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DIELECTRIC BEHAVIOR OF 2-METHYL-2-PROPANOL AND BUTANOL ISOMERS IN SOLUTIONS

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The principal relaxation times of four isomeric butanols were measured at 25 °C in cyclohexane solutions by the TDR method and compared with those obtained in solutions of benzene and pyridine. The dielectric behavior of 2-methyl-2-propanol is found to be vastly different from other butanols.

Dielectric measurements on four butanol isomers were carried out in cyclohexane solutions at 25 °C in the frequency region between 10 MHz and 5 GHz by the time domain reflectometry (TDR) method.[1-3] The obtained principal relaxation times τ of the alcohols are plotted against the mole fraction f (see Fig. 1). In contrast to the small changes in τ for other butanols, τ of 2-methyl-2-propanol drops sharply on dilution by cyclohexane. The τ-f curves of four butanol isomers in solutions of cyclohexane, benzene and pyridine[4)] are compared in Fig. 2. This figure indicates again a marked difference in the dielectric behavior between 2-methyl-2-propanol and the other three alcohols; the τ-f curves of the cyclohexane, benzene and pyridine solutions of 2-methyl-2-propanol show a sharp and similar decrease on dilution while the curves of the other alcohols

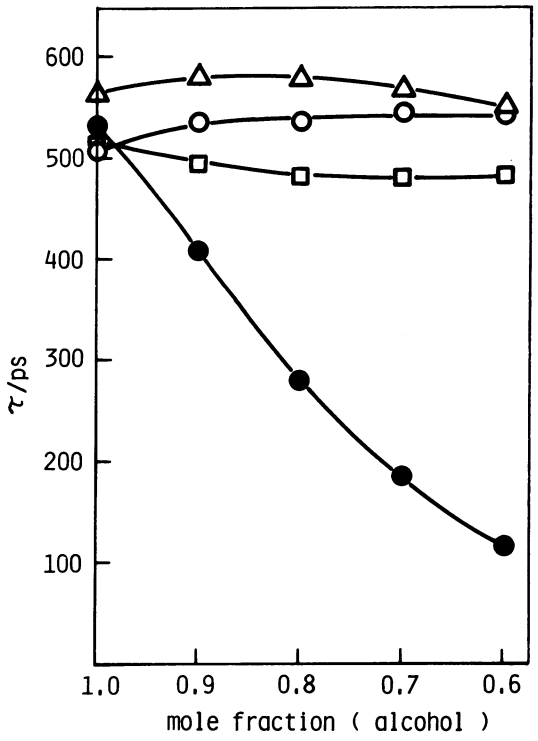

Fig. 1. Variation of the principal relaxation times of alcohols in cyclohexane with mole fraction at 25 °C.
─○─ : 1-butanol; ─△─ : 2-methylpropanol;
─□─ : 2-butanol; ─●─ : 2-methyl-2-propanol.

depend largely on the kind of solvents.

The decrease in the principal relaxation time observed for the butanol solutions has been interpreted as arising from deformation or destruction of hydrogen bonded clusters of the alcohols.4-6) The above feature of 2-methyl-2-propanol proves that the stability of the cluster formed by the alcohol is smaller than that of the other alcohols. According to Nishikawa,7) an X-ray diffraction pattern of liquid 2-methyl-2-propanol reported by Narten and Sandler8) can be explained on the basis of a structure model similar to that of liquid 2,2-dimethylpropane, which means that the steric hindrance of the methyl groups plays an important role in determining the liquid structure of 2-methyl-2-propanol. Nishikawa's explanation is consistent with the above-mentioned dielectric property of 2-methyl-2-propanol because the explanation suggests that the hydrogen-bonding of 2-methyl-2-propanol is weaker than that of the other alcohols, where a linear OH···O hydrogen-bonding is supposed to be an important factor in determining their liquid structure.

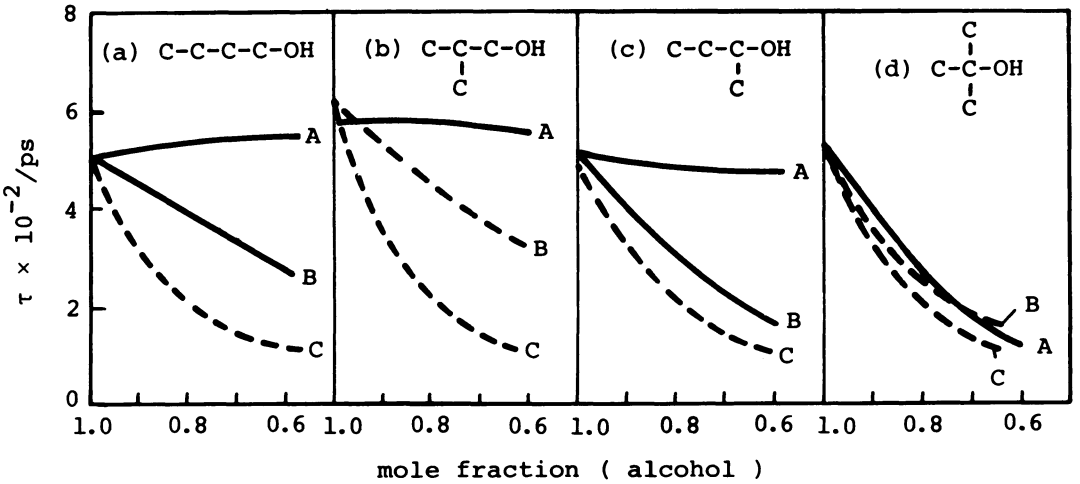

Fig. 2. Variation of the relaxation times of 1-butanol, 2-methylpropanol, 2-butanol and 2-methyl-2-propanol (from left to right) with alcohol mole fraction at 25 °C in cyclohexane (A), benzene (B) and pyridine (C) solutions. —— : obtained by the present work; ---- : obtained from the preceding paper.4)

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