

ION PAIRS AS A THEORETICAL LIMIT CASE CONCEPT AT HIGH DILUTION
FOR EQUILIBRIUM AND TRANSPORT EXCESS PROPERTIES

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Abstract - After presenting the various assumptions implied in the classical ion-pair association model, recent developments are reviewed which help to show in which conditions the chemical model is realistic. The results obtained from fundamental bases like the activity expansion equation are discussed. Some general properties concerning ion-pair distribution functions are analyzed. A generalisation of the echo effect in conductance is proposed which is applicable to electrolyte mixtures in solutions. These results explain the large success of the association concept for excess thermodynamic and transport properties of electrolyte solutions where strong interactions occur.

INTRODUCTION

Among the most striking features of the concept of ionic association (Ref.1), one can point out the following characteristics.

- The simplicity of the basic idea and of its analytical representation.
- The large appeal of this concept to chemists due to its obvious tight chemical analogy.
- The surprising success met when it is tested against experimental data (Ref.2), or compared to more refined theoretical developments (Ref.3,4).
- The easiness with which it can be generalized to any model hamiltonian (Ref.5).

And yet, few concepts have been more misunderstood, criticized, altered or misused. What is really amazing is that the most efficient definition of the concept is the original 1926 statement of Bjerrum which it seems appropriate to recall here for the special case of a single symmetrical electrolyte.

1) In dilute solutions, all short range configurations involving one anion and one cation of opposite charges at a distance from each other less than a distance R will be considered as behaving as a non electrolyte entity, without interaction with the other ionic solute particles. The stoichiometric activity coefficient of the electrolyte thus reads

$$f_{\pm} = \gamma f'_{\pm} \quad (1)$$

where γ and f'_{\pm} are the fraction and the activity coefficient of non associated electrolyte, respectively.

2) The probability density of such a type of configuration is approximated by the Boltzmann function $\exp(-U_{+-}/kT)$ where U_{+-} is the direct potential in the pure solvent.

3) These ion pairs are considered to be in equilibrium with the rest of the ions. This leads to the mass action law expression

$$(1-\gamma)/\gamma^2 c f_{\pm}'^2 = K_A^B = 4 \pi N 10^{-3} \int_0^R r^2 \exp(-U_{+-}/kT) dr \quad (2)$$

4) For the activity coefficient f'_{\pm} of the free ions, any theoretical expression may be used which reasonably takes into account the long-range nature of the corresponding interactions. But for sake of consis-

tency in this expression an ionic Restricted Primitive Model of characteristic distance R must be used together with concentration $c \gamma$ of free ions. Thus, the activity coefficient f_{\pm}^{\dagger} becomes

$$f_{\pm}^{\dagger} = f_{\pm}(R, c \gamma) \quad (3)$$

This does not imply that the sphere of radius R is a hard sphere. Free ions cease to be free ions as soon as they enter the sphere R and associated ions become free ions as soon as they leave the sphere of radius R . On the average the two flows of ions are equal but of opposite directions so that the result is the same as if free ions of concentration $c \gamma$ were indeed bouncing on a hard core sphere of radius R . Hard core sphere encounters would imply a $f_{\pm}(R, c \gamma)$ formulation but the reciprocal is much less restrictive as illustrated in the present case.

The exact correspondence rule for the analytical expression of the long range contribution f_{\pm}^{\dagger} to f_{\pm} will be proved below from more rigorous considerations leading to eqs. (19-21). Surprisingly this rule is independent of the type of interactions between the ions as well as of their properties in the long and short range regions.

5) In 1926 the Debye and Hückel theory was the only theory available, so that Bjerrum chose

$$f_{\pm}^{\dagger} = \exp \{-\kappa q \gamma^{1/2} / (1 + \kappa R \gamma^{1/2})\} \quad (3 \text{ bis})$$

6) The choice of the cut-off distance R must obviously be a compromise which tends to minimize the effect of the two different approximations used on each side of this cut-off distance. Bjerrum proposed to choose

$$R = q \equiv z^2 e^2 / 2DkT \quad (4)$$

since this minimizes the integrand of eq.(2). Using now the hard sphere model of distance of closest approach \underline{a} for anion and cation the Bjerrum association constant is given by

$$K_A^B = 4 \pi N 10^{-3} \int_a^R r^2 \exp \left(\frac{2q}{r} \right) dr \quad (5)$$

and the function f_{\pm}^{\dagger} becomes

$$f_{\pm}^{\dagger} = \exp \{-\kappa q \gamma^{1/2} / (1 + \kappa q \gamma^{1/2})\} \quad (6)$$

The above decomposition of the Bjerrum definition into six steps of decreasing importance as to the consequences of the restrictions they bring, will help to discuss the various criticisms often encountered and also to foresee in which direction the association concept may be complemented to be useful in a large range of applicability.

First, the choice of the cut-off distance, if the concept is correct and the range of concentration in which it is used adequate, must not be critical. Indeed it has been shown (Ref.6) that if exactness is to be achieved at the level the linear contribution in concentration of the $\log f_{\pm}$ function the best choice for this "book keeping" should be $R = 1.1 q$. This shows that Bjerrum's proposal, though not based on the same criterion is indeed quite satisfying. This also shows that this "cut-off" distance is in no way a "critical distance" as it was often called and thereafter subsequently criticized. Indeed the cut-off distance must be such that the errors due to the application of either two short and long range theories used in the vicinity of R are less than experimental precision requires. The answer to this is mainly a matter of experimental verification until more refined theoretical developments either confirm or reject the former assumptions. For instance the HNC theory has indeed confirmed that activity coefficients calculated by Bjerrum's formula are quite realistic in all cases where a comparison can be achieved.

It is often said that the Bjerrum theory concerns only the restricted primitive model like the original Debye-Hückel theory. In fact this is quite inexact since the direct potential U_{+-} used in eq.(2) can easily represent any model. Experiments have shown that, indeed, in this respect, the specific short range parameters which can be derived from eq.(2) do exhibit close correlations with the same parameters issued from HNC calculations: ref.5.

It may seem inconsistent that the Bjerrum theory does not explicitly take into account the short range U_{ij} potential. This is to be expected since in dilute solutions the short range ++ or -- configurations are, for most simple symmetrical electrolytes such as alkali halides or alkylammonium salts, largely outweighed in number by the corresponding +- configurations (there may be some exceptional cases where some chemical complexation occurs between ions of the same charge; but these are outside the field of applications of the association concept discussed here). It was shown elsewhere (Ref.6,7) from considerations concerning the evaluation of the second virial coefficient of electrolyte solutions that the contribution of ++ and -- short range configurations may be explicitly accounted for analytically. These results will be discussed and generalized below.

More important and crucial is the legitimization of the basic statement of the association concept which specifies that the short-range anion-cation pairs do lose their electrolyte activity even in dilute solution. Bjerrum's idea was based on the fact that those pairs in dilute solution were far from any other ion of the solution so that these interactions could be assimilated to ion-dipole interactions which could be neglected. One must admit that this view is not unrealistic. This is but an approximation though and the real question is: how good is this approximation and under which particular conditions for the concentration range and electrolyte-solvent system considered? Obviously for any system the more dilute is the concentration the better is the approximation. A good discussion of this point may be to refer to the average distance of the free ions from the reference ion and state that the ratio of the Debye radius $(\kappa\gamma^{1/2})^{-1}$ to the Bjerrum length q be larger than 2. It thus comes

$$\kappa q \gamma^{1/2} < 0.5 \tag{7}$$

to define the maximum concentration beyond which the Bjerrum expression may become unrealistic. Beyond this concentration one may expect the number of three-ion-short-range clusters to become significant and no longer negligible.

EXCESS PROPERTIES AT EQUILIBRIUM

After a brief summary of the results previously obtained and discussed in a former review (Ref.13) we shall present our more recent developments.

From the Rasaiah-Friedman compressibility equation (Ref.8)

$$d \ln f_{\pm} / d \ln c = - c G / (1 + c G) \tag{8}$$

where $G = G_{+-} + \frac{1}{2} (G_{++} + G_{--})$ (9)

and $G_{ij} = 4\pi \int_0^{\infty} r^2 (g_{ij}(r) - 1) dr$ (10)

in which $g_{ij}(r)$ is the ion-pair distribution function, the following result could be reached (Ref.7)

$$\left\{ \begin{array}{l} \ln f_{\pm} = \ln f_{\pm}^L(R, c) + \ln \gamma_{ij} + \ln \gamma_{++} + \ln \gamma_{--} + O(c^{3/2}) \end{array} \right. \tag{11}$$

$$\left\{ \begin{array}{l} (1 - \gamma_{ij}) / \gamma_{ij} = c G_{ij}^S \end{array} \right. \tag{12}$$

where G_{ij}^S is the short range part of the integral defining G_{ij} (integration from 0 to R) and where f_{\pm}^L is the value of f_{\pm} obtained by using the compressibility equation with the long range parts of the integrals G_{ij} (integration from R to infinity). It could be shown that all neglected terms in the process are of order $3/2$ in concentration. The above result for f_{\pm} is indeed a first step toward the legitimization of the Bjerrum formulation. This result was itself at the time the generalization of a former result (Ref.6) obtained for the second virial coefficient which reads

$$\ln f_{\pm} = - \kappa q + \kappa q \kappa R \{ 1 - \delta(q/R) + \delta'(q/R) \} - K_{+-} c - \frac{1}{2} (K_{++} + K_{--}) c + O(c^{3/2}) \tag{13}$$

with $K_{ij} = 4\pi N 10^{-3} \int_0^R r^2 \exp(-\psi_{ij}/kT) dr$ (14)

- 1) all $n > 2$ contributions
- 2) K_{++} and K_{--}
- 3) the excluded volume term in K_{+-}^S integral eq. (24)

The f_{\pm}^S identifies with the fraction γ of free ions as defined originally by Bjerrum. Using the Debye approximation for f_{\pm}^L was the only possibility offered in 1926.

Before the introduction of these approximations for f_{\pm}^S and f_{\pm}^L , the choice of R is arbitrary. Given the approximations for f_{\pm}^S and f_{\pm}^L , the choice of R becomes restricted, but it is not critical around the value of $R = q$ and leads to errors not higher than the experimental errors in the range of dilute concentration defined by $\kappa q \gamma^{1/2} < 0.5$.

The system of eqs.(19-21) constitutes a generalization of the former system of eqs (11,12). One way to obtain a better evaluation from the compressibility eq.(8) would be to substitute there the unknown zeroth moment function G by $\gamma G_M(c, \gamma)$ in which G_M represents the Meeron approximation. The compressibility equation then reads

$$d \ln f_{\pm} / d \ln c = - c \gamma G_M(c \gamma) / (1 + c \gamma G_M(c \gamma)) \tag{25}$$

which would lead straightforwardly to the following modification of eqs.(11,12)

$$\left\{ \begin{array}{l} \ln f_{\pm} = \ln f_{\pm}^L(R, c \gamma) + \ln \gamma_{+-} + \ln \gamma_{++} + \ln \gamma_{--} + O(c^{3/2} \gamma^{3/2}) \\ (1 - \gamma_{ij}) / \gamma_{ij} = c \gamma G_M(c \gamma) \end{array} \right. \tag{26}$$

$$(1 - \gamma_{ij}) / \gamma_{ij} = c \gamma G_M(c \gamma) \tag{27}$$

which is much closer to the exact system of eqs.(19-21).

This means that the distribution function of the type $\gamma g_M(c \gamma)$ represents indeed a good analytical expression for the distribution functions. This expression does not tend to 1 as r goes to infinity as it should. By adding empirically the necessary complement $1 - \gamma$, the distribution function then reads

$$g_{+-} = \gamma \exp \left(- \frac{U_{+-}^*}{kT} \pm \frac{2q}{r} e^{-\kappa r} \right) + 1 - \gamma. \tag{28}$$

If γ represents the fraction of free ions then $1 - \gamma$ represents the fraction of associated pairs for the g function. The quantity $1 - \gamma$ should represent distribution function of anion-cation ion pairs which is a constant independant of r if these pairs behave ideally. Since free ions or paired ions are the only two exclusive possibilities for an ion their probabilities should indeed be added as done in eq. (28). One thus reaches a selfconsistent formulation.

SOME REMARKS ON DISTRIBUTION FUNCTIONS

Statistical mechanics tells us that distribution functions must meet certain conditions which are often used to overcome various mathematical undeterminacies or as selfconsistency test

A) The most frequent condition used is the electroneutrality condition which states that the charge of the ionic atmosphere should be opposite to that of reference ion. This gives

$$c_i (G_{ii} - G_{ij}) = -1 \text{ with } i \neq j \tag{29}$$

These relations were used by Debye and Hückel to remove one of the undeterminacies in the integration of the linearized Poisson-Boltzmann equation. This condition is also called the zeroth moment condition.

B) Another condition is the second moment condition due to Stillinger and Lovett (Ref.11).

$$\frac{1}{6} \frac{\kappa^2}{\epsilon_i} \sum_j c_j e_j G'_{ij} = -1 \quad (30)$$

$$\text{with } G'_{ij} = \int (g_{ij}(r) - 1) r^2 dr \quad (31)$$

which is used as a test in the HNC approximation by Friedman et al (Ref.12).

C) We have seen that

$$g_{ij}(r) \rightarrow 1 \quad \text{as } r \rightarrow \infty \quad (32)$$

which simply means that at infinity there is no correlation between the ions. This condition was used by Debye and Hückel to remove the second undeterminacy of their integration.

D) There is another condition which so far has been little used which states that at infinite dilution the distribution function should tend to the direct Boltzmann function of the direct potential U_{ij}

$$g_{ij}(r) \longrightarrow \exp(-U_{ij}/kT) \quad \text{as } c \rightarrow 0 \quad (33)$$

In other words the mean potential must tend to the direct potential at infinite dilution when two ions i and j are left alone in the solvent.

It is quite interesting to notice that the Meeron distribution function

$$g_M = \exp\left(-\frac{U_{ij}^*}{kT} \pm \frac{2q}{r} e^{-\kappa r}\right) \quad (34)$$

is in agreement with this requirement like the HNC distribution functions. Also all treatments based on the complete Poisson-Boltzmann equation implicitly assume this condition. The same is true with the Bjerrum calculation through the association constant which makes explicit use of the Boltzmann function. Let us note that the Meeron functions do not satisfy conditions A and B but lead however to much more exact evaluation than the Debye-Hückel functions. This is the evidence that, though theoretically important, the two conditions A and B are not crucial for the evaluation of excess thermodynamic functions at least in dilute solution and condition D is more important for practical efficiency in this field.

E) It is our belief that the function g_B defined above by eq.(28) may constitute a further condition. As concentration decreases the distribution functions should tend to the g_B formulation before leading ultimately to the Boltzmann $\exp(-U_{ij}/kT)$ expression at zero concentration. (Let us note that the g_B functions also follow condition D). Expressed in terms of correlation functions

$$h = g - 1 \quad (35)$$

one obtains

$$h_B = \gamma h_M(c\gamma) \quad (36)$$

so that

$$G_B = \gamma G_M(c\gamma) \quad (37)$$

which was the starting point of this development.

CONDUCTANCE

Let us now turn to the problem of conductance. Classical low field conductance is an irreversible process where the response of the system is linear versus the external perturbation. Like all linear irreversible processes the coefficient of proportionality must be independent of the external perturbation and be a function only of the state of the system at equilibrium. In other words the conductance coefficient

$$f_{\Lambda} = \Lambda/\Lambda_0$$

where Λ and Λ_0 are the molar conductances at finite and zero concentration respectively, should lead to the same kind of information concerning the electrolyte-solvent system as the activity coefficient f_{\pm} . This has already been checked in terms of short-range Gurney cosphere overlap free energy parameters (Ref. 4,13). Another consequence is that in conductance the concept of ion pair must also be a very efficient theoretical tool. This point consequently deserves close attention. We shall now briefly summarize the situation in this particular respect.

A close analysis of the basic equation of transport processes

$$\nabla_P g_{jQ}^{iP} \vec{v}_{jQ}^{iP} + \nabla_Q g_{iP}^{jQ} \vec{v}_{iP}^{jQ} = - \frac{\partial}{\partial t} g_{iP}^{jQ} = - \frac{\partial}{\partial t} g_{jQ}^{iP} \quad (38)$$

shows (Ref.14) that the perturbation $g_{ij}^i(\vec{r})$ on the distribution function of an ion of type i in the vicinity of a reference ion of type j is not only proportional to the external force acting on the ions but more generally is proportional to the difference in the velocity impressed on them in the linear irreversible process.

$$g_{ji}^i(\vec{r}) = Y_{ji}(r) \cos\theta \frac{(\vec{v}_i^i - \vec{v}_j^j) \vec{X}/X}{kT(\omega_i + \omega_j)} \quad (39)$$

where \vec{r} is the vector $\vec{r}_i - \vec{r}_j$

θ is the angle between \vec{r} and the external field \vec{X}

ω_i is the mobility of the ion i

\vec{v}_i^i is the mean velocity vector of the ions of type i

\vec{X} is the external field

Expressed in terms of ionic conductance quantities the above result can be rewritten

$$g_{ji}^i(\vec{r}) = Y_{ji}(r) \cos\theta v_{ji} \frac{e_i X}{kT} \quad (40)$$

where e_i is the charge of the ions of type i and v_{ji} is the "echo" factor given by

$$v_{ji} = \frac{1}{z_i} \frac{\lambda_i/z_i - \lambda_j/z_i}{\lambda_i^0/z_i^2 + \lambda_j^0/z_j^2} \quad (41)$$

For symmetrical electrolytes the echo factor reduces to

$$v_{ji} = \Lambda/\Lambda_0 \quad (42)$$

which was so far always neglected. (This was equivalent to approximating ionic conductances λ_i by their limiting value λ_i^0 in Onsager continuity equation, i.e. in the v_{ji} coefficient).

For symmetrical electrolyte, taking into account the echo factor v_{ji} leads to the following reformulation (Ref.14) of the molar conductance

$$\left\{ \begin{aligned} \Lambda &= f_{\Lambda}^S \Lambda_0 \left(1 + \frac{\Delta X_C^L}{X} + \frac{\Delta X_h}{X} + \frac{\Lambda_e}{\Lambda_0} \right) \end{aligned} \right. \quad (43)$$

$$\left\{ \begin{aligned} \frac{1 - f_{\Lambda}^S}{f_{\Lambda}^S} &= - \frac{\Delta X_{IC}^S}{X} \end{aligned} \right. \quad (44)$$

where $\frac{\Delta X_C^L}{X}$ is the long range coulombic part of the relaxation effect; $\frac{\Delta X_h}{X}$ is the hydrodynamic part of the relaxation effect; Λ_e is the electrophoretic conductance and $\frac{\Delta X_{IC}^S}{X}$ is the "unechoed" short range part of the relaxation effect. The quantity f_{Λ}^S is here an intermediary variable which has the following interesting numerical property.

$$0 \leq f_{\Lambda}^S \leq 1 \quad (45)$$

The analogy with the Bjerrum formulation is obvious. Using the strong coupling approximation Justice and Ebeling (Ref.15) could show that

$$\frac{\Delta X_{IC}^S}{X} = -c \int_0^R r^2 \exp(-\psi_{+-}/kT) + O(c^{3/2}) \quad (46)$$

so that the result for f_{Λ} is now quite analogous to the set of eqs.(11,12) and also of eqs.(26,27) at equilibrium. Another interesting feature of the above system is that the conductance coefficient can be represented by a product

$$f_{\Lambda} = f_{\Lambda}^S \times f_{\Lambda}^L \quad (47)$$

in close analogy with the result for activity coefficient given in eq.(19). Another consequence is the fact that the perturbation on the pair distributions function can be rewritten

$$g'_{ji}(\vec{r}) = \gamma g'_{ji}(\vec{r}) \times f_{\Lambda}^L \quad (48)$$

since according to the result of the strong coupling approximation

$$f_{\Lambda}^S \longrightarrow \gamma \quad (49)$$

like f_{\pm}^S at low concentrations.

This result must be closely related to the above result for the equilibrium distribution functions which states that the quantity γ should also appear explicitly as a factor of the distribution functions. In other words the quantity γ which at low concentration identifies with Bjerrum's fraction of free ions is a permanent factor whether the distribution function is at equilibrium or slightly perturbed.

Introducing this last result in the Onsager continuity equation leads ultimately to the following result

$$\left\{ \begin{array}{l} f_{\Lambda} = \gamma f_{\Lambda}^L(c, \gamma, R, a) \\ (1 - \gamma)/\gamma = c \gamma G_{M+}^S(c\gamma) \end{array} \right. \quad (50)$$

$$(1 - \gamma)/\gamma = c \gamma G_{M+}^S(c\gamma) \quad (51)$$

where R , the cut-off distance, controls the leading term $\frac{\Delta X_C^L}{X}$ in eq.(43) and a still controls the minor contributions $\frac{\Delta X_h}{X}$ and Λ_e/Λ_0 . However the calculation shows that these two quantities are practically independant of a as soon as a is less than the Bjerrum distance q , a result which constitutes an independant confirmation of the Strong Coupling Approximation (Ref.16).

It was recently possible to generalize these results to the case of mixtures of any electrolyte to obtain the following formulation for the specific conductance χ of such solutions (Ref.17).

$$10^3 \chi = \sum_i c_i \gamma_i \lambda_i^0 (1 + \Delta X_{ic}^L/X + \Delta X_{ih}/X + \lambda_i^e/\lambda_i^0) + \sum_i \sum_{j>i} c_i \gamma_i c_j A_{ij}^S (z_i + z_j)^2 / (z_i^2/\lambda_i^0 + z_j^2/\lambda_j^0) B_{ij} \quad (52)$$

$$\text{with } (1 - \gamma_i)/\gamma_i = \sum_k c_k A_{ik}^S \quad (53)$$

and

$$B_{ij} = \{z_i (1 + \Delta X_i/X + \lambda_i^e/\lambda_i^0) + z_j (1 + \Delta X_j/X + \lambda_j^e/\lambda_j^0)\} / (z_i + z_j) \quad (54)$$

$$A_{ik}^S = 4\pi \int_0^R r^2 g_{ik}^0 dr + O(c^{3/2}). \quad (55)$$

The interesting new feature of this result is that the second term on the right hand side of eq.(52) identifies with the conductance of ion pairs of net charges $Z_i + Z_j$ existing in the solution at a concentration $(1-\gamma_i)c_i$ and characterized by an intrinsic limiting conductance Λ_{ij}^0

$$\Lambda_{ij}^0 = (Z_i + Z_j)^2 / (Z_i^2 / \lambda_i^0 + Z_j^2 / \lambda_j^0) \quad (56)$$

a result which is in close agreement with what the chemical model would predict.

CONCLUSION

Two very similar formulations are now reached for activity coefficient f_{\pm} and conductance coefficient f_{Λ} which are valid for dilute solutions of electrolytes and quite efficient specially when anion-cation interactions are large.

They are based on a space partition of integrals into short-range and long-range terms. In the long-range terms concentration expansion treatments are used whereas in the short-range terms activity expansion treatments turn out to be much more adequate. Depending on the different approximations used in both treatments the concentration range of validity will vary as well as the range of possibilities for the cut-off distance R defining the space partition. If the Debye approximation is used in the long-range term (linearized Poisson-Boltzmann equation) and if the Mayer integrals of order three and higher as well as those concerning ++ and -- clusters are neglected in the short-range term, then a Bjerrum type formulation is obtained. Experiment shows (Ref.5) that a) the range of validity for concentration is then such that $\kappa R \gamma^{1/2} < 0.5$ and b) the value of R may vary around the Bjerrum distance q without significantly altering the numerical results in terms of f_{\pm} and f_{Λ} .

Surprisingly enough, the short-range contribution is represented in terms of a mass action law even though they do not concern tightly bonded entities as is the case for real chemical equilibria. Indeed, the mass action law formulation found is an approximation but not in the usual assertion; it is not a more or less justified extrapolated view of a chemical model, as the Bjerrum original presentation of the concept might lead to think, which thus would need a more or less drastic revision before enabling to proceed further in theoretical developments; it is rather an exact formulation in terms of functional expansion (just like the virial expansion is) which can be improved by adding more terms (just like introducing the third virial coefficient is an improvement relative to the same expansion truncated at the second virial term).

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