ion pair

A pair of oppositely charged ions held together by Coulomb attraction without formation of a *covalent bond*. Experimentally, an ion pair behaves as one unit in determining conductivity, kinetic behaviour, osmotic properties, etc.

Following Bjerrum, oppositely charged ions with their centres closer together than a distance:

$$q = 8.36 \times 10^6 z^+ z^- / (\varepsilon_r T) \text{ pm}$$

are considered to constitute an ion pair ('Bjerrum ion pair'). [z^+ and z^- are the charge numbers of the ions, and ε_r is the relative permittivity (or dielectric constant) of the medium.]

An ion pair, the constituent ions of which are in direct contact (and not separated by an intervening solvent or other neutral molecule) is designated as a 'tight ion pair' (or 'intimate' or 'contact ion pair'). A tight ion pair of X^+ and Y^- is symbolically represented as X^+Y^-.

By contrast, an ion pair whose constituent ions are separated by one or several solvent or other neutral molecules is described as a 'loose ion pair', symbolically represented as $X^+\|Y^-$. The members of a loose ion pair can readily interchange with other free or loosely paired ions in the solution. This interchange may be detectable (e.g. by isotopic labelling) and thus afford an experimental distinction between tight and loose ion pairs.

A further conceptual distinction has sometimes been made between two types of loose ion pairs. In 'solvent-shared ion pairs' the ionic constituents of the pair are separated by only a single solvent molecule, whereas in 'solvent-separated ion pairs' more than one solvent molecule intervenes. However, the term 'solvent-separated ion pair' must be used and interpreted with care since it has also widely been used as a less specific term for 'loose' ion pair.

See also *common-ion effect, dissociation, ion-pair return, special salt effect.*
1994, *66,* 1126; 1995, *67*, 1344