simultaneously subjected to forces emanating from the surface and from the cations bound to the surface, both simultaneously reducing the free energy of the water. At most one might be able to determine that for certain cations the major portion of the reduction in free energy for the first water molecules is due to the cations and for the later water molecules due to the surface, depending on the relative hydration energies of surface and cations.

I feel that expression of thermodynamic data on a gram-ion basis of exchangeable ion as Kittrick attempted, interesting as it may be in regards to fixation mechanisms, must await better data on the hydration of the ions. The hydration of ions in solution is still unresolved [e.g. (3), and ref. 15 in (1), page 70]. The degree of hydration of exchange ions could remain unknown even longer.

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References


The two questions raised by Dr. Kijne concern the hydration number and the entropy and enthalpy of hydration of interlayer cations as compared to bulk solution. The evaluation of the strong force model for vermiculite (2) was carried out “with vermiculite layers and interlayer cations initially at infinite distance in bulk solution.” At this point interlayer ions are essentially ions in bulk solution. After the vermiculite layers have contracted around the interlayer ions, dehydrating them to the point where only one or two interlayers of water remain, it seems obvious that the interlayer ions are not going to be as hydrated as they were in bulk solution (with corresponding changes in their remaining hydration number, entropy and enthalpy of hydration). In evaluating the strong-force model, bulk solution properties were used only for calculating purposes, so that opposing energy contributions could be evaluated prior to their mutual diminution.

Considering several additional comments by Dr. Kijne, the hydration number of 6 for Na ions in Na-vermiculite was not assumed by Kittrick (2), but was determined experimentally by Van Olphen (3). Further, the hydration energy of interlayer Na⁺ was calculated by Van Olphen from a condenser formula as work against electrostatic attraction. Discussing this formula, Kittrick (2) did point out that “For vermiculite, this formula predicts ΔH of contraction to be lower than ΔH of hydration of the interlayer cation alone.”

Dr. Kijne apparently does not object to the TΔS values for vermiculite determined by Van Olphen, or their use in (2). Since the evaluation of the strong-force model was for vermiculite only, it is perhaps best left to Dr. Kijne to evaluate the data for other minerals in his letter and in (1).

The strong-force model and its quantitative evaluation (2) still appear to fit the data presently available for vermiculite rather well. It was hoped that the model would stimulate new thinking on the subject and when the model can no longer fit vermiculite data, I will mourn its passing but briefly.

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Determining Diffusivity from the Redistribution of Soil-Water

As Cassel, Warrick, Nielsen and Biggar (1) have recently suggested, there is a need in soil physics for accurate and convenient techniques to measure soil-water transport characteristics at intermediate moisture contents. The redistribution method they describe for diffusivity determination may be useful in this regard, but a limitation not discussed in their paper should be recognized.

Due to hysteresis in the dependence of capillary potential (Ψ) on moisture content (θ), the diffusion description of water transfer fails when different parts of a uniform soil are first wet to different moisture contents and then drained (3, 6, 2). This is a consequence of the different Ψ(θ) relations at different positions in the draining soil: at each point the Ψ(θ) relation is a primary draining scanning curve which depends on the moisture content at the point at the instant of reversal from wetting to draining.

Thus in those parts of soil columns where the moisture content is decreasing during redistribution the diffusion analysis and equations [1] and [2] of Cassel et al. are not applicable. The correct equations are

\[ \int_{x_0}^{x_0} \frac{\partial \theta}{\partial t} \, dx = (K \frac{\partial \psi}{\partial x})_{x_0}, \quad [1] \]

\[ \int_{x_0}^{L} \frac{\partial \theta}{\partial t} \, dx = (K \frac{\partial \psi}{\partial x})_{x_0}. \quad [2] \]

K is the hydraulic conductivity of the soil. Since K enters the above equations as a point value, they are not affected by hysteresis in K(θ).