Although the suggested explanations[2-4] in terms of heavy radicals or complex ions may be correct, it is clear that the parameters directly responsible for the minimum velocity are the density, and the adiabatic compressibility, β, of the solution. These are related by the equation:

$$v^2 = 1/\rho\beta$$

where v is the ultrasonic velocity. The variation in v with molarity may then be expressed:

$$dv/dc = -v/2 . (1/\rho . d\rho/dc + 1/\beta . d\beta/dc) \quad (1)$$

The terms $d\rho/dc$ and $d\beta/dc$ are of opposite sign; hence the relative magnitudes of the terms within brackets on the right-hand side of equation (1) may produce monotonic increase or decrease of v with concentration, or, as in the case of silver nitrate, a minimum velocity.

It is interesting that ammonium nitrate solutions, which show similar variations with molarity of electrical conductance and of mean-ion activity coefficient to those of silver nitrate, do not exhibit a minimum ultrasonic velocity; the curve for ammonium nitrate is included in Fig. 1. Presumably the ion-pairing in these solutions[5] does not always result in a velocity minimum.

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Complexes of Vermiculite with Amino-Acids

ORGANIC substances, either as neutral molecules or as cations, form 'sandwich' complexes with the expanding-lattice silicate minerals in which films of the organic substance a few Angstroms thick alternate with silicate layers 10 Å. thick. Recent work has shown that macroscopic vermiculite crystals complexed with butylammonium ions absorb large quantities of water and swell in the direction perpendicular to the plane of the silicate layers[1,2].

We have observed that macroscopic vermiculite crystals complexed with various amino-acids also swell anisotropically to many times their original size. Two apparently different swelling mechanisms are involved, depending on whether the amino-acid is present as the cation or as the dipolar ion; in both instances, swelling is confined to the direction perpendicular to the plane of the silicate layers (Fig. 1). In the jelly-like swollen crystals, the silicate layers remain effectively parallel to one another and, under optimum swelling conditions, may be some hundreds of Angstroms apart.

One type of swelling resembles that exhibited by the butylammonium–vermiculite complexes, and occurs after the amino-acid has been introduced as the interlayer cation replacing the magnesium or other inorganic cations present in the natural minerals. Treatment with 0·5 M aqueous solutions of the hydrochloride of the acid for two or three days at 80° C.
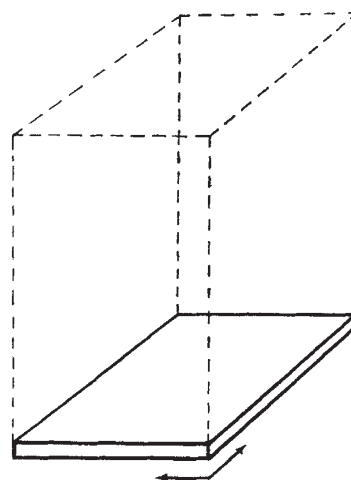

Fig. 1. Representation of the dimensional change in a vermiculite–amino-acid crystal before swelling (full line) and after swelling (dashed line). Silicate layer plane indicated by arrows

is usually sufficient for complete exchange with crack-free crystals of dimensions 1 mm. × 1 mm. × 0·1 mm. The amount of amino-acid taken up is close to the cation exchange capacity of the minerals, that is, in the range 120–180 m.equiv./100 gm. Swelling develops when the amino-acid solution, in which the crystals are immersed, is diluted to a critical value which varies with the amino-acid and the vermiculite used. Swelling increases with decreasing solution concentration and is maximal at infinite dilution. The initiation of swelling is thought to coincide with 'hydration' of the interlayer amino-acid cations[2] and their dissociation from the negatively charged silicate surfaces, while subsequent swelling appears to be osmotically controlled. This type of swelling has been observed with ornithine, lysine and γ-aminobutyric acid.

A second type of swelling occurs when natural vermiculite crystals are immersed in strong amino-acid solutions containing the acid in the dipolar form. In this type, replacement of the interlayer inorganic cations is inappreciable and swelling may take place at room temperature in a few minutes. Swelling develops only in solutions of sufficiently high concentration and increases directly with concentration. Considerable amounts of amino-acid are taken up into the interlayer regions of the mineral, the intracrystalline concentration being of the same order as that of the external solution. Here the dielectric constant of the immersion solution appears to be the controlling factor. The mechanism is thought to involve the masking of the charge on the interlayer cations so that the effective electrostatic attraction between them and the silicate layers is reduced. Swelling of this type has been observed with solutions of glycine, β-alanine, γ-aminobutyric acid and ε-aminocaproic acid.

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