Common Features in the Ultrasonic Relaxations of Aqueous Mixtures: the Importance of Water Structure

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THE ultrasonic absorption of water–t-butyl alcohol mixtures over the alcohol mole-fraction range $0 < x_2 < 0{\cdot}04$ and the frequency range 1·5 to 230 MHz is not significantly different from that of pure water.[1–3] This is a common feature of many alcohol–water mixtures[3,4] although the extent of this insensitive region is a function of the nature of the alcohol. At t-butyl alcohol mole fractions greater than 0·04, the ultrasonic absorption increases, rising to an intense maximum close to

$x_2 = 0{\cdot}1$.[1,3] A similar pattern is observed for mixtures of other alcohols.[4,5] We report a summary of ultrasonic relaxation frequencies which are remarkably similar for a range of aqueous mixtures.

The ultrasonic absorption over the frequency range 1·5 to 230 MHz has been fitted to a general equation of the form

$$\alpha/f^2 = B + A_1/[1 + (f/f_{c_1})^2] + A_2/[1 + (f/f_{c_2})^2]$$

where α is the amplitude absorption coefficient, f the frequency, B the non-relaxing component, and A_1 and A_2 the relaxing components having relaxation frequencies f_{c_1} and f_{c_2}. The two relaxation frequencies have minima close to the alcohol mole fraction where the ultrasonic absorption, (α/f^2), at a given frequency is a maximum.

Minimum ultrasonic relaxation frequencies and corresponding mole fractions, x_2 for aqueous mixtures

Non-aqueous component	Temp.	x_2 at $(\alpha/f^2)_{max}$	f_{c_1} $(f_{c_1})_{min}$ MHz	x_2	f_{c_3} $(f_{c_2})_{min}$ MHz	x_2
Bu^{t}OH	5°	0·10	4·5	0·2	60	a
	25	0·10	5	0·15	50	0·15
	45	0·10	7	0·15	50	0·15
Pr^{n}OH	0	0·11	6·5	0·2	70	a
	10	0·11	7	0·15	70	0·125
	20	0·11	7	0·15	65	0·15
Pr^{i}OH	0	0·15	11	0·2	100	a
	20	0·15	11	0·2	110	0·2
Allyl alcohol	0	0·15	8	0·15	80	0·15
Et_2NH	0	0·10	—	—	90	0·10
	25	0·10	—	—	160	0·10

[a] Mole fractions corresponding to $(f_{c_2})_{min}$ are less well defined at low temperatures.

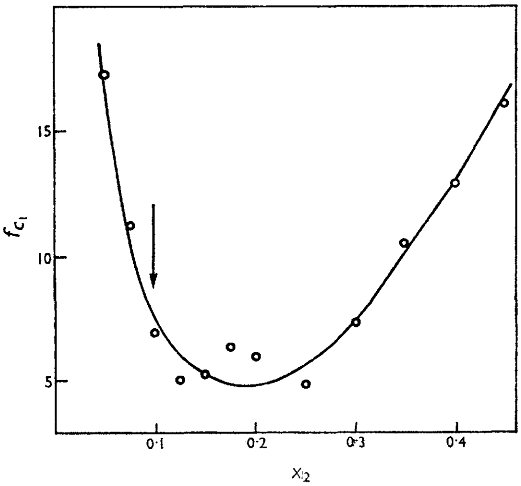

FIGURE. *Variation in relaxation frequency, f_{c_1}, with alcohol mole fraction for mixtures of water and t-butyl alcohol at 5°; the arrow indicates the mole fraction at which (α/f^2) is a maximum.*

A typical plot is given in the Figure. The minimum frequencies together with the mole fractions at which they occur are given in the Table which also lists the mole fractions at which (α/f^2) is a maximum. Both minimum relaxation frequencies are almost independent of temperature.

The similarities suggest that, since bulk water is the only common component, the two relaxation frequencies must be associated with a reorganisation of water structure. It has previously been suggested[1,2] that a water–clathrate model can satisfactorily accommodate the results in the very low mole fraction region and it seems possible that the relaxations under consideration involve co-operative reorganisation of similar structures. This co-operative nature of the process accords with the small temperature coefficient of the relaxation frequencies.

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