, the authors, in our opinion, made a mistake of generalization of characteristics of the object modeling. Yes, in complex of chestnut soil the moisture can be as high as the authors have shown in Table 1, however, this state of soil humidity is less common than the typical condition of low humidity. Soil moisture of solonetzic complex, especially in the summer, may be less than 10%, and for the sufficiently long period of time. Is the real soil moisture and aeration zone is consistent with the model and its interpretation, the authors proposed?

Answer We agree with the reviewer that used to provide input data to test models the physical modeling method has drawbacks. We agree with the reviewer's position on the details of these shortcomings. But the method is common, and many researchers are very satisfied using this method. That is why we used this way of displacement of soil solution from soil samples. Other methods, on our opinion, have further disadvantages. The disadvantage of the method at the low soil moisture, which is indicated by the reviewer, is obvious for us too. We are grateful to the referee for an opportunity to justify fully our approach, basing on his observations. Respectively to the reviewer's remark to the "Discussion" section of the final version of the article we add the following text:

To obtain the baseline data for thermodynamic model's testing was used a standard physical modeling method. The method has drawbacks. Instead proper soil, is used the substrate of soil and sand, otherwise the extraction of soil solution from the native soil of heavy structure and corresponding granulometric composition is impossible. The presence of sand in the substrate dramatically increases the hydraulic conductivity of the artificial system. It distinguishes from natural chestnut soil. The next lack of direct soil solution extraction methods is that links are broken in the system "solid phase – liquid phase". Chestnut soil has low humidity. But at low soil moisture the soil solution displacement method is useless, so in experiment the high soil moisture was applied. This leads to inadequate generalization of the object's simulation, but another version of the direct study of soil solution composition is not currently available. The disadvantage of method at the low soil moisture is obvious. It is a reason for thermodynamic model development, which allows extrapolation of the solution's state in the soil and vadose zone at low humidity of soil complex components.

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