Absorption Spectra of Iodide in Aqueous Mixed Salt Solutions: Shifts of Absorption Maxima and a Cross-square Rule

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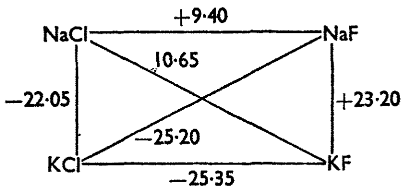
Summary The energies of absorption maxima, $E_{\max}$, of iodide in water containing two salts are compared with those predicted assuming that the effect of each salt is additive, and the differences between observed and calculated shifts in $E_{\max}$ follow a cross-square relationship.

WHEN a salt, *e.g.* sodium chloride, is added to a solution of potassium iodide (6×10^{-5}M at 293 K), the energy of the first absorption maximum for the charge-transfer-to-solvent transition of iodide shifts to higher energies.[1] We have examined these shifts for a number of single and mixed salt solutions at constant total ionic strength ($I = 1{\cdot}0$). For a mixed salt solution containing equimolal amounts of, for example, potassium chloride and potassium fluoride, the shift, $\Delta E_{\max}$(obs) [$=E_{\max}$(KI in salt solution, $I = 1$) $-$ $E_{\max}$(KI in water) at 293 K] did not equal that predicted, $\Delta E_{\max}$(calc). The latter were obtained from $\Delta E_{\max}$(obs) for single salt solutions ($I = 1{\cdot}0$) by assuming that the effect of each salt on the overall shift was additive. The differences, $\mathrm{d}\Delta E_{\max}$cal.mole^{-1} [$=\Delta E_{\max}$(obs) $-$ $E_{\max}$ (calc)] are shown below on the lines joining the pairs of salts in each mixed aqueous salt solution. The sum of the values for systems containing common ions, $\Sigma\square$, is $+ 9{\cdot}40 + 23{\cdot}20 - 25{\cdot}35 - 22{\cdot}05 = - 14{\cdot}80$ and the sum of the values for systems containing no common ions, ΣX, is $10{\cdot}65 - 25{\cdot}20 = - 14{\cdot}55$. In other words, $\Sigma\square \sim \Sigma$X.

A number of thermodynamic quantities for salt solutions follow a cross-square rule.[2] The present example is slightly different in that it concerns the spectroscopic properties of a "tracer" ion, iodide, in these systems. The cross-square rule does, however, link together our data and this is the first example of which we are aware in which this rule has been successfully applied to spectroscopic quantities.



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