# Ultrasonic Absorption Properties of t-Butanol–Water Mixtures at 25°

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RECENT interest[1,2] in the properties of alcohol–water mixtures prompts us to report new details concerning the ultrasonic absorption properties of the t-butanol–water system. The general features of the absorption of sound in alcohol–water mixtures are well documented.[3,4] At a fixed frequency $f$, a plot of $\alpha/f^2$ (where $\alpha$ is the absorption per cm.) against mole fraction of t-butanol, $x_2$, passes through a maximum at approximately 0·1 (Figure 1). Our more detailed investigation of the sound absorption properties in the frequency range

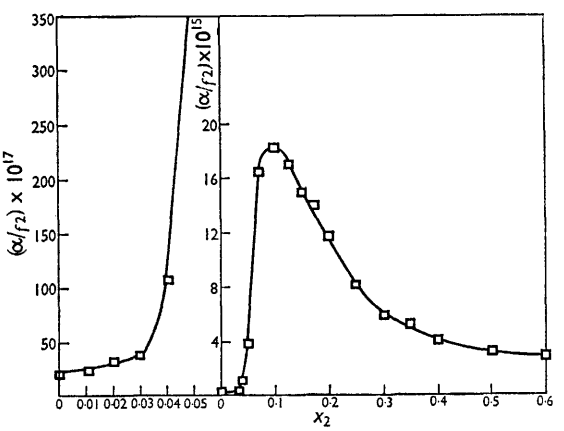


FIGURE 1. *Sound absorption of t-butanol–water mixtures at 7·5 Mc./sec. as a function of mole fraction of alcohol* $x_2$.

1·5 to 230 Mc./sec. has revealed a greater complexity than was previously recognised. In particular, the following aspects are noted. At low alcohol concentrations, $x_2 < 0{\cdot}04$, $\alpha/f^2$ is not significantly different from that of water at the same temperature ($21 \times 10^{-17}$ n. sec.$^2$cm$^{-1}$). Over the concentration range $0{\cdot}04 < x_2 < 0{\cdot}08$, $\alpha/f^2$ increases dramatically to a value of $1760 \times 10^{-17}$ n. sec.$^2$ cm.$^{-1}$ (Figure 1). For $x_2 > 0{\cdot}04$ there are two distinct relaxation frequencies both of which show a large increase in relaxation strength[5] ($\mu$) with a maximum at $x_2 = 0{\cdot}1$ (Figure 2).

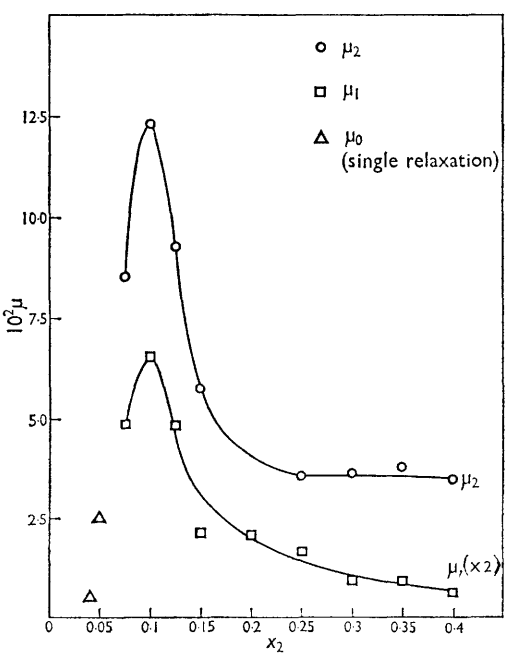


FIGURE 2. *Relaxation strengths for the low-frequency,* $\mu_1$, *and high-frequency,* $\mu_2$, *relaxation processes in t-butanol–water mixtures.*

Other evidence that there are major structural changes occurring in the $0{\cdot}03 < x_2 < 0{\cdot}06$ range includes a maximum in the sound velocity[4] at $x_2 = 0{\cdot}045$ (27°), a minimum in the partial molal volume of t-butanol[6] at $x_2 = 0{\cdot}03$ (20°) and a maximum in the partial molal heats of solution for several salts[7] in the $x_2 = 0{\cdot}04$ region.

The independence of $\alpha/f^2$ on $x_2$ over the range $0 < x_2 < 0{\cdot}04$ and the rapid increase over the range $0{\cdot}04 < x_2 < 0{\cdot}08$ can be understood in terms of a structural model described by Franks and Ives.[1] In this model, when t-butanol is added to water, it is initially accommodated interstitially with significant loss of volume, the solution resembling a liquid water clathrate. However with further addition of alcohol (and concomitant removal of water), the interstial sites become saturated and the alcohol dissolves by substitution in the water lattice. This latter process resembles that for the dissolution of methanol in water,[1] the dissolution being accompanied by little loss in volume. When t-butanol is dissolved both interstitially and substitutionally, transfer of t-butanol between two sites must be accompanied by a large change in volume and will therefore be sensitive to the pressure perturbation of an ultrasonic wave.

Previous models which have related the relaxation with hydrogen bond interactions between the solution components of the type[8] $AA + BB \rightleftharpoons 2AB$ cannot account for the independence of $\alpha/f^2$ on $x_2$ over the range $0 < x_2 < 0{\cdot}04$.

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