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PHYSICS

Discontinuities in the Thermal Properties of Water and Aqueous Solutions

THERE is considerable controversy at present on discontinuities in various properties of water as a function of temperature¹⁻⁵. In particular, the discontinuities postulated in the region of 37° C, that is, body temperature, have important biological implications. These discontinuities, however, are in the main so subtle that their very existence is questioned.

We have studied the ultra-violet absorption spectrum of the first charge-transfer-to-solvent band of iodide in water over the range of temperature 15°-75° C in the hope that these ions would act as "probes" of their environ-ment⁶ and that the spectrum would be sensitive to these discontinuities. While for many systems the band maximum, E_{max} , is a linear function of temperature⁷, small deviations from linearity have, in fact, been detected in aqueous solution and we shall present evidence elsewhere which seems to us to show conclusively that the discontinuities in shift are greater than experimental error.

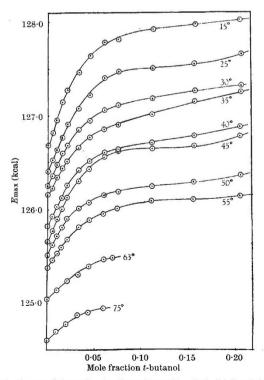


Fig. 1. Energy of absorption band maximum, E_{\max} for iodide in mixtures of water and t-butanol (mole fraction x_2) at various temperatures.

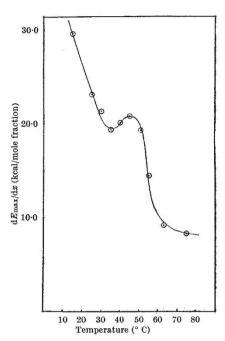


Fig. 2. Sensitivity of the absorption band maximum of iodide to addition of added t-butanol, dE_{max}/dx_s over the range $0 \le x_s \le 0.02$, as a function of temperature.

When small quantities of t-butanol (mole fraction x_{*}) are added to the system, however, the discontinuities are greatly magnified in the plot of dE_{max}/dx_2 as a function of temperature, and it is to this aspect of our work that we direct attention. The results are summarized in Fig. 1 and the effects depicted there are very large compared with experimental error. In particular, it will be seen that there is a reversal in the trend of the initial slope in the region 35°-45° C, Fig. 2. Because these effects extrapolate back to the pure aqueous solution we feel that this lends strong support to the hypothesis that there are discontinuities in the properties of water in this temperature region.

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Sub-millimetre Wave Spectra of Non-polar Liquids and Crystals

IN a previous publication, the sub-millimetre wave spectra of polar liquids-and in particular chlorobenzene-were discussed¹. It was shown that in addition to the Debye absorption process at very low frequencies $(< 10 \text{ cm}^{-1})$ there existed a more intense absorption at frequencies characteristically in the range 20-100 cm⁻¹. This absorption, which was in the form of a very broad (half width ≈ 40 cm⁻¹) band with peak heights in the range 10-30 nepers/cm,