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DIELECTRIC RELAXATION OF 1-PROPANOL IN 1,4-DIOXANE AND CYCLOHEXANE

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Dielectric relaxation times of 1-propanol were measured in 1,4-dioxane and cyclohexane at 25 °C by the TDR method. Dielectric behavior of this alcohol varied greatly according to the nature of the solvent. A single relaxation process was observed when the hydrogen bonding solvent was employed, while two separate relaxation processes were found in the inert solvent.

We have reported how the principal relaxation time of 1-propanol changes with concentration in a variety of solvents in the frequency range of $(0.35—2.1)\times10^9$ Hz at 25 °C.[1,2] In this work we studied the concentration dependence of this alcohol in two typical solvents, i.e., 1,4-dioxane and cyclohexane, for a wider concentration range at 25 °C in a wider frequency range of $10^7—10^{10}$ Hz by the use of a new equipment[3] of the time domain reflectometry(TDR) method.[4] TDR measurements can be carried out with remarkable speed and data obtained can be plotted uniformly on the complex plane diagram. Three examples of the Cole-Cole plots for cyclohexane solutions of 1-propanol obtained by the present work are shown in Fig. 1.

As is seen in Fig. 1, two relaxation processes were found clearly in cyclohexane solutions of 1-propanol. The complex dielectric constant ε^* of this solution is assumed to be the sum of Cole and Debye contributions.[5]

$$\varepsilon^* = \varepsilon_\infty + \frac{\Delta\varepsilon_p}{1 + (i\omega\tau_p)^\beta} + \frac{\Delta\varepsilon_s}{1 + i\omega\tau_s} \qquad (1)$$

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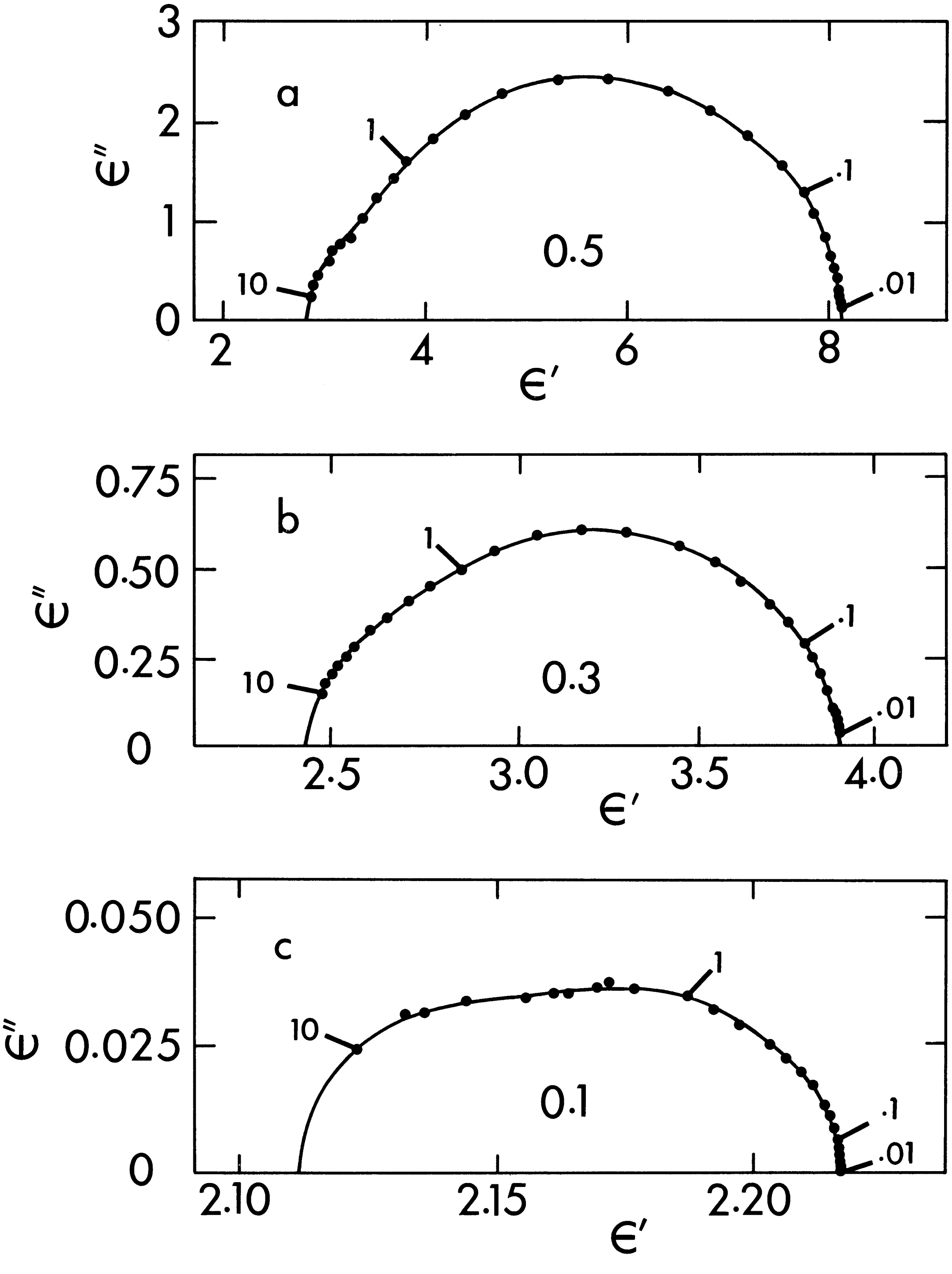

Fig. 1. Cole-Cole plots for cyclohexane solutions of 1-propanol with mole fractions 0.5, 0.3, and 0.1 of the alcohol. ●: the dot is obtained from the TDR measurement. —: the curve is obtained by calculations from Eq. 1. The number near the curve denotes the frequency at the related dot in GHz.

where ε_∞ is the high frequency limit of dielectric constant, $\Delta\varepsilon$ is the dielectric increment, ω is the angular frequency, τ is the relaxation time, β is the Cole-Cole parameter and subscripts p and s refer to the primary and the secondary relaxation processes, respectively. For 1,4-dioxane solution we set $\Delta\varepsilon_s$=0 because no secondary relaxation process was detected.

Plots of the relaxation times τ of 1-propanol are made against the concentration f of the alcohol in Fig. 2. As 1-propanol exhibits two separate processes in cyclohexane, we have two τ versus f curves in Fig. 2; τ_p is for the primary process

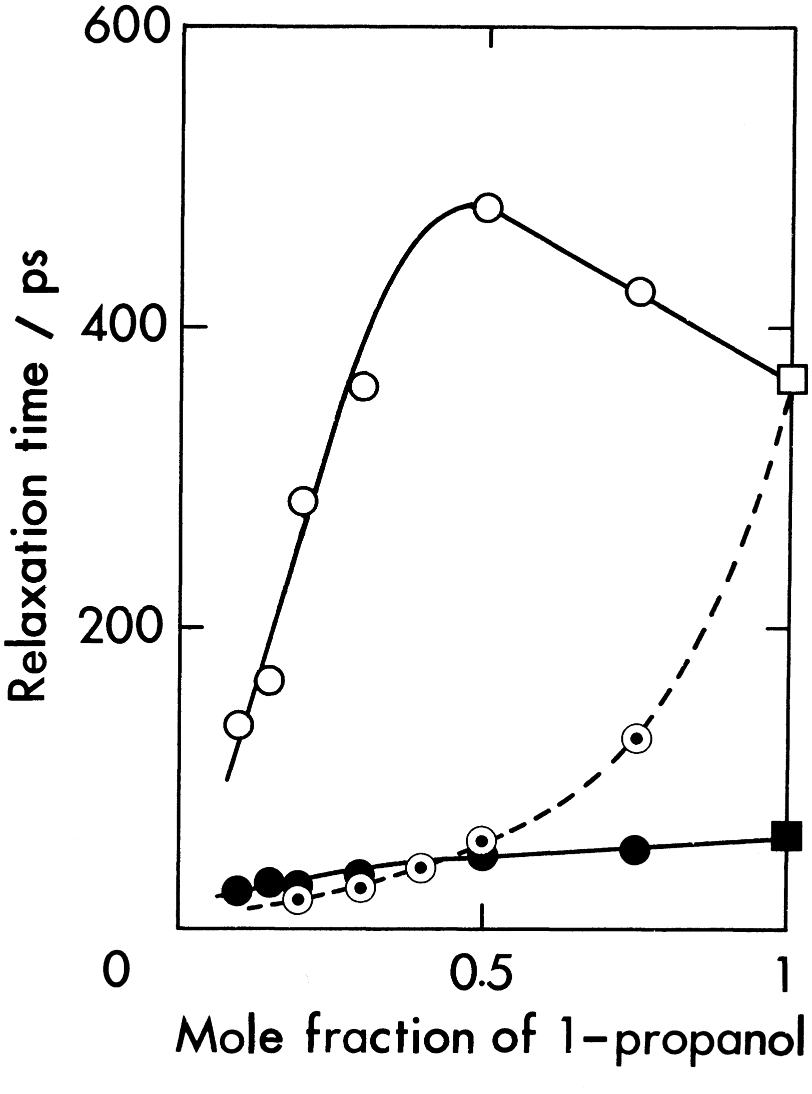

Fig. 2. Variation of the relaxation time of 1-propanol with concentration.

-○-: τ_p in cyclohexane; -□ : τ_p in pure alcohol;

-●-: τ_s in cyclohexane; -■ : τ_s in pure alcohol;

-⊙-: τ in 1,4-dioxane.

and τ_s for the secondary process. Both τ_p and τ_s were observed for pure 1-propanol while τ_s was not detected in pure methyl and ethyl alcohols. The relaxation time of 1-propanol in solution of 1,4-dioxane corresponds to τ_p and it decreases with decreasing concentration of the alcohol.

The primary relaxation is believed to be a cooperative process in large multimers of alcohol molecules arranged in a straight chain.6) The dependence1,2,7) of observed τ_p upon the alcohol concentration has been explained from the above viewpoint8) for a variety of solvents. Figure 2 provides us with distinctive features of this effect for two typical solvents. After examining a few other simple alcohols by use of the same TDR equipment we shall present a discussion in detail9) on the mechanism of the primary relaxation.

The secondary relaxation may be due to rotation of small alcohol multimers. The present work made clear the existence of this relaxation first for 1-propanol.

Lastly we shall turn to the Cole-Cole parameter: β was found to be equal to unity except in the dilute region of the alcohol $f=0.10$—0.30 in cyclohexane. The maximum deviation is: $\beta=0.91\pm0.02$ at $f=0.15$.

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