DIELECTRIC BEHAVIOR OF 1-PROPANOL IN A VARIETY OF HYDROGEN-BONDING SOLVENTS

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The dependence of the principal relaxation time of 1-propanol upon hydrogen-bonding solvent has been carefully studied by use of water and four ketones as solvent. It was found that the molecular weight of the hydrogen-bonding solvent is fairly important in the solvent effect.

Dielectric measurements on mixtures of 1-propanol with water, acetone, 3-pentanone, cyclohexanone and camphor were made at 25°C in the frequency range of 350-1000 MHz by a slotted line type equipment. The principal relaxation time of the alcohol in a mixture was obtained from the Cole-Cole plots of ϵ' and ϵ'' of the solution; and the distribution parameter α was found to be zero in the range of frequencies and concentrations employed in the present experiment.

The relaxation time of the alcohol for a given concentration expressed in the units of mol fraction appears to increase with an increase in the molecular weight of the solvent, water being an exception (Table 1).

Table 1. Relaxation times of 1-propanol in various solvents (units: ps)

Solvents (mol. wt.)	Concentration of 1-propanol (mol fraction)			
	0.95	0.90	0.80	0.70
Water (18)	293	246	188	141
Acetone (58)	240	195	119	85
3-Pentanone (86)	265	217	137	110
Cyclohexanone (98)	273	238	168	116
Camphor (152)	278	229	180	145

The anomalous behavior of water will become normal if the concentration of the alcohol is expressed in the units of mol per liter (Fig. 1). It has been reported 2)

that the points for pyridine and dioxane lie in a single curve instead of two (see curve (e)). The molecular weights of pyridine and dioxane are 79 and 88, respectively, while their molecular volumes are similar, 81 vs. 83 cm³. The amalgamation of two curves might be due to the similarity of the two molecules in shape and size. It is interesting to note that the curve (d) for 3-pentanone is near the curve (e) for these molecules. The solvent effect appears to depend approximately on the molecular weight, or possibly, it is governed by both size and shape of the hydrogen-bonding solvent. The polarity of the solvent is of much less importance.

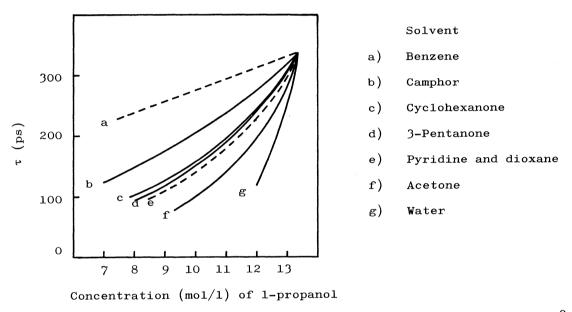


Fig. 1. Dependence of the Relaxation Time upon Dilution by Solvents at 25°C.

—— obtained by this experiment; —— from a preceding paper.²)

REFERENCES

- 1) T. Koshii, E. Arie, M. Nakamura, H. Takahashi and K. Higasi, Bull. Chem. Soc. Japan, 47, 618 (1974)
- 2) E. Arie, M. Nakamura, H. Takahashi and K. Higasi, Chem. Lett., 1973. 533.

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