Application of Spectroscopic and Relaxation Techniques to the Study of t-Butyl Alcohol–Water Mixtures

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ATTENTION has recently been focused upon many anomalous properties of aqueous solutions of alcohols in the water-rich region.[1,2] We have studied the near-infrared spectra of solutions of t-butyl alcohol in water and the ultraviolet and e.s.r. spectra of various ions in low concentration in water–t-butyl alcohol mixtures and find marked changes in the 0·04—0·10 mole-fraction region. These changes are compared with the very marked concentration-dependence of the absorption of ultrasound in this mole-fraction region.[3]

Our results are summarised in the Figures.

The systems fall into two categories, namely those with added ions whose spectra are monitored and which act as "probes" of their environment (Figure 1B, 2B, 2C) and those without such additions (Figure 1A, 2A). These results are divided into those showing a "plateau" in the 0·00 < X_2 < 0·04 region (X_2 being the mole fraction of t-butyl alcohol) and a sharp change in the 0·4 < X_2 < 0·10 region (Figure 1) and those showing a sharp change in the 0·00 < X_2 < 0·04 region and a levelling off in the 0·04 < X_2 < 0·10 region (Figure 2).

The two types of behaviour shown in Figure 1 and 2 are connected in the sense that the marked changes initially observed on adding t-butyl alcohol, shown in Figure 2, are diminished (or cancelled) in the mole-fraction region corresponding to the large changes shown in Figure 1.

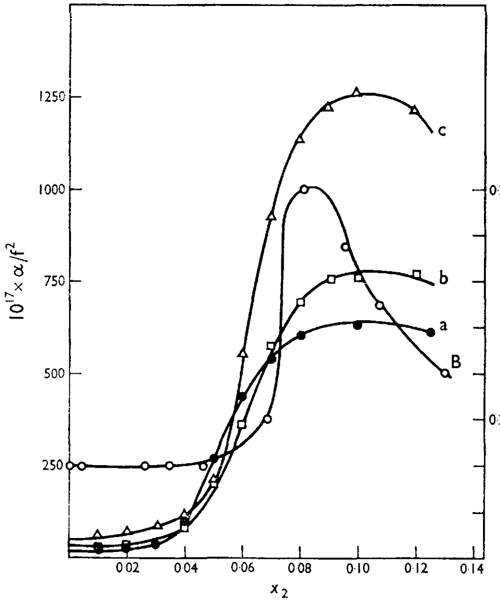

FIGURE 1(A). *Effective intensity,* α/f^2, (*ref.* 3) *of the ultrasonic absorption for water–t-butyl alcohol mixtures at* 70 *Mc./sec. for* (a) *water at* 25°, (b) *deuterium oxide at* 25°, (c) *water at* 5°.

(B). *Difference between the methyl and ring proton hyperfine coupling constants,* Δa, *of* 2,6-*dimethyl*-p-*benzosemiquinone in water–t-butyl alcohol mixtures at room temperature.*

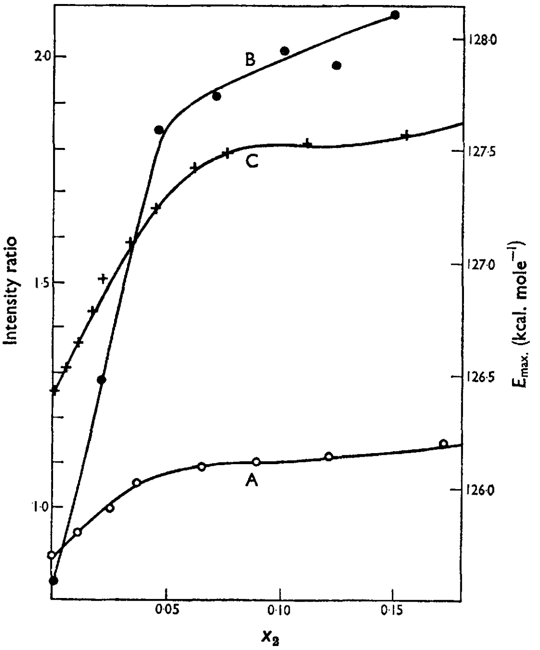

FIGURE 2. *Effect of t-butyl alcohol on*:

(A). *Ratio of intensities of the infrared absorption bands at* 1·556μ *and* 1·416μ *for* HOD(6M) *in* D_2O *at* 25°. [*The bands at* 1·556μ *and* 1·416μ *have been assigned* (*ref.* 5) *to the intermolecularly bonded and nonbonded* O–H *stretch overtone, respectively.*]

(B). *The ratio of the intensities of the visible absorption bands of Methylene Blue chloride assigned* (*ref.* 6) *to the cation monomer* (M) *and dimer* (H) *in water at* 25°.

(C). *Energy,* E_{max}, *of the first charge-transfer-to-solvent absorption band for iodide ion in water at* 25°.

The infrared results show unambiguously that there is an enhancement in the water–water interaction in the initial mole-fraction region whereas the ultrasonic results suggest that when $X_2 > 0{\cdot}04$ there is a dramatic breakdown of this structure. The absorption spectrum of iodide ion is sensitive to the former whereas the spin distribution of the semiquinone is sensitive to the latter. The situation for Methylene Blue is more complex since it involves a change in an equilibrium between monomeric, D^+, and dimeric, D_2^{2+}, species. One possible description is that there is a competition for the dye cations between t-butyl alcohol and other dye cations.

The contrast between the results for Methylene Blue (Figure 2B) and the results reported[4] recently for Brookers Dye VII, the absorption spectrum of which seems to follow the pattern of Figure 1, is, in our opinion, misleading. Our results on Brookers Dye VII suggest that the solvent effect is quite comparable in the two cases. The apparent shift is in reality a change from a spectrum characteristic of one species to a spectrum characteristic of another, these species probably being the dimer and monomer, respectively. This has been established by dilution experiments[7] and if our interpretation is correct then the results are better expressed by a figure similar to Figure 2B.

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