RESPONSE TO MacCARTHY'S COMMENTS ON THE DERIVATION OF SCHUBERT'S ION-EXCHANGE EQUATIONS

Dear Sir:

In a letter published in *Soil Science* (123: 207, 1977), MacCarthy says that our interpretation of the ion-exchange method for calculating stability constants (Zunino et al. 1972) arose from a literal translation of a misprint in Schubert's paper of 1948. According to MacCarthy's views, Schubert's equation is restricted to mononuclear complexes because Schubert "equated the molar concentration of the complex M_xC_y to the concentration of complexed metal (M_c) rather than to $(M_c)/x$, thus omitting the stoichiometric factor, x."

A proper answer to MacCarthy's criticisms can be based upon a simultaneous examination of his letter and the paper wherein MacCarthy and Mark originally gave their thoughts (MacCarthy and Mark 1977). In their paper they say that in Schubert's treatment (Schubert 1948) two misprints and a number of simplifications and oversights render the ion-exchange equation applicable only to mononuclear complexes. Even though in Schubert's paper there are more than two misprints, MacCarthy and Mark's statement is difficult to accept since it suggests that Schubert did not develop his equation based on the scientific method, but on accidental formal facts.

We ratify in this letter that Schubert implicitly introduced two assumptions that are not valid, but that, when simultaneously introduced into the derivation treatment, do algebraically cancel each other when the complex is mononuclear. When complexes contain more than one metal ion per molecule (M_xC_y or M_xC-types), however, they do not algebraically cancel out, since the free metal ion concentration at equilibrium will be raised to the stoichiometric factor x. The approach we developed gets rid of these two nonvalid assumptions and shows the influence of the factor x on the ion-exchange equation. This had not been the case in other derivations, e.g., Schubert (1948); Li, Doody, and White (1957); and Martell and Calvin (1952).

MacCarthy and Mark's work is an excellent example to show how the assumptions we characterized as "erroneous" in 1972 have been improperly used. To derive the ion-exchange equation, they define:

$$\lambda_0 = \frac{(M_r)}{(M)} \qquad (1)$$

$$\lambda = \frac{(M_r)}{(M_c) + (M)} \qquad (2)$$

where λ_0 and λ are the distribution coefficients in the absence, and in the presence, of the complexant, respectively; (M) is the free-metal ion concentration in solution; (M_r) is the number of moles of metal per unit weight of air-dried resin; and (M_c) is the concentration of complexed metal in solution.

Then they *combined* Eqs. (1) and (2) to obtain:

$$\frac{\lambda_0}{\lambda} - 1 = \frac{(M_c)}{(M)} = \frac{m(M_mL_n)}{(M)}$$

Evidently when combining Eqs. (1) and (2) it is being assumed that the terms (M_r) and (M) are the same in both equations, i.e., the amount of metal bound to the resin at equilibrium is the same in the presence, and in the absence, of the complexant, and that the free metal ion concentration in solution at equilibrium is the same in the presence or absence of complexant. This would be true only if no complex formation had taken place. It seems that MacCarthy and Mark missed the meaning of our paper since, surprisingly, some equations they gave, e.g., $(MmLn) = (Mc)/m$, and $\beta = (Mc)/m(M)^m(L)^n$, are exactly the same, except for different symbols, as those we deduced in 1972.

In his letter MacCarthy says that "for the polynuclear case, Zunino et al. (1972) do unwittingly incorporate the stoichiometric factor, which Schubert had omitted, into their equations." This statement is surprising since it implies that we found the correct procedure just by chance and that Schubert consciously based his deduction on simplifications and oversights! According to basic principles of chemistry the molar concentration of an M_xC_y complex, ex-

pressed as a function of complexed metal, is undoubtedly Mc/x.

The ion-exchange equilibrium method is no doubt one of the best available for determining the stability of simple mononuclear complexes. We think that it is important to study the analytical limiting factors of this method, however, and, accordingly, we have recently demonstrated that the accuracy of the experimental data is strongly dependent on the range of the complexant concentration used (Galindo and Zunino 1978). The knowledge of the limiting factors of the ion-exchange method, together with a clear derivation of its equations, should help analysts to make better use of this simple experimental procedure.

So far, the suitability of the ion-exchange equilibrium method to determine stability or stoichiometry of soil organic matter metallic complexes has been widely discussed. It is our opinion that the role of soil organic matter in soil genesis, plant nutrition, and environmental metal pollution cannot be investigated only by determining formation constants of soil organic matter metallic complexes (Zunino et al. 1975). The complexity of some systems and the many variables involved may render the majority of such analytical methods as ion-exchange and continuous variations inapplicable for this purpose. It seems important that the advantages of using different approaches that measure potential metal-binding ability of the macromolecular complexant rather than the apparent stability constants of its individual metallic complexes (Zunino and Martin 1977 a and b) be discussed and worked out.

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