

SECTION E

E-43

RELATING SPECTROSCOPIC AND ELECTROCHEMICAL STUDIES. THE CHARGE-TRANSFER-TO-SOLVENT (ctts) SPECTRUM OF IODIDE IN CONCENTRATED ALKYL AMMONIUM SOLUTION CORRELATED WITH THE ACTIVITY COEFFICIENTS

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The absorption maximum E_{\max} of dilute ($< 10^{-4}M$) aqueous iodide solutions shifts progressively to higher energies on addition of various tetra (Alkyl ammonium Chlorides. For concentrations greater than 1M solutions, these observations are interpreted as arising from a combination of the Debye—Hückel charge cloud and the quasi—(diffuse, expanded) lattice interactions ; the relative proportions of these are determined using the molar volume in the solid state of the added salt. This interpretation is based on the observed linearity of E_{\max} with \sqrt{C} , ($C =$ concentration of added electrolyte) between 1 and 4 M and with $\sqrt[3]{C}$ in the same range. The activity data of these salt solution and E_{\max} data yields linear relationships having the same slope. The combination of these observations leads to structural data on concentrated salt solutions.