

Ion Activities: An Historical and Theoretical Overview¹

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ABSTRACT

A knowledge of ion activities in soil-water systems is essential to a proper understanding of the physicochemical behavior of soils and to the environment of plant roots in the soil. However, with the notable exception of soil acidity, perhaps no other topic in soil chemistry has provoked such fierce arguments as the meaning of ionic activities as they apply to the soil solution. The purpose of this paper is to present an historical and theoretical overview of the use of ion activities in soil chemistry. Attempting to incorporate ionic species into a thermodynamic analysis of the soil solution is a convenient mathematical device, since an ionic species cannot be described in thermodynamic terms. Ionic species are strictly molecular or microscopic concepts. It is demonstrated in this paper that when ionic equilibria between aqueous solutions and solid phases are investigated, the division of the electrochemical potential into a term in electrical potential (ϕ) and a term in chemical potential (μ) is entirely arbitrary. Additionally, the early 1950s arguments of Jenny, Marshall, Peech, Coleman, Overbeek, and Babcock dealing with junction potentials, suspension effects, and mobilities of ions is reviewed. The importance of soil solution activities in relation to nutrient uptake and plant growth is also presented.

Additional Index Words: thermodynamics, electrochemistry, chemical potential, electrochemical potential, suspension effect.

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IT HAS BEEN 32 YEARS since some of the giants of soil chemistry initiated intense discussions on the meaning of ionic activities as they applied to the soil solution. Perhaps no other topic in soil chemistry, with the notable exception of soil acidity, has provoked such fierce arguments.

Yet in 1983, many of the questions posed by such illustrious soil and surface chemists as Jenny, Coleman, Overbeek, Peech, Marshall, and Babcock remain unresolved. Yet, no one denies the fact that a knowledge of ion activities in soil-water systems is essential to a proper understanding of the physicochemical behavior of soils and ionic environment of plant roots in the soil.

THEORETICAL ASPECTS OF ION ACTIVITIES

The chemical potential of a substance can be expressed as (Babcock, 1963; Sposito, 1981)

$$\mu = \mu^\circ + RT \ln f/f^\circ \quad [1]$$

where μ = chemical potential, μ° = chemical potential in the Standard State, f = fugacity, f° = Standard State fugacity, and R and T = universal gas constant and absolute temperature, respectively. Eq. [1] applies

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to any substance, in any phase, in any kind of mixture at equilibrium. The ratio f/f° in Eq. [1] can be given the symbol a and defined to be the relative activity, or, the thermodynamic activity of the substance:

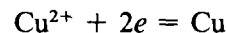
$$a \equiv f/f^\circ \quad [2]$$

The activity is a dimensionless quantity that serves as a measure of the deviation of the chemical potential from its value in the Standard State. By definition the activity of any substance in its Standard State is equal to 1. The combination of Eq. [1] and [2] produces the expression

$$\mu = \mu^\circ + RT \ln a \quad [3]$$

Attempting to incorporate ionic species into a thermodynamic analysis of the soil solution is a convenient mathematical device, since an ionic species cannot be described in thermodynamic terms. Ionic species are strictly molecular or microscopic concepts.

Consider two teflon beakers, each of which contains an aqueous solution of 0.01M $\text{Cu}(\text{NO}_3)_2$ along with a wire made of pure copper that is immersed in the solution. Each of the two identical copper wires, in turn, is connected to one pole of a dry cell, such that an electrical potential difference V exists between the wires. Within either wire, the reaction (Sposito, 1981)



(or its reverse) takes place. This reaction can be described by the expression

$$\mu(\text{Cu}) = \mu(\text{Cu}^{2+}) + 2\mu(e)$$

at equilibrium. In this case, $\mu(\text{Cu}) = \mu^\circ(\text{Cu})$ and the Standard State chemical potential of copper metal in the wire is zero by definition (Sposito, 1981). Thus the expression above is reduced to

$$\mu(\text{Cu}^{2+}) = -2\mu(e) \quad [4]$$

between the chemical potentials of Cu^{2+} and the electron in each wire. If N denotes the wire connected to the negative pole of the dry cell and P denotes the wire connected to the positive pole,

$$\mu^N(e) - \mu^P(e) = -FV \quad [5]$$

relates the electrical potential difference to the chemical potential difference between the electrons in the two identical wires (F is the Faraday constant). The combination of Eq. [4] and [5] gives

$$\mu^N(\text{Cu}^{2+}) - \mu^P(\text{Cu}^{2+}) = 2FV \quad [6]$$

Since an equilibrium exists with respect to the transfer of Cu^{2+} between each copper wire and the solution of $\text{Cu}(\text{NO}_3)_2$ bathing it, Eq. [6] can be written in another form

$$\mu^N[\text{Cu}^{2+}(\text{aq})] - \mu^P[\text{Cu}^{2+}(\text{aq})] = 2FV \quad [7]$$

where N and P now refer to the aqueous solutions in which the copper wires labeled N and P , respectively, are immersed.

Suppose now that the copper wires are removed very carefully from the two solutions without perturbing them. In that case, Eq. [7] still must relate the chemical potentials of Cu^{2+} in the two solutions of $0.01M$ $\text{Cu}(\text{NO}_3)_2$. Thus, the value of $\mu[\text{Cu}^{2+}(\text{aq})]$ will depend not only on the chemical properties of the solution of $\text{Cu}(\text{NO}_3)_2$, which in this example are exactly the same in each beaker, but also on the electrical state of the solution. This dependence on the electrical state does not exist for neutral species. Therefore, it is more precise to call $\tilde{\mu}[\text{Cu}^{2+}(\text{aq})]$ the electrochemical potential of Cu^{2+} in an aqueous solution and to denote it with a tilde, while reserving the name chemical potential for $\mu[\text{Cu}(\text{NO}_3)_2(\text{aq})]$ and generally for μ , which refers to any neutral species (Sposito, 1981).

The possibility that the electrochemical potential of an ionic species can differ between two chemically identical aqueous solutions, by virtue of a difference in electrical potential, suggests that the formal definition

$$\tilde{\mu} \equiv ZF\phi + \lambda^\circ + RT \ln a \quad [8]$$

should be examined as to its general applicability to a species of valence Z that is subjected to an electrical potential ϕ . The quantity λ° is a function only of the Standard State temperature and pressure, as well as of the "purely chemical" nature of the substance whose activity is a . For a neutral species, $Z \equiv 0$ and Eq. [8] reduces unambiguously to Eq. [3], with $\lambda^\circ = \mu^\circ$. In the case of the two solutions of $\text{Cu}(\text{NO}_3)_2$ just discussed,

$$\begin{aligned} \tilde{\mu}^N [\text{Cu}^{2+}(\text{aq})] &= 2F\phi^N + \lambda_N^\circ + RT \ln (\text{Cu}^{2+})_N \\ \tilde{\mu}^P [\text{Cu}^{2+}(\text{aq})] &= 2F\phi^P + \lambda_P^\circ + RT \ln (\text{Cu}^{2+})_P \\ \lambda_N^\circ &= \lambda_P^\circ \quad (\text{Cu}^{2+})_N = (\text{Cu}^{2+})_P \end{aligned}$$

and

$$\tilde{\mu}^N [\text{Cu}^{2+}(\text{aq})] - \tilde{\mu}^P [\text{Cu}^{2+}(\text{aq})] = 2F(\phi^N - \phi^P) \quad [9]$$

which is consistent with Eq. [7]. Here again there is no ambiguity in the separation of $\tilde{\mu}$ into "purely electrical" and "purely chemical" parts. If, instead of two $0.01M$ $\text{Cu}(\text{NO}_3)_2$ solutions, Eq. [8] is applied in turn to $\text{Cu}^{2+}(\text{aq})$ in solutions of $0.1M$ $\text{Cu}(\text{NO}_3)_2$ and $0.001M$ $\text{Cu}(\text{NO}_3)_2$, the difference in electrochemical potential of $\text{Cu}^{2+}(\text{aq})$ is given by Eq. [10]:

$$\begin{aligned} \tilde{\mu}'' [\text{Cu}^{2+}(\text{aq})] - \tilde{\mu}' [\text{Cu}^{2+}(\text{aq})] &= 2F(\phi'' - \phi') + RT \ln \{ [\text{Cu}^{2+}]'' / [\text{Cu}^{2+}]' \} \\ &+ RT \ln (\gamma'_{\text{Cu}} / \gamma''_{\text{Cu}}) \end{aligned} \quad [10]$$

where '' refers to the $0.1M$ $\text{Cu}(\text{NO}_3)_2$ solution, ' refers to the $0.001M$ $\text{Cu}(\text{NO}_3)_2$ solution, and γ_{Cu} refers to the single-ion activity coefficient. The left side of Eq. [10] is well defined because it is measurable, for example, by means of a volt-meter and a pair of suitable electrodes. The molar concentrations on the right side of Eq. [10] also are measurable. The extent to which the electrical potential difference, $(\phi'' - \phi')$, which cannot be measured directly, has chemical meaning depends entirely on whether the ratio of single-ion activity coefficients, $\gamma'_{\text{Cu}}/\gamma''_{\text{Cu}}$, in Eq. [10] can be evaluated unambiguously. If, for example, this ratio can be calculated accurately with the Davies equation, the

electrical potential difference becomes well defined. If, on the other hand, the ratio of activity coefficients could not be represented accurately with some model expression, or, if the activity ratio for Cu^{2+} in the two solutions could not be measured, there would be no chemical significance to the separation of the electrochemical potential into "purely electrical" and "purely chemical" parts as in Eq. [8]. This conclusion applies to the problem of defining the electrical potential difference between an aqueous solution in the pore space of a soil and a supernatant solution contacting the soil, or the so-called Donnan potential. Unless the ratio of activity coefficients on the right side of Eq. [10] is well defined, the Donnan potential, $\phi'' - \phi'$, is without empirical significance.

Sposito (1981) makes the above point well through a consideration of the equilibrium between Cu^{2+} in an aqueous solution and in a solid phase [e.g., a solid cupric electrode, or $\text{Cu}_2(\text{OH})_2\text{CO}_3(\text{s})$, or Cu-montmorillonite]. Even though $\tilde{\mu} [\text{Cu}^{2+}(\text{s})] - \tilde{\mu} [\text{Cu}^{2+}(\text{aq})]$ may be well defined, there is no known experimental means by which the terms in ϕ and λ° can be distinguished from one another unambiguously. Therefore the definition in Eq. [8] cannot be applied usefully to this example and only the electrochemical potential itself may be used to describe thermodynamic equilibrium.

The important conclusion one can draw from the above examples is that *an electrical potential difference between two phases of different chemical composition cannot be defined thermodynamically*. The electric potential is a concept that has meaning only when identical phases (e.g., two pieces of copper wire) are under consideration, or when it is possible to determine unambiguously the ionic activity coefficient ratios in two aqueous solutions that contain the same components. In all other situations and, in particular, when ionic equilibria between aqueous solutions and solid phases are investigated, the division of the electrochemical potential into a term in ϕ and a term in λ° is entirely arbitrary.

DISCUSSIONS ON THE SUSPENSION EFFECT

The observation that when a mixture of soil and water is stirred and the solid particles are allowed to settle that a higher pH is usually measured with the electrodes placed in the supernatant solution than when they are placed in the sedimented soil particles (Fig. 1) or the "suspension effect" was first noted by Wiegner (1931). Earlier, Bradfield (1924) first demonstrated potentiometrically the "suspension effect" with electrodyalized clays which constituted evidence for the dissociation of H^+ ions in colloidal clay suspensions. The suspension effect itself was not questioned by anyone but its causes and implications have been given widely different interpretations.

In 1950, Jenny et al. touched off a controversy concerning the cause of the suspension effect and the resultant potential that was argued heatedly for four years by a number of eminent soil and surface chemists. Jenny et al. (1950) ascribed the potential difference to a "liquid junction potential," E_j . One would assume that the use of KCl in the salt bridge would eliminate

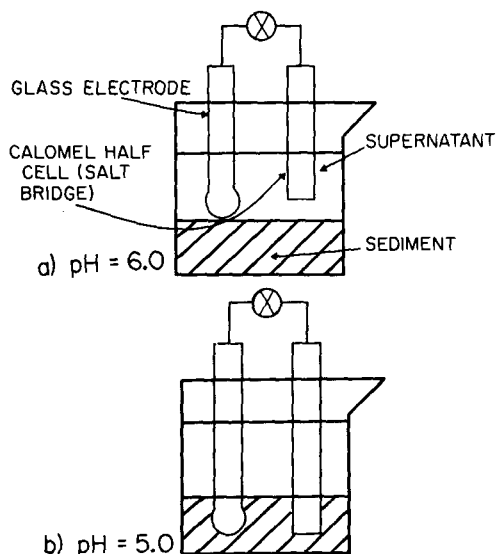


Fig. 1—Illustration of the suspension effect in colloidal systems.

any junction potentials because the mobility of K^+ and Cl^- ions in aqueous solution is very similar and theory would predict a E_j would not arise. However, in cation exchange systems, Jenny et al. (1950) hypothesized that the mobility of K^+ ions may be quite different from that of Cl^- ions, giving rise to a E_j at the KCl bridge.

Marshall (1950, 1964) believed that exchangeable H^+ ions of clay ionized to a degree and the glass electrode responded to the ionized H^+ . He felt the pH should decrease as the concentration of soil or clay in the suspension rises, because the concentration of ionized H^+ goes up as well. Marshall believed that for a system consisting of sedimented clay and a supernatant solution or a clay suspension separated from an equilibrium dialysate by a membrane, that there was an electrical potential difference across the boundary which he called a Donnan potential. Marshall argued that the junction potential of an irreversible reference electrode would be the same in the soil suspension, soil solution, and in standard solutions. Therefore, any difference in ionic activity between the suspension and solution phases must be due to a difference in the electrical potentials between the two phases.

Marshall (1964) felt the good agreement between ionic activities calculated from potentiometric measurements, conductance measurements, and the rate of sugar inversions in clay suspensions supported the extrathermodynamic assumption of a constant E_j . However, one must view these conclusions with a certain degree of suspicion. The increase of sugar inversion in clay suspensions as compared to the equilibrium solution may have been due to the catalytic activity of the clay surface rather than to increased ionic activity. The calculation of ionic activity data from Donnan equilibrium data or from mean salt activity measurements involves unverifiable extrathermodynamic assumptions which do not resolve the issue. Other investigators also concurred with Marshall that the salt-bridge-clay junction potential should be negligibly small and considered the measured potential was a Donnan membrane potential (Peech and Scott, 1951; Low, 1954).

Jenny et al. (1950) had earlier hypothesized that the mobility of K^+ ions may be quite different from that of Cl^- ions when one dealt with cation exchange systems. This difference in ion mobility would give rise to a junction potential at the KCl bridge. However, Marshall disagreed. He felt that when the KCl of a salt bridge is so concentrated that it carries the greatest proportion of current across a boundary in a colloidal system, E_j must be small. Jenny et al. (1950) and Coleman et al. (1950) attempted to counter this argument by saying that K^+ and Cl^- ions carried 95 to 100% of the current but the amount of current carried by K^+ , i.e., its transference number, was much greater than that carried by Cl^- . Peech and McDevit (1950), however, argued that ascribing the sole variation of the observed transference numbers, viz., the decrease in the transference number of Cl^- based on the assumption that the relative mobilities of K^+ and Cl^- ions were changed significantly in the presence of negatively charged colloids, was erroneous. Peech and McDevit (1950) felt that Coleman et al. (1950) had ignored the fact that as the number of cations relative to anions was increased due to dissociation of cations from the clay, the proportion of total current carried by cations must be increased. Also, they reasoned that the transfer number of ions in a solution containing a mixture of electrolytes tells nothing about the relative mobility of ions.

In the wake of these intense arguments, Overbeek (1953) developed an equation relating the Donnan potential to the reduced mobility of counter ions. There was good agreement between Donnan potentials and those calculated using Overbeek's equation. This was also later confirmed by Bower (1961).

Babcock and Overstreet (1953) and Overbeek (1953) used calomel half cells to measure Donnan potentials. They showed that even where transference numbers at the KCl bridge were assumed to be equal, a calomel half cell does not measure a membrane potential in a Donnan system. If an emf was obtained for such a cell, the authors reasoned this would indicate that the transference numbers were not equal at all bridge junctions.

Overbeek (1953) preferred to call the Donnan membrane potential a Donnan emf which was the sum of all interface potentials including the Donnan potential. He recognized well, along with Coleman and Jakobi (1954), that for any electromotive cell, all that can be measured is the total potential. There is no a priori way in which the total potential can be divided and the various potentials assigned to particular regions in the cell (Babcock et al., 1951). Thus, Overbeek concurred with Jenny and Coleman that most if not all of the Donnan potential was due to a liquid junction potential resulting from the reduced mobility of counter ions in the colloidal phase.

Nothing more was done to resolve the suspension effect issue until the elegant work of Olsen and Robbins (1971). Through osmotic pressure and freezing point depression measurements, they concluded that the suspension effect was attributable to a junction potential at the interface between the suspension and the supernatant solution which corroborated work of Jenny and his co-workers. They found that the freez-

ing points of the slurry and supernatant solution were identical, providing evidence that the activity of ions in the two media were identical.

What can one conclude from all of these different viewpoints about the cause of the suspension effect? Perhaps Gast (1977) answered the preceding question best when he wrote: "At present there does not appear to be any rigorous way of resolving which of these interpretations is correct and the true significance of the Donnan potential remains in question. The consequence of this uncertainty is more than academic for it enters into all measurements using a reversible single ion electrode in conjunction with a reference electrode employing a salt bridge such as the calomel electrode."

ION ACTIVITIES AND PLANT GROWTH

One of the main reasons for the initial interest in measuring ion activities was to determine the validity of the "contact exchange theory" proposed by Jenny and co-workers (Jenny and Overstreet, 1939). According to this theory, a plant root in the close proximity of a clay particle actually penetrates a zone (ion swarm) in which the activity of a cation may be 10 to 100 times higher than the activity of a cation in the bulk soil solution. Most research workers agree that the activity of an ion is a better measurement of intensity (I) than is concentration. However, this is limited to solutions only, and may stop when one is dealing with suspensions.

There is a difference of opinion as to the driving force for ion uptake when roots are immersed in soil or clay suspensions. Is it a gradient in the chemical potential of the ion as given by Eq. [3] or is it a gradient in the electrochemical potential as defined by Eq. [8]? Proponents of Eq. [3] found that uptake of a nutrient was often higher when roots were submerged in a clay or resin suspension than when they were placed in a solution that was at equilibrium with the suspension (Khasawneh, 1971). This was ascribed to the greater cation activity in suspensions than in their equilibrium dialysate. Proponents of uptake based on Eq. [8] reported contradictory experimental evidence showing uptake by roots was equal from suspension and from equilibrium dialysates (Khasawneh, 1971).

Olsen and Peech (1960) compared the rate of uptake of Rb^+ and Ca^{2+} by excised roots of barley and mung beans from a suspension of clay or cation-exchange resin with that from the corresponding equilibrium dialysate. The authors found that the rate of uptake of Rb^+ or Ca^{2+} by roots was exactly the same from both suspensions and equilibrium dialysates. The significance of this was that the composition of the soil solution or of the equilibrium dialysate should completely characterize the ion environment of plant roots in soil-water systems, at any selected time.

Many attempts have been made to relate plant growth to ion activity in the soil solution. The earliest attempts dealt with soil pH and soil acidity in the 1920s and early 1930s (Adams, 1974; Khasawneh, 1971).

Adams and co-workers (Adams, 1974) were among the first to successfully relate the ionic activity of the soil solution to plant uptake. Adams and Lund (1966)

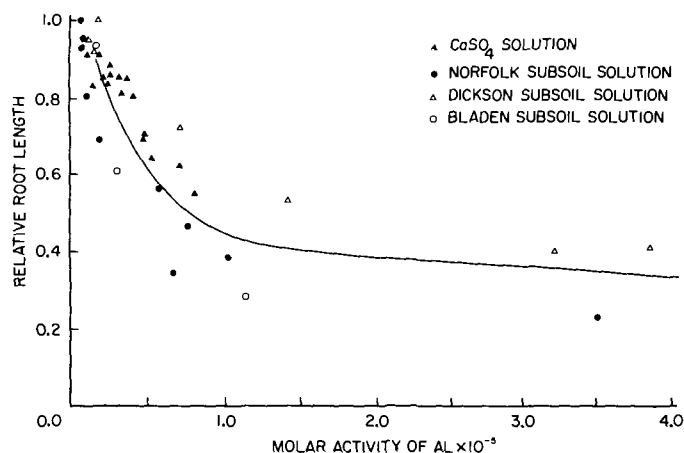


Fig. 2—Effect of molar Al activity on relative cotton root growth in nutrient and soil solutions in situ. Figure taken from Adams and Lund (1966).

measured the growth rate of cotton primary roots in culture solutions containing Al and in acid soils of varying Al contents. If culture solution Al and soil solution Al concentrations were corrected to molar activities, no difference in root growth rate in the two media at equal solution Al activities was observed (Fig. 2). They found the "critical" value of solution Al for cotton roots was an Al^{3+} activity of about $2\mu M$. The data points for all growth media fell on the same line. This critical value for soil Al was later verified by Adams et al. (1967) and by Richburg and Adams (1970).

Brenes and Pearson (1973) demonstrated that Al^{3+} activity was a good index of Al toxicity for corn (*Zea mays* L.) and sorghum (*Sorghum vulgare* L.). Helyar (1978) also called attention to the use of Al activity as an index of Al toxicity for lucern (*Medicago sativa* L.) and subterranean clover (*Trifolium subterraneum* L.). Pavan and Bingham (1982) conducted a solution culture experiment with coffee seedlings (*Coffea arabica* L.). At a constant Al concentration, seedling growth was reduced with dilution of the nutrient solution. This decrease in growth best correlated with

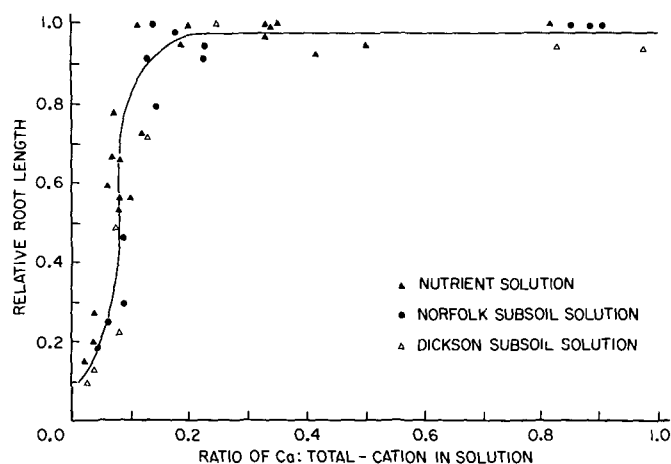


Fig. 3—Effect of Ca: total-cation in solution on cotton root growth in nutrient solutions and soil solutions in situ. Figure taken from Howard and Adams (1965).

an increase in the activity of Al^{3+} . An Al^{3+} activity value of 1.2×10^{-5} was associated with a 10% reduction of coffee seedling growth. This compared favorably with values quoted by Adams and Lund (1966) and by Brenes and Pearson (1973).

Howard and Adams (1965), using soil solution data, found that Ca deficiency could also be found in non-acid soils. They showed that the critical Ca level for cotton (*Gossypium hirsutum* L.) root growth was the same in culture solutions as in soil solutions in situ (Fig. 3). Subsequently, Adams (1966) and Bennett and Adams (1970a) found that Ca-deficient levels even in limed soils were defined by this same quantitative relationship. However, the Ca-plant interrelation necessitated that soil solution cations be expressed as ionic activities rather than ionic concentrations. The critical Ca level in soil solution was defined as:

$$a_{Ca}/\sum a_{cation\ i} \approx 0.15$$

where a_{Ca} = molar activity of Ca^{2+} , and $\sum a_{cation\ i}$ = sum of cationic activities. Thus, for each growth medium, there was a critical level of Ca activity below which root elongation was reduced. However, these critical levels were different for different media. Changing the method of expressing the intensity of Ca from concentrations to activities could not account for the differences in the critical levels of Ca.

In studies with NH_3 , Bennett and Adams (1970), with soil solution and culture solution data, defined the "critical" toxic concentrations of solution NH_3 for cotton roots and sudangrass (*Sorghum bicolor* L.) seedlings. They further showed that the "critical" NH_3 concentration in soil solution was identical to the value in culture solutions. However, a quantitative evaluation of the "critical" toxic concentration of 0.2 mM NH_4OH , which applied to all systems, required that the electrolytic composition of the solutions be expressed as ionic activities and not as ionic concentrations.

The soil solution experiments of Adams and co-workers were the first to show that some ionic effects on root growth were the same in culture solutions as in soil solutions in situ. The experiments further demonstrated the advantage of expressing soil solution and culture solution compositions as ionic activities rather than as measured concentrations. As Khasawneh (1971) stated: "There seems to be general agreement that plant growth is related to nutrient ion activity in the soil solution, but in many cases each soil has a different set of parameters that define this relationship. Data and conclusions cannot always be extrapolated from one soil to another merely on the basis of solution ion activities—other parameters may be needed."

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