Chapter 15

Debye–Hückel Relations and Neighboring Relations: Calculation of the Activity Coefficient of an Ion

Abstract The value of the activity of an ion cannot be determined experimentally, contrary to that of an uncharged species. However, it is accessible through a calculation, at least in some conditions of concentrations. Hence, this possibility is of utmost importance from the theoretical standpoint and, also, from the practical one as well. An example of such an importance is provided by the most commonly and quasi-universally used scale of pH which is based on the estimation of the *activity* of the solvated proton in the studied medium.

The calculation of the activity of ions is performed by applying Debye–Hückel or a very neighboring relation.

The chapter is focused on the presentation of these relations and on the results and conclusions to which they lead. (Their setting up is described in another chapter.) Here are also mentioned the properties of the mean activity coefficients of electrolytes which, contrary to those of their constitutive ions, can be measured. They have the great virtue to permit to indirectly verify the Debye–Hückel relations. However, the using of these relations imposes to know the ionic strength of the solution. This notion is introduced at the beginning of the chapter but, just before, the impossibility of the measurement of the activity of an ion is explored.

Keywords Ion activity (determination?) • Ionic strength (influence on the nonelectrolytes) • General behavior of the activity coefficient of the whole electrolyte • Guntelberg's relation • Guggenheim's relation • Davies' relation • Broomley's relation • Debye–Hückel's relation • pH scale

The value of the activity of an ion cannot be determined experimentally, contrary to that of an uncharged species. However, it is accessible through a calculation, at least in some conditions of concentrations. Hence, this possibility is of utmost importance from the theoretical standpoint and, also, from the practical one as well. An example of such an importance is provided by the most commonly and quasi-universally used scale of pH which is based on the estimation of the *activity* of the solvated proton in the studied medium.

The calculation of the activity of ions is performed by applying Debye–Hückel relations. In this chapter, we not only focus ourselves on their presentation but also on the results and conclusions to which they lead. Here, we also mention the properties of the mean activity coefficients of electrolytes which, contrary to

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those of ions, can be measured. They permit to indirectly verify the Debye–Hückel relations.

Using these relations imposes to know the ionic strength of the solution. We introduce this notion at the beginning of the chapter. But, just before, we come back on the notion of impossibility of measurement of the activity of an ion.

15.1 Impossibility of an Experimental Measurement of the Activity of an Ion

As we have already and briefly said it (viz. Chap. 6) and as we shall specify it below, activity coefficients quantify the electrostatic interactions between the chemical species constituting the studied system, notably the interaction ions/ions. Let us also mention the interaction ions/dipoles, dipoles/dipoles, etc. They result in a Gibbs energy change of the whole solution under study for a mole of ions added to it. It is impossible to determine this Gibbs energy change because of the following two reasons:

- We do not have a chemical species constituted by only one kind of ions at our disposal. This is for a reason of electroneutrality. A salt is always neutral from the electrical standpoint. It is also the case of a solution. In brief, an ion is always accompanied by a counterion to ensure the electroneutrality of the medium. Hence, it is quite impossible to add an ion into the studied solution and as a result to determine the change in the chemical potential during this virtual process.
- The second reason is that, if even the previous process was possible, the corresponding measured change in Gibbs energy would then comprise a supplementary term from electrostatic origin which adds to the search for one concerning the interactions of the ions, which is only of interest for our purpose. It would correspond to the work necessary to perform (in the conditions of reversibility) in order to add a charged particle to an already charged solution.

Hence, in order to measure the activity coefficient of an ion, it should be necessary to think up a process which would be able not only to add only one kind of charged ion but also to evolve at a constant electrical charge of the solution.

Hence, all that is possible from the experimental viewpoint consists in adding an ion and its counterion together. Certainly, while doing that, the studied ion is added at the constant charge (null) of the solution, but the measured Gibbs energy change is vitiated by the proper Gibbs energy of addition of the counterion. Actually, here, one finds the same impossibility as that encountered for the measurement of the solvation heat of one ion. It is, indeed, impossible to add only one kind of ions without adding its counterion.

However, the opinion of some authors is that the activity of an ion is potentially measurable but only when an infinitely weak number of ions would be transferred into the solution and, that, provided that the net electrical charge of the solution would be measured at every moment. For some others (Guggenheim), the very notion of activity of an ion is devoid of any physical significance.

To sum up, only some mathematical combinations of activities of ions can be measured (viz. Chap. 12, paragraph 3). Fortunately, if the activity of an ion cannot be experimentally measured, its value can be approached through calculations, at least in some conditions.

From the historical viewpoint, it is interesting to know that the physico-chemical literature is endowed with writings asserting that this determination is possible.

15.2 Ionic Strength

A rapid mention concerning the notion of ionic strength has already been given (viz. Chap. 12). It has been introduced in 1921 by Lewis and Randall on purely empirical bases but its introduction into the realm of the study of solutions has been theoretically justified some years later within the framework of Debye–Hückel theory (viz. Chap. 46).

The ionic strength is a function, the value of which expresses the charge "in ions" of a solution. It is defined as being the half sum of the terms obtained by multiplying the molality m_j of each ion present in solution by the square of its relative charge z_j that is to say

$$I_m = 1/2\sum_j m_j z_j^2 \tag{15.1}$$

where I_m is the ionic strength of the solution on the scale of molalities. The index j indicates that the sum is over all the ions of the solution. It is expressed in mol kg^{-1}. It can also be defined in terms of molarities:

$$I_c=1/2\sum_j c_j z_j^2 \tag{15.2}$$

Then, it is expressed in mol L^{-1}. Given the fact that the notion of ionic strength is only handled in the cases of dilute and very dilute solutions and since, then, the numerical values of molalities are very close to those of molarities, the numerical values of the ionic strengths expressed in both unities are very close to each other:

$$I_m \approx I_c \text{ (dilute solutions)}$$

(The symbol μ has also been used formerly in order to symbolize the ionic strength. It is no longer recommended.)

It is very important to highlight the fact that the "concentration" m_j or c_j is the true "concentration" of the ions and not their total "concentration." As a result of this point, the calculation of the ionic strength entails to take into account the incomplete dissociation of some electrolytes. This is not without setting up some calculation problems (viz. Chap. 19).

Let us confine ourselves, at the present time, to deduce the following conclusions relative to the fully dissociated electrolytes from relations (15.1) and (15.2):

- For those of the type 1/1, the ionic strength is equal to its molar concentration. For example, for a solution c molar of sodium chloride

$$I = 1/2\left([\mathrm{Na}^+]1^2 + [\mathrm{Cl}^-]1^2\right)$$
$$I = c\,\mathrm{mol\,L}^{-1}$$

- For the multivalent ones, it is larger than the molar concentration. Its value is larger all the more the charges of the ions are themselves larger, since there are changes with the square of these ones. For example, for 1 M solution of magnesium sulfate

$$I = 1/2\left(\left[\mathrm{SO}_4^{2-}\right]2^{\mathbf{2}} + \left[\mathrm{Mg}^{2+}\right]2^{\mathbf{2}}\right)$$
$$I = 4c\,\mathrm{mol\,L}^{-1}$$

In direct relation with the use of all Debye–Hückel relations (viz. under), the question coming in mind is this: What are the ions which must be into account in order to calculate the ionic strength of the solution containing the ion under study. The answer is simple: *all*.

15.3 Influence of the Ionic Strength on the Activity of Nonelectrolytes

We know that, in dilute solutions, the activity coefficients of nonelectrolytes are quasi-equal to 1 and hence their activities are quasi-equal to their concentrations in numerical values (viz. Chap. 13). Although the principal subject of this chapter is the solutions of electrolytes, it is interesting, in passing, to study the influence of the ionic strength on the activity coefficients of the nonelectrolytes. We are concerned, here, with aqueous solutions.

It is an experimental fact that one finds the following relation:

$$\ln(\gamma/\gamma_0) = kI_m \tag{15.3}$$

where γ is the activity coefficient of the nonelectrolyte when its solubility is m when it is in presence of some quantity of electrolyte and γ_0 its activity coefficient in pure water in which its solubility is m_0. This relation is found by measurements of solubilities of numerous nonelectrolytes in the presence of electrolytes. I_m is the ionic strength of the solution based on the scale of molalities. Hence, ln γ appears as being proportional to the ionic strength of the solution. The relation seems to be obeyed up to large ionic strengths such as 5 mol kg^{-1}. The value of the proportionality coefficient k depends on the nature of the nonelectrolyte and also of that of the electrolyte added in order to fix the ionic strength. For the major part of electrolytes, the k value is located between 0 and 0.1. For an ionic strength such as $I_m < 0.1$ mol kg^{-1}, the ratio γ/γ_0 changes in the range of 1000–1023. This result justifies the fact that, as a rule, one attributes the value 1 to the activity coefficient of a nonelectrolyte or of the undissociated part of a weak electrolyte in calculations, even when they must be refined (viz. Chap. 19).

An interesting point to underline is that the solubility m of a nonelectrolyte in the presence of an electrolyte is weaker as that m_0 it exhibits in the presence of pure water. This is a point easy to justify. Let us compare two solutions of the same nonelectrolyte, one in pure water where its solubility is m_0 and its activity coefficient γ_0 and the other in water containing an electrolyte where its solubility is m and its activity coefficient γ. At saturation, in both solutions, there is equilibrium between the nonelectrolyte in the solid pure state and itself in solution. Moreover, its fugacity is the same in the solid state, whatever the solution is and the standard state in solution (necessary to quantify whether its activity is the same in both solutions).

Hence, the fugacity in the standard state is the same for both solutions. As a result, the activity of the nonelectrolyte is the same in both solutions. By introducing the activity coefficients, we obtain

$$m_0\gamma_0 = m\gamma$$

and

$$\gamma = (m_0/m)\gamma_0$$

Since the ratio γ/γ_0 is larger than 1, it is also the case of the ratio m_0/m.

The solubility of a nonelectrolyte in water is weakened by the addition of an electrolyte in the solution. It is the base of the phenomenon called “salting out” which is one of the processes used to resolve liquid phases into their constituents in proximate analysis.

It is also interesting to notice that, according to relation (15.3), ln γ is proportional to the ionic strength. This is not the case for the electrolytes as it is evidenced by the Debye–Hückel relations (viz. under).

15.4 General Behavior of the Mean Ionic Activity Coefficients of Electrolytes

In Table 15.1, we mention the experimental values of the mean ionic activity coefficients of several electrolytes in water at 25 °C as a function of their molalities. (Their methods of determination have been described in Chap. 13.)

Table 15.1 Mean ionic activity coefficients in aqueous solutions at 25 °C

Molality	0.001	0.005	0.01	0.05	0.1	0.2	0.5	1.0	2.0
HCl	0.966	0.928	0.905	0.830	0.796	0.767	0.757	0.809	1.009
NaCl	0.966	0.929	0.904	0.823	0.778	0.732	0.679	0.656	0.670
NaBr	0.966	0.934	0.914	0.844	0.800	0.740	0.695	0.686	0.734
KCl	0.965	0.927	0.901	0.815	0.769	0.717	0.650	0.605	0.575
$CaCl_2$	0.888	0.789	0.732	0.584	0.531	0.482	0.457	0.509	0.807
Na_2SO_4	0.887	0.778	0.714	0.530	0.450	0.360	0.270	0.200	–
$ZnSO_4$	0.734	0.477	0.387	0.202	0.148	0.104	0.063	0.044	0.035
$LaCl_3$	0.853	0.716	0.637	0.417	0.356	0.298	0.303	0.387	0.954

According to S. Glasstone, Thermodynamics for chemists, 11th ed., D. Van-Nostrand, Inc., 1960, Princeton

These values clearly show the following points:

- When the molalities are weak, the numerical values of the activity coefficients decrease all the more quickly as the electrolyte is constituted by the most charged ions. This result justifies the definition and introduction of the ionic strength. For example, for a molality of 0.01 mol kg^{-1}, the activity coefficient of lanthanum chloride is 0.637, whereas for sodium chloride at the same molality, it is 0.904. The lanthanum chloride activity is $a_{\mathrm{LaCl3}} = 0.637 \times 0.01 = 6.37 \times 10^{-3}$. Its value falls very quickly with respect to its concentration. From the standpoint of its thermodynamic behavior, the occurrence of interactions from several origins, in particular due to the interaction ions/ions in the bulk solution (viz. Chap. 6), decreases its *effective* presence.
- The mentioned values show that when the molality of the electrolyte is weak, the activity coefficients of the same kind of electrolytes (from the standpoint of the charges of the ions constituting them) are quasi-equal.
- When the molality of the electrolyte increases, the values of the mean ionic activity coefficients begin decreasing, then reach a minimum, and after end up increasing.

The general behavior of the mean ionic activity coefficient is shown in Fig. 15.1 where it is exemplified by three kinds of electrolytes.

Sometimes, when the concentration of the electrolyte is very large, the mean ionic activity coefficient may take incredibly large numerical values. For example, for a molality $m = 20$ mol kg^{-1} of lithium bromide in water, the value of its activity coefficient $\gamma_\pm$ reaches 485!

It is interesting to notice that there exists one concentration (more rigorously: ionic strength) at which the activity coefficient exhibits the value unity, as if the solution would be ideal. This particular concentration varies with the nature of the electrolyte. In aqueous solution at 25 °C, it is located in the range about 3–4 mol kg^{-1}. This phenomenon has a practical application. Some authors take it into account in order to quickly approach the values of the equilibrium thermodynamic constants. Let us recall (viz. Chap. 6) that the latter are expressed in terms of activities. By fixing

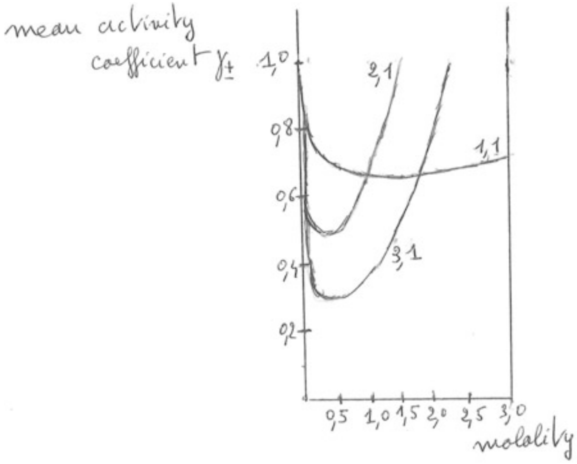

Fig. 15.1 General behavior of the mean ionic activity coefficients as a function of their molalities and according to the kind of electrolyte (symbolism *i*, *j*: *i* metallic ion charge, *j* anion charge)

the ionic strength of the solution under study in the above range of molalities, the different activity coefficients are close to unity and hence the values of equilibrium constants calculated by handling concentrations may not frankly differ from the thermodynamic ones. Calculations taking into account the activities, as they must do in all scientific rigor, may be indeed tedious (viz. Chap. 19). With such a trick, they can be, at least in part, avoided.

Let us also notice in passing that all these behaviors in water we have already mentioned are also recognized in nonaqueous media (ethanol, methanol) and in hydro-organic ones such as the mixtures ethanol-water and dioxan-water.

The Debye–Hückel theory and the equations resulting from it, at least in part, account for these results.

15.5 Debye–Hückel's Relations

Usually, one distinguishes the limit Debye–Hückel relation (1923) and the extended Debye–Hückel one and some others which are very close to the previous ones.

15.5.1 The Limit Equation Law

In this chapter, let us confine ourselves to mention that in order to obtain the limit equation, Debye and Hückel have adopted the hypothesis that ions are electrically charged points dispersed in a continuous medium, the permittivity of which is constant and equal to that of the pure solvent. In these conditions, the equation stemming from it, called the limit Debye–Hückel law, is for a binary electrolyte, the charges of its ions being z_+ and z_-:

$$-\log \gamma_{\pm} = A\left|z_{+}z_{-}\right|\sqrt{\mathrm{I}} \tag{15.4}$$

where I is the ionic strength of the solution expressed in molalities or molarities. This distinction does not matter given the conditions in which the relation can legitimately be used (viz. under). A is a constant, the value of which only depending on the temperature and on the solvent permittivity ε, according to the relations[1]

$$A = 1.825\,10^{6}\,(\varepsilon \mathrm{T})^{-3/2}$$
$$A = 0.509\,\mathrm{mol}^{-1/2}\mathrm{l}^{1/2} \quad (\text{water}: \ 25\,°\mathrm{C})$$

The comparison of the calculated values through the expression (15.4) with those experimentally found for the mean ionic activity coefficients shows that the limit law is only verified for ionic strengths lower than 10^{-3} mol L^{-1}.

The Debye–Hückel theory also provides us with the relation (15.5) which permits the calculation of the activity coefficient of one ion only of charge z in a sufficiently dilute solution:

$$-\log \gamma = A\,z^{2}\sqrt{\mathrm{I}} \tag{15.5}$$

As it has been already said, the expression (15.5) cannot be directly compared with an experimental measurement, but it can be indirectly compared (viz. Chap. 46). However, indirectly, it confirms what has been experimentally found by studying the behavior of the whole electrolyte (viz. the paragraph 4 above). The activity coefficient of an ion, cation, or anion only depends on the ionic strength of the solution. This assertion is exact for the sufficiently diluted solutions. It has been proposed, once in 1923, by Lewis and Randall.

15.5.2 Extended Debye–Hückel Relation

The previous Debye–Hückel's relation (15.4) leads to markedly too weak values of the activity coefficients for the intermediary concentrations of electrolytes. A change in the limit equation enhancing the range of its applications is obtained by adopting the hypothesis that ions are spheres of finite radius, the other hypothesis prevailing in the setting up of the limit law remaining the same. For a binary electrolyte, the new Debye–Hückel's relation, called the extended Debye and Hückel's law, is

$$-\log \gamma_{\pm} = A\left|z_{+}z_{-}\right|\sqrt{\mathrm{I}}/\left(1 + \mathrm{Ba}\sqrt{\mathrm{I}}\right) \tag{15.6}$$

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[1] Other numerical values (but close to the latter ones) may be found in the literature. The discrepancy depends on the chosen value of the solvent permittivity (viz. Chap. 46).

and for only one ion

$$-\log \gamma = Az^2 \surd \mathrm{I} / \left(1 + \mathrm{Ba} \surd \mathrm{I}\right) \tag{15.7}$$

In both expressions, B is a function of the temperature and of the permittivity ε of the solvent. B has for expression

$$B = 50.3\ (\varepsilon \mathrm{T})^{-1/2}$$
$$B = 0.328\,10^8\ \mathrm{cm}^{-1}\,\mathrm{mol}^{-1/2}\,\mathrm{l}^{1/2} \quad (\text{water}:\ \ 25\,°\mathrm{C})$$

In (15.6) and (15.7), a is an adjustable parameter approximately corresponding to the effective radius of the hydrated (solvated) ion, measured in Å (10^{-10} m). The a parameter is called "ion size parameter" or "minimal approach distance" by the other ions of the solution of the ion, the activity coefficient of which is considered. The parameter A of both limit and extended relations is the same. In the case of a binary electrolyte constituted by monovalent ions, the extended Debye–Hückel's relation is

$$-\log \gamma = Az^2 \surd m \,/ \left(1 + \mathrm{Ba} \surd m\right)$$

given $m = I$.

As a first rule, we can conceive that the parameter a is related to the radius r of the ions. By comparing the expressions (15.5) and (15.7), one can notice that it is the presence of the denominator in (15.7) which differentiates them. This finding may be correlated to the fact that, when the concentration of the ion (the ionic strength of the solution) increases, the electronic cloud gets closer to the considered ion, as it is shown by the Debye–Hückel's theory itself (viz. Chap. 46). As a result, the electrical interactions called "long-range interactions" are no longer the only ones to be efficient. "Short-range interactions" are then added to the previous ones. One author (Kielland) has compiled the values of the parameter a for 136 inorganic and organic ions in water. They have not been, of course, directly measured. The values result from the comparison of mean ionic activity coefficients already known, adjusted according to an empirical manner in such a way that the activity coefficient of an electrolyte can be forecasted in a mixture of other electrolytes. A calculation of the activity of a given ion can, then, be possible (viz. Appendix E). It is interesting to notice, through the values of the Kielland's table, that the activity coefficients do vary few little with the parameter a.

The extended Debye–Hückel is satisfactory for ionic strengths varying up to 0.1 mol L^{-1}.

The calculations of the mean ionic activity coefficients of binary monovalent electrolytes lead to accurate values at the level of 1 p 100 whereas the use of the limit equation leads to errors of the order of 10 p 100 in the same conditions.

According to several authors, it seems that the meaning of hydrated radius of the ion under study given to the parameter a is devoid of any thermodynamic base. In addition, inverse calculations of the parameter a as a function of $\sqrt{m}$ by introducing experimental values of $-\log \gamma_{\pm}$ show that a is not a constant.

The worst is that for some concentrations, a is endowed with fully aberrant values. For examples, for molalities of 1.8 mol kg^{-1} in HCl and 2.5 mol kg^{-1} in lithium chloride, the respective values of a are -41.12 nm and -14.19 nm!!

This is the reason why, today, a is only considered as being an adjustable parameter permitting to obtain the best fit between the experimental values of the mean activity coefficients and the extended Debye–Hückel relation.

Finally, from another viewpoint, it must be noticed that, for some authors, it seems that the activity coefficients calculated through the Debye–Hückel relations are related to the scale of molar fractions, although the ionic strength values used for their calculations are expressed in molalities or molarities.

15.5.3 Other Relations Permitting the Calculation of the Mean Activity Coefficient of an Electrolyte

Numerous relations which are more and less related to those of Debye–Hückel have been proposed. Either they stem from minor modifications of the extended Debye–Hückel equation or they differ from the extended relation by the presence of supplementary terms. In connection with this subject, it is interesting to notice that from the mathematical standpoint, the Debye–Hückel relations (both limit and extended) cannot, at all, explain the occurrence of minima in the curves $-\log \gamma_{\pm}/\text{I}$ or $-\log \gamma_{\pm}/c$ or m, as it can be proved definitively by an elementary calculation of derivatives.

Let us mention, like other equations, the

- Guntelberg's relation

By adopting the unique numerical value $a = 3.0$ Å for all the ions, Guntelberg, starting from the extended Debye–Hückel relation, leads to the expression

$$-\log\gamma_{\pm} = A|z_{+}z_{-}|\left[\sqrt{\text{I}}/\left(1 + 1\sqrt{\text{I}}\right)\right] \tag{15.8}$$

The factor unity of $\sqrt{\text{I}}$ in the denominator is a real stroke of luck since at 25 °C, $B = 0.328$ whence $\text{Ba} \approx 1$ with $a = 3$ Å. The Guntelberg's relation seems to give too weak values $\gamma_{\pm}$, even in the range of ionic strength values less than 0.1 mol L^{-1}. Another relation very close to that of Guntelberg plays a fundamental part in the anchoring of the pH scale of the National Bureau of Standards (pH scale of Bates and Guggenheim).

- Guggenheim's relation (1935)

$$-\log\gamma_{\pm} = A\left|z+z-\right|\left[\sqrt{I}/\left(1+\sqrt{I}\right)\right] - \mathrm{bI} \tag{15.9}$$

In this relation, there exists the empirical linear term—bI. For ionic strengths larger, supplementary linear terms may be added to the Guggenheim's equation, whence the relations of the kind are derived:

$$-\log\gamma_{\pm} = A\left|z+z-\right|\left[\sqrt{I}/\left(1+\sqrt{I}\right)\right] + \mathrm{bI} + \mathrm{cI}^2 + \mathrm{dI}^3 \tag{15.10}$$

Quite evidently, the greater the number of terms added, the better the fit between the calculated and experimental values is. But, then, the latter added terms cI^2, dI^3, etc. do possess a statistical weight which is less and less.

A more elaborate form of the Guggenheim's relation is

$$\log\gamma_{\pm} = -A\left|z+z-\right|\left[\sqrt{I}/\left(1+\sqrt{I}\right)\right] + \left[2\nu_{+}\nu_{-})/(\nu_{+}+\nu_{-})\right](2\beta m)$$

Its applies to only one electrolyte. m is the molality of the electrolyte and ν_{+} and ν_{-} the charges of the cation and of the anion. β is a parameter specific of each electrolyte. This relation is exact for an ionic strength up to 0.1 mol l^{-1} with univalent, bi-univalent, and uni-bivalent electrolytes. The coefficient β of the linear term is adjustable according to the nature of the electrolyte. Guggenheim's equations are semiempirical relations.

– Davies' relation (1938)

Davies' relations are

$$-\log\gamma_{\pm} = A\left|z+z-\right|\left[\sqrt{I}/\left(1+\sqrt{I}\right)\right] - 0.2\mathrm{I} \tag{15.11}$$

or

$$-\log\gamma_{+} = A\, z^2\left[\sqrt{I}/\left(1+\sqrt{I}\right)\right] - 0.2\ \mathrm{I} \tag{15.12}$$

It has been largely used in order to estimate the activity coefficients of ions "alone" at ionic strengths relatively large. It seems that for ionic strength of 0.5 mol L^{-1}, the error made by using it on the estimation of the activity coefficient is lower than 8°/°.

Concerning all these relations comprising one or several linear terms, it is interesting to notice that the presence of this term may, mathematically, justify the existence of the minimum of the curves $\gamma_{\pm}/m$.

– Broomley's relation (1972)

According to this theory, the mean activity coefficient of an electrolyte in a binary solution is given by the relation

$$-\log\gamma_{\pm} = A\left|z_{+}z_{-}\right|\left[\sqrt{I}/\left(1+\sqrt{I}\right)\right] + \mathrm{B}_{12}\mathrm{I}$$

with

$$\mathrm{B}_{12} = [(0.06 + 0.6\,\mathrm{B})(z_1 z_2)]/(1 + (1.5/z_1 z_2)\mathrm{I})^2 + \mathrm{B}$$

B is the Broomley's parameter. z_1 and z_2 are the charges of both ions of the electrolyte. A is the Debye–Hückel's constant A ($A = 0.509$). Broomley's relation is also a semiempirical relation since it is based, on the one hand, on those of Debye and Hückel and on the other on arbitrary terms. Some extensions of Broomley's relation exist. They permit to study some mixtures of electrolytes.

Let us also mention the theory of Meissner and Kusik (1978), the mainspring of which is the reduced activity coefficient Γ_{AC} defined by

$$\Gamma_{\mathrm{AC}} = \gamma_{\pm}(1/z_+ z_-)$$

The idea behind this relation is that the reduced activity coefficient is mainly influenced by the interactions between the anions and cations.

Other relations of Debye–Hückel's kind, but less used than the previous ones, are also proposed (viz. Chap. 46). Others, which are not of Debye–Hückel's kind, are also proposed. The most interesting are those based on the radial distribution functions (viz. Chap. 47). The theory leading to them stems from considerations of statistical thermodynamics.