Significance of Isosbestic Points in the Charge-transfer-to-solvent Spectra of Iodide in Water–t-Butyl Alcohol Mixtures

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Summary Spectrophotometric measurements show that iodide in water containing small amounts of added t-butyl alcohol exists in two discrete local environments.

THE addition of low concentrations of a variety of organic solvents to dilute (10^{-5} M) aqueous solutions of alkali-metal iodides causes a marked shift of the charge-transfer-to-solvent (c.t.t.s.) absorption band[1] to high energies. This shift is particularly marked when t-butyl alcohol is added over the range $0 \leqslant c_2 \leqslant 0{\cdot}03$ (where x_2 is the mole fraction of alcohol), further addition being ineffective up to $x_2 = 0{\cdot}6$.[2,3] As shown in the Figure, well defined isosbestic points at 44050 and 47750 cm^{-1} are generated in the range $0 \leqslant x_2 < 0{\cdot}03$ at 298·1K. A similar pattern occurs in the spectra measured at 274·6K, the isosbestic points being at 44720 and 47500 cm^{-1}. These isosbestic points almost certainly indicate an equilibrium between two well defined iodide species in these systems.

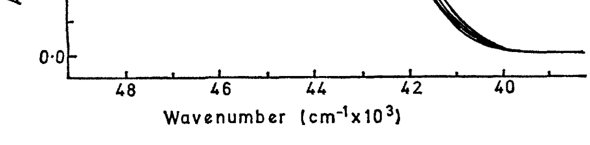

FIGURE. *Charge-transfer-to-solvent spectra of potassium iodide* (*ca.* 5 × 10^{-5}M) *at* 298K *in water containing different mole fractions of t-butyl alcohol;* (a) $x_2 = 0{\cdot}06$, (b) $x_2 = 0{\cdot}04$, (c) $x_2 = 0{\cdot}02$, *and* (d) $x_2 = 0$.

The fact that broad lines are observed is taken to indicate the presence of a range of closely similar solvates in both regions but the isosbestic points indicate two quite distinct types of solvates. We tentatively suggest that the new form involves iodide incorporated into the water lattice of a clathrate hydrate structure in a manner analogous to the incorporation of fluoride and chloride ions in solid alkylammonium salt clathrate hydrates. The fact that the band narrows markedly on going to the new form suggests that the solvation is more precise than in pure water. The high energy shift on going from aquated iodide to iodide in the new environment means, in terms of our normal description of c.t.t.s. bands, that either the cavities are smaller or the hydrogen bonding is stronger as well as being more precise.

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