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IONIC ASSOCIATION:

ION PAIRS

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Abstract

The concept of *ion pair* and the way it has been presented in the literature is critically discussed.

Key words: ion pairs, complexes, electrolytes

The concept of ion pair

The presence of ion pairs is frequently invoked not only by those primarily interested in the behaviour of electrolyte solutions, but also by those concerned with the rates and mechanisms of both inorganic and organic reactions. However, it has been referred in the literature in different ways not equally clear.

This concept was introduced by Bjerrum in 1926 [1] to account for the behavior of ionophores in solvents of low dielectric constant and in his 1930 book Newman [2] says:

"(...) Bjerrum has come to the conclusion that certain electrolytes, among them potassium nitrate and the iodates of potassium and sodium, cannot be completely dissociated. His argument is that a certain proportion of the ions will form pairs which will act osmotically as single molecules if one, or both, of the ions has a radius smaller than a critical value. Under these conditions the ions will approach so near to each other that the attraction of a positive ion for a negative ion will be, for short periods, greater than the combined attractions of all the surrounding positive ions on the negative ion. (...)".

An identical idea is presented by Robinson and Stokes [3]:

"(...) Similarly we use the idea, due to Bjerrum [1], that the average effects of ion-pair formation may be calculated on the basis that all oppositely charged ions within a certain distance of one another are "associated" into ion-pairs, though in reality a momentarily fast-moving ion might come within the distance of another and pass by without forming a pair. (...)".

Also, Bockris [4] says:

"(...) The ions of the pair together form an ionic dipole on which the net charge is zero. Within the ionic cloud, the locations of such uncharged ion pairs are completely random, since being uncharged, they are not acted upon by the coulombic field of the central ion (...)
(...) It is only short-range coulombic interactions that lead to ion-pair formation (...)".

However, in 1958, Fuoss [5] presents an alternative picture of ion pairs. He suggests that two ions should be counted as a pair only if they are in contact, with no solvent molecule intervening. "(...) If they are not in immediate contact, we shall count them as free ions. In this way, we avoid the Bjerrum predicament of counting as pairs those ions not in actual contact (...)"

Gurney in 1953 [6] discusses the nature of the forces involved in the formation of the ion pair:

"(...) In 1926 the idea was put forward by Bjerrum [1] that, when discussing the solute particles of a weak electrolyte, we do not have to choose between free ions and neutral molecules but there is a kind of intermediate state. To this third state Bjerrum gave the name *associated ion pair*. An associated ion pair is a pair of oppositely charged ions caught in each other's field, in the manner described above; one or more solvent molecules may separate the two ions, between which only the usual long-range electrostatic forces are operative. A solute will behave as a completely dissociated electrolyte only provided that associated ion pairs are not formed; in addition, short-range forces of attraction like those in $(PbCl)^+$ must be absent. The problem then is to decide under what conditions associated ion pairs will be present. In the solution of a uni-univalent or of a di-divalent substance an associated ion pair will be electrically neutral and in important respects will behave like a neutral molecule: 1 - it will not contribute to the electric current, and 2 - there will be a dissociative equilibrium in the solution between the free ions and the neutral ion pairs; this equilibrium can be described by means of a dissociation constant just as for neutral molecules. (...)"

Robinson and Stokes in 1959 [3] also refer to the nature of the forces as follows:

"(...) We shall use the term "ion-pairing" in discussing a class of electrolytes in which association occurs as a result of purely electrostatic attraction between oppositely charged ions (...) that an ion-pair must be long-lived enough to be a recognizable kinetic entity in the solution (...)"

MacInnes [7] in 1961 presents the concept in the following way:

"(...) Ion pairs, AB, are considered to form *entirely by electrostatic forces* from the charged ions A^+ and B^-, and the complexes are assumed to take no part into the conduction. Though no sharp division has been made experimentally these ion pairs are considered to differ from the undissociated portion of a weak electrolyte in that no electron shift has occurred in their formation. (...)"

Diamond [8] in 1963 considers the case of large ions:

"(...) More importantly for the present paper, we might consider what would happen when both the cation and anion are large and do not contain specific hydrophilic groups. Both ions now require a considerable loss in water-water interactions to create their cavities and both contribute to a tightening up of their surrounding water structure; that is, to a corresponding loss in entropy of the solvent. So there would be a tendency for the water structure to force a large cation and anion pair into a single larger cavity in order to again decrease the disturbance to itself. But now, in contrast to the case of the micelles of the sodium salts of the fatty acids, there is no minimum critical concentration, as there is no coulombic interaction impeding the association. On the contrary, the opposite charges on the anion and cation facilitate the association of a pair in the same cavity, and contribute to a lowering of the ionic free energy of the associated pair.
However, this type of ion-pairing (and possibly higher ion-association) is primarily not due to an electrostatic ion-ion interaction such as the usual Bjerrum-type ion-pair, but is an association forced by the water structure itself in trying to minimize the disturbance to its structure. This suggested new type of ion-pairing, which we shall call water structure-enforced ion-pairing for want of a better name, can occur only in water solutions, or in other highly structured (bonded) solvents, and has, in fact, the opposite type of dependence on charge and size compared to electrostatic ion-pairing. The latter is least likely to occur in a solvent with as high a dielectric constant as water, and is greater the smaller the ions and the higher their charge [1]. (...)
(...) However, the type of ion-pairing suggested in this paper as occurring in aqueous solutions of large cations and anions is due principally to the strength of

the hydrogen-bonded water structure in forcing the cation-anion pair together so as to minimize their disturbance of the water structure, and should show the opposite behavior; an association increasing with size from NMe_4^+ to NAm_4^+, and from Cl^- to I^-, etc. The resultant ion-pairing should lead to a negative correction to the osmotic and activity coefficients of large ion salt solutions, and the effect should be larger the higher the concentration and the larger the ions of the salts. It should not occur with highly charged ions which interact strongly with the surrounding water molecules.

Ion-pairing between large ions in aqueous solution is quite strange on the basis of the usual consideration of the electrostatic interaction between the ions, but is a very natural consequence of the ideas discussed above.

Such water structure-enforced association may also be the explanation, or part of the explanation, for the phenomenon of hydrotropism, for the "salting in" of neutral molecules in water that occurs with electrolytes containing large ions, either cations or anions [9, 10]. In this case the desire of the water structure to minimize its contacts with hydrophobic molecules and to minimize the number of molecular cavities forces the neutral molecule into the same cavity with the large ion, at least for a period of a few molecular collisions, creating a transitory ion-molecule pair. Obviously, this associated species adds to the solubility of the neutral molecule in the aqueous solution, leading to the observed salting in (...)".

Viscosity studies by Davies [11], in 1964, contribute to the understanding of ion pairs:

"(...) In some almost completely dissociated electrolytes the effect of ion-pairing on the viscosity is too small to measure. In every other case the effect is to cause a reduction in viscosity. (...)

(...) Ion-pairing is least in lithium sulphate and greatest in potassium sulphate, and the effect of ion-pairing on viscosity increases in the same order. It would seem that the strong hydration of the lithium ion is virtually unaffected by association with the sulphate ion, but that the increasing interaction between the ions in sodium and potassium sulphates leads to increasing reductions in the viscosity.(...)"
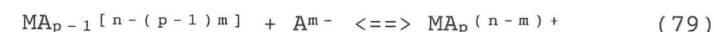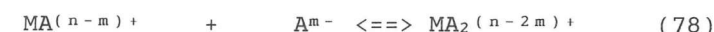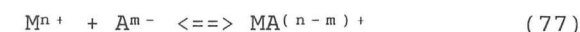
Denaro [12] in 1965 attempts to use ion pairs to justify the deviations of the experimental data on conductance relative to Onsager's theory:

"(...) For concentrated solutions, and even for dilute ones of some multivalent electrolytes, however, the Onsager equation breaks down. One of the reasons for this breakdown was originally pointed out by Bjerrum who showed that, as the concentration of ions increased, pairs of oppositely charged ions could occur in the solution. These ion pairs are formed when oppositely charged ions approach

each other sufficiently closed to be considered more or less as a single entity. The net charge on the single entity is zero, and thus an ion pair will contribute nothing to the conductance of the solution. It must be pointed out, however, that these ion pairs are not stable and continually exchange partners. Ion association in strong electrolytes has been examined mostly by Bjerrum and by Fuoss and Kraus. These workers have deduced equations which account accurately for the conductance of strong electrolytes up to concentrations of 0.1 N. (...)"
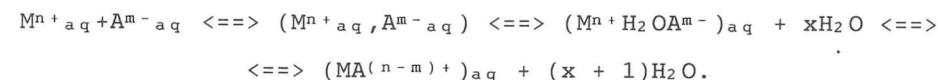
Nancollas [13] in 1966 says:

"(...) The ion association can be regarded as a stepwise process involving the equilibria

$$M^{n+} + A^{m-} \iff MA^{(n-m)+} \qquad (77)$$

$$MA^{(n-m)+} + A^{m-} \iff MA_2^{(n-2m)+} \qquad (78)$$

$$\cdot \qquad \cdot \qquad \cdot$$
$$\cdot \qquad \cdot \qquad \cdot$$

$$MA_{p-1}^{[n-(p-1)m]} + A^{m-} \iff MA_p^{(n-m)+} \qquad (79)$$

In equations (77) to (79), associated water is omitted and p is the maximum coordination number of the metal ion M^{n+}. The principal of stepwise formation of such mononuclear complexes was first proposed by Abbeg [14] and was established by the pioneering work of Niels and Jannik Bjerrum [15]. As early as 1915, Niels Bjerrum was able to show that in chromium(III) thiocyanate solutions six complex species, $CrSCN^{2+}$, $Cr(SCN)_2^+$, ..., $Cr(SCN)_6^{3-}$ coexisted ..."

Based in Smithson [16] Nancollas also presents a formal distinction of ionic pairs:

"(...) The interaction between a hydrated metal ion and an anion or neutral ligand may involve a number of partially solvated species which participate in a series of equilibria represented by

$$M^{n+}_{aq} + A^{m-}_{aq} \iff (M^{n+}_{aq}, A^{m-}_{aq}) \iff (M^{n+}H_2OA^{m-})_{aq} + xH_2O \iff$$

$$\iff (MA^{(n-m)+})_{aq} + (x+1)H_2O.$$

Thus the ion-pairs formed in the solution need not be identical, and we can make a formal distinction between outer- and inner- sphere species. In the former, one, or at most two, solvent molecules are interposed between the interacting ions, whilst in the latter, the ions are adjacent to one another (...)"

"(...) In place of the terms outer-sphere and inner-sphere, many workers have used "ion-pair" and "complex" respectively, to distinguish between the two types of

species. It is preferable, however, to retain the terms outer- and inner-sphere to describe the type of association in question but to attach a rather wider meaning to "ion-pair", regarding this species as one in which the bonding is almost entirely due to the long range electrostatic forces between the oppositely charged ions. Under these circumstances, solvent molecules may or may not be interposed between the ions. In complexes, on the other hand, short-range or covalent forces will contribute to the stability, and such species will certainly involve inner-sphere interaction with the elimination of one or more solvent molecules from the co-spheres of the ions. (...)"

"(...) When the K values for the bivalent metal sulphates are inserted into the Bjerrum equation (23) p17, the values of a are 3.7 ± 0.2 Å for the sulphates of magnesium, calcium, copper, zinc, cobalt and nickel. A distance of closest approach of 3.7 Å, however, is equal to that in the anhydrous metal sulphates and as such is inconsistent with the evidence that most of the ion-pairs are present as outer-sphere species for which a could hardly be less [17] than about 6 Å. One explanation which has been advanced to explain this inconsistency is that of "localised hydrolysis" [18]. The octahedrally situated water molecules in the inner coordination sphere of the cation will be strongly polarised, and the hydrogen atoms at one face of the octahedron are well placed for forming strong hydrogen bonds with a sulphate ion in contact with the face. For a large class of 2:1 electrolytes such as the alkaline earth halides, the Bjerrum Theory predicts ion-pairing but no ion-pairs can be detected; and Davies has suggested that definite classification into ion-pairs and complexes on this basis should not be made [19]. (...)"

" (...) Experimentally determined association constants can vary over a very wide range of values, and it is useful to try to classify the metal ions in terms of their complex-forming ability. If they behaved as rigid non-polarisable particles, then it would be a relatively simple matter since only purely electrostatic bonding need be considered. In practice, however, we must also consider the deformability of the metal ion, or the way in which the electronic structure is modified by interaction with the ligand. Various classifications have been proposed and we will briefly outline that due to Schwarzenbach [20] who divided the metal ions up into three classes.

Class A. In this group are included the cations with a noble gas configuration such as the alkali and alkaline earth metal ions together with Al^{3+}, Sc^{3+}, Y^{3+}, La^{3+}, Ti^{4+}, Zr^{4+}, Hf^{4+}, Th^{4+}, Nb^{5+} and Ta^{5+}, for which purely electrostatic bonding predominates. The association constants will be expected to increase with decreasing cationic size and increasing charge. (...)"

"*Class B*. Metal cations with completely filled d subshells (18 electrons; *e.g.* Cu^+, Ag^+, Au^+, Tl^+, Zn^{2+}, Cd^{2+}, Hg^{2+}) are included in this group. They undergo predominantly covalent interactions and the factors governing ion-pair formation in class A no longer hold. The extent of complex formation is largely determined not by the charge and radius but by the difference in the electronegativities of the metal ion and the donor atom of the ligand. (...)"

"*Class C*. Into this group fall the transition metal ions with incomplete subshells in which the characteristics of both classes A and B can be distinguished. (...)"

Davies [21] in 1967 clarifies the concept as follows:

"(...) We therefore have a uniform theory for strong and weak electrolytes in sufficiently dilute solutions, in which a long-range interaction between the ions is accounted for by the Debye and Onsager equations of interionic attraction, and the short-range forces between them by the dissociation constant. The nature of these short-range forces may vary greatly from one electrolyte to another, and may be difficult to identify. At one extreme we have a typical weak electrolyte, in which an undissociated molecule is formed by chemical bonding between the ions; at the other extreme we have the typical strong electrolytes shown in Fig. 21, in which the ion-pairs may be held together purely by electrostatic forces. (...)"

Spiro [22] in 1968 raises an important problem:

"(...) Of further interest is the possibility that volume changes might be of aid in the resolution of a recurrent and troublesome structural question about ion association: namely, whether a given pair of associated ions is in contact or separated by one or more solvent molecules or, in the language of coordination chemistry, whether a given complex ion is inner or outer sphere [23]. (...)"

However, in 1969 Justice [24] transmits an idea similar to that of Davies [21]:

"(...)It is now possible to make a clear distinction between Debye's long-range and Bjerrum's short-range electrostatic interactions. (...)"

In the same year, Szwarc [25], also says:

"(...) Contrary to Bjerrum's expectation, the pairing of ions often leads to the formation of new, thermodynamically distinct species possessing properties strikingly different from those of the free ions (...)"

Later, Pikal [26], when developing a theory of mutual diffusion for binary electrolytes, says:

"(...) A theory of mutual diffusion in a binary electrolyte is developed using the conventional charged sphere-in-continuum model. However, instead of approximating the Boltzmann exponential by a truncated power series, the calculations are performed retaining the full Boltzmann exponential. As a result of this procedure, a term representing the effect of ion-pair formation appears in the theory as a natural consequence of the electrostatic interactions. The mobility of an ion pair is not an adjustable parameter but is determined by the theory. (...)"

"(...) Physically, the truncation approximation ignores close range electrostatic interactions, and therefore one cannot expect ion-pair formation to be predicted by the Onsager-Fuoss theory. Thus, if the full Boltzmann exponential is retained in the development of a diffusion theory, one might expect ion-pair formation to be a natural result of the theory (...)"

Hampel [27] points out the case of a molecule and an ion pair formed by the same species:

"In the equation

$$C^+ + A^- \iff [C^+A^-]^° \iff CA \qquad (7)$$

the reaction of the ions C^+ and A^- to form $[C^+A^-]^°$ represents just such an ion pair formation, the pair being held together by coulombic forces only. In contrast, CA is a molecule joined by electronic interactions, to which Bjerrum's approach is not applicable. Further reactions which will also remove ions from solution are possible, as

$$[C^+A^-]^° + A^- \iff [A^-C^+A^-]^- \qquad (8)$$

$$[C^+A^-]^° + C^+ \iff [C^+A^-C^+]^+ \qquad (9)$$
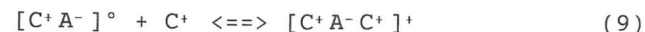
and others leading to more complex aggregates such as

$$\begin{bmatrix} C^+A^- \\ A^-C^+ \end{bmatrix}^°$$
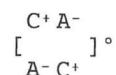
Robbins [28] discusses the conductivity in connection with the formation of ion pairs:

"(...) *Ion pair formation, or ion association*, in which ions of opposite charge tend to aggregate by electrostatic attraction, the formation of the ion pair diminishes the net contribution to the conductivity of the electrolyte. Such species exist to an appreciable extent

in relatively concentrated solutions (and particularly in molten salts) but are easily dispersed on dilution, so that the molar conductivity rises as concentration decreases. (...)"

Crow [29] points out that ion pairs are distinct kinetic species:

"(...) Ion-pairs consist of *associated* ions, the formation of which must be regarded as a time-averaged situation since in any such system there will be a continual interchange of ions amongst the pairs. For a species to be regarded as an ion-pair it must be a "kinetically distinct" species. That is, although it is an unstable and transient entity, if nevertheless has a lifetime of such duration that it can experience a number of kinetic collisions before exchanging an ion partner. (...)"

Burgess [30] says:

"(...) The formation of ion-pairs [31], otherwise known as outer-sphere complexes, can be treated as a problem in electrostatics. (...)"

However, Fuoss [32] clarifies the situation:

"(...) 1 - those which find an ion of opposite charge in the first shell of nearest neighbours (contact pairs); 2 - those with overlapping Gurney cospheres (solvent separated pairs); and 3 - those which find no other unpaired ion in a surrounding sphere of radius R, where R is the diameter of the cosphere (unpaired ions). Thermal motion and interionic forces establish a steady state, represented by the equilibria $A^+ + B^- \iff (A^+ ... B^-) \iff A^+B^-$ where the concentration of unpaired ions is $c\gamma$, *that of solvent separated pairs is* $c(1 - \gamma)(1 - \alpha)$ and that of contact pairs is $\alpha c(1 - \gamma)$. (Contact pairs of ionogens may rearrange to neutral molecules, $A^+B^- \iff AB$; e.g., H_3O^+ and acetate ion). (...)"

"(...) The contact pairs react as dipoles to an external field X and contribute only to changing current. Both contact pairs and solvent separated pairs are felt as virtual dipoles by unpaired ions; their interaction with unpaired ions is therefore neglected in calculating long-range effects (activity coefficients, relaxation field ΔX, and electrophoresis $\Delta \Lambda_c$). (...)"

Wright [33] in 1988 may be the author transmitting the best information about the ion pair:

"(...) By an ion-pair we mean a physical entity with no specific intimate chemical interactions between the ions. The ions of the ion-pair move together a single unit and are held together by electrostatic forces of the

coulomb type acting over the short distance that the ions are apart in the ion-pair. These coulombic forces impose a certain degree of cohesion on the unit and this is sufficiently great to overcome the tendency for normal thermal motion to cause the ions to move around as separate independent particles each with is own translation degrees of freedom.

Because the forces holding the ions together are of this physical nature, they depend on three factors:

The charges on the ions.
The sizes of the ions; these are taken to imply the distance over which the forces act.
The relative permittivity of the solvent in the vicinity of the ion.

It is very important to realise that these forces are therefore independent of the chemical nature of the ions.

We would, therefore, expect that electrolytes which have ions of the same charge and similar size would have equilibrium constants of similar magnitude if the associated species is an ion-pair. (...)

(...) The charge on an ion is usually unambiguous (for example Mg^{2+} or NO_3^-) and the charge distribution for such ions is probably approximated spherical symmetrical. But the charge and the charge distribution for some ions may not be so clearly definite. (...)

(...) An ion-pair of zero overall charge must not be treated as though it were a neutral molecule. At best it can be regarded as a dipolar molecule but it is probably more like a charge separated ...

(...) When the ion-pair has an overall charge it should not be treated as though it were a single charge with a spherical symmetrical distribution of charge. Again it is probably more like a dipolar charge ion ... or a charge separated ion-pair ...

"Likewise, the ion-pair will be solvated, and we must get some estimate of its size. Furthermore, the change in solvation pattern on forming the ion-pair is of crucial importance.

Three limiting situations can be envisaged, but other intermediate situations are possible:
   (1) An ion-pair is formed with no disruption of the individual solvation sheaths of the individual ions, so that in the ion-pair these solvation sheaths are in contact and solvent is present between the ions.
   (2) An ion-pair is formed with total disruption of the individual solvation sheaths of the individual ions, so that in the ion-pair the bare ions are in contact and there is no solvent present between the ions.
   (3) An ion-pair is formed with partial disruption of the individual solvation sheaths of the individual ions, so that in the ion-pairs some solvent has been squeezed out but there is still some solvent present between the ions.

The ion-pairs which can be formed are thus not necessarily identical, and we must consider the possibility that different experimental methods may pick out and detect only one kind of ion-pair -- for instance, detect contact ion-pairs but not solvent-separated ion-pairs.

A further formal definition can be proposed:
An **outer-sphere** ion-pair: is one where **one** or at most **two** solvent molecules lie between the ions.
An **inner-sphere** ion-pair: is one where the bare ions are in contact -- all solvents sheaths have been eliminated from **between** the ions.

However, both inner-sphere and outer-sphere ion-pairs are still solvated as the **composite** unit.

Although our **definitions** can be quite unambiguous, **experimental** classification into inner-sphere and outer-sphere ion-pairs most certainly is not unambiguous, and may even, at best, be only a guess. This is exactly the same problem as will be encountered when discussing the formal and experimental distinctions between complexes and ion-pairs. (...)

(...) Where a complex is formed there is an intimate chemical interaction between the ions. Some electronic rearrangement is occurring and this results in covalent interactions, in contrast to the purely physical coulombic electrostatic interactions involved in the formation of an ion-pair.

Discussion and conclusions

As we see, the scientific literature does not present a consistent concept of ion pairs. For example, the applicability of short and long range forces attracting the different species is not always considered in the same manner.

In an electrolyte solution, we may, merely for formal reasons, consider three "categories" of ions: free ions, complex ions, and ion pairs. Ion pairs may be considered as associations of ions attracted by mainly coulombic forces, that, though being unstable species, are still recognized as kinetic entities with a long life-time compared with the number of collisions they suffer before changing partners. Their electrical charge depends on the nature of the electrolytes involved, symmetrical or not. Even in the cases where they may be considered neutral (e.g. in certain cases of symmetrical electrolytes), we think, from our studies on diffusion [34], they still may contribute to the conductance of the electric field, due to the loose nature of their bonding. As showed in the previous section, many authors think otherwise.

Concerning the size of the ion pairs, the perspective presented by Wright [33], previously indicated, seems to be the best option.

The distinction between ion pairs and complex ions may eventually be difficult to make. In fact, it may not

be feasible to clarify clearly, for a specific case, the nature of the forces binding the species which constitute the ion pair (or complex ion) as is the case of class C, indicated in Nancollas book [13]. However, we would say that what normally is more important for the knowledge of the structure of the electrolyte solutions is the thermodynamic behaviour of the involved species, not so much the complex question of the nature of their internal binding forces.

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