CHEMISTRY LETTERS, pp. 491-494, 1975. Published by the Chemical Society of Japan

DIELECTRIC BEHAVIOR OF 2-METHYL-2-PROPANOL IN BENZENE AND PYRIDINE SOLUTIONS. II

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Dielectric measurements have been made for 2-methyl-2-propanol in benzene and pyridine solutions at four temperatures. The activation enthalpy and entropy of the principal relaxation of the alcohol decrease upon the addition of these solvents. The mechanism of the principal relaxations of alcohols is discussed from the viewpoint of cluster formation by hydrogen bonds.

The origin of the principal relaxations of alcohols is still in dispute. The activation enthalpies ΔH^* and entropies ΔS^* of the principal relaxations of primary alcohols are known to increase slightly upon the addition of inert solvents (benzene, cyclohexane, hexane, and carbon tetrachloride).[1-3] The observed increase of ΔH^* has been discussed with special regard to the relative size of the solvent molecule to that of the alcohol. Recently, both the ΔH^* and ΔS^* values of 1-propanol were found to decrease upon the addition of hydrogen-bonding solvents (1,4-dioxane and pyridine).[4] This result showed, for the first time, that the hydrogen-bonding capacity of the solvents could be a very important factor in determining the principal relaxation of the alcohol. On the other hand, the dielectric behavior of long-chain alcohols is governed largely by their isomeric configurations.[5-7] The purpose of this letter is to report the dependence of the two parameters ΔH^* and ΔS^* of the principal relaxation of 2-methyl-2-propanol upon the addition of hydrogen-bonding and non-hydrogen-bonding solvents.

The dielectric constants ε' and losses ε'' of the mixtures of 2-methyl-2-propanol with benzene and pyridine have been measured in the frequency range of 1-0.35 GHz,

in the temperature range of 25-40°C, and in the concentration range of 1-0.7 mol fractions of the alcohol, by the use of a UHF slotted-line-type apparatus.[8] All the measured ε' and ε'' values, when plotted in a complex plane, lie on Debye semicircles; and they are considered to be all associated with the principal dispersion of the alcohol.[8]

The principal relaxation times τ were calculated on the basis of the Debye equation.[8] Fig. 1 shows the plots of τ against the concentration. On dilution, τ decreases similarly in both solutions. This result makes a sharp contrast to the behavior of other isomeric butanols. The corresponding curves for other isomeric butanols greatly depend upon the nature of the solvent.[9]

The activation enthalpies ΔH^* and entropies ΔS^* of the principal relaxation were calculated from the temperature dependence of the relaxation times.[4] For liquid 2-methyl-2-propanol, ΔH^* is obtained as 11.7 kcal/mol and ΔS^* as 11.7 e.u. Fig. 2 shows the dependence of ΔH^* upon the concentration; both ΔH^* and ΔS^* of the two solutions similarly decrease on dilution. At the concentration of 0.7 mol fraction of the alcohol, ΔH^* is 5.7 kcal/mol in benzene, and 2.7 kcal/mol in pyridine. At the same concentration, ΔS^* is 3.0 e.u. in benzene, and -2.1 e.u. in pyridine.

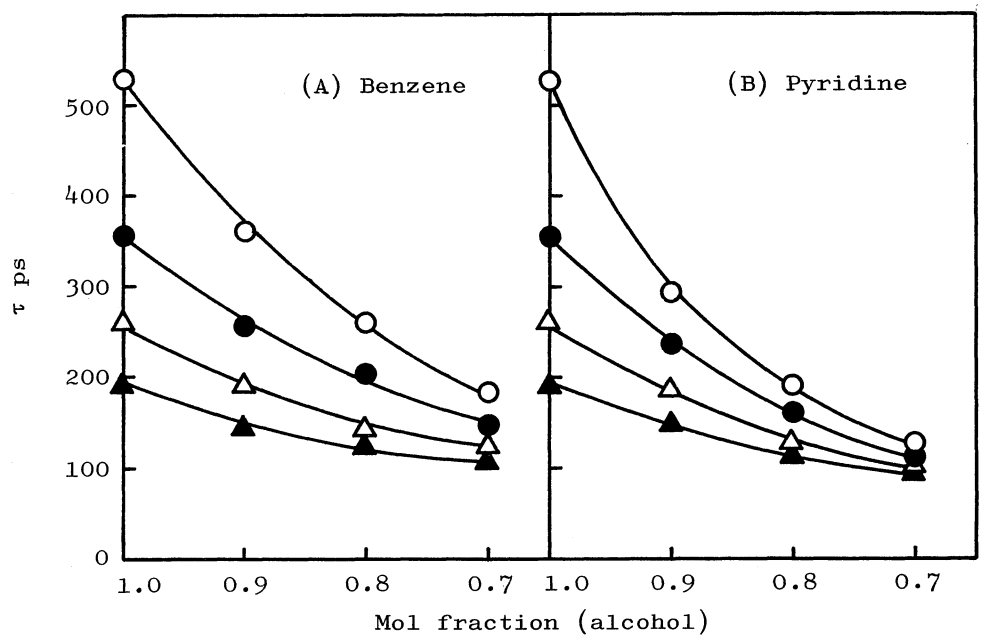

Fig. 1 Variations of principal relaxation times τ with mol fractions; 2-methyl-2-propanol mixed with (A) benzene and (B) pyridine.
○, 25; ●, 30; △, 35; ▲, 40°C

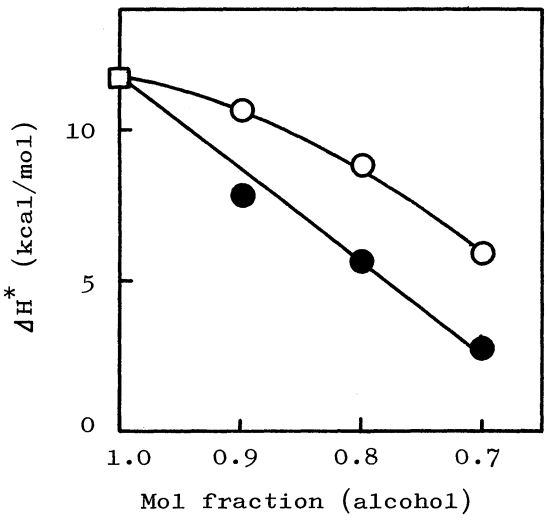

Fig. 2 Activation enthalpy ΔH^* of 2-methyl-2-propanol (○) in benzene and (●) in pyridine.

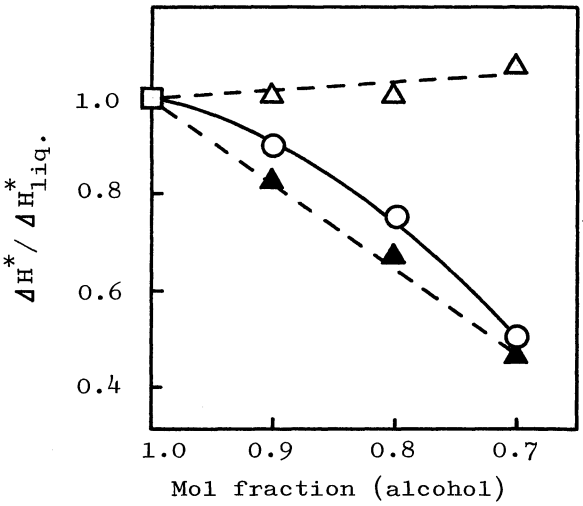

Fig. 3 Ratio of activation enthalpies of (△) 1-propanol in benzene, (▲) in pyridine and (○) 2-methyl-2-propanol in benzene.

On the other hand, both ΔH^* and ΔS^* of 1-propanol are known to depend more strongly upon the nature of the solvent. That is, they show a slight increase on the addition of non-hydrogen-bonding benzene, while they decrease upon the addition of hydrogen-bonding pyridine.[4] Hence, it can be concluded that pyridine behaves similarly for both 1-propanol and 2-methyl-2-propanol, while benzene behaves quite in a different way for the two alcohols. The ratio of the activation energy of a solution to that of the pure liquid, $\Delta H^*/\Delta H^*_{liq.}$, is taken for 2-methyl-2-propanol in benzene and compared with those of 1-propanol in benzene and pyridine in Fig. 3. It will be seen that the points ○ for $\Delta H^*/\Delta H^*_{liq.}$ of 2-methyl-2-propanol in benzene lie close to the lower dotted line for the points ▲ of 1-propanol in pyridine.[4] In this graph of $\Delta H^*/\Delta H^*_{liq.}$ plotted against the mol fraction, non-hydrogen-bonding benzene in 2-methyl-2-propanol appears to behave as if it were a hydrogen-bonding solvent in 1-propanol.

In case of 1-propanol, the changes of ΔH^* and ΔS^* [4] with two different solvents are in the same direction with those of the correlation factor g and the reduced relaxation time τ/η.[10] The large ΔH^* and ΔS^* values in benzene are accompanied by the large g and τ/η, and the small ΔH^* and ΔS^* in pyridine by the correspondingly small g and τ/η. Hence, it might be argued that the principal relaxation is associated with multimers, or molecules in the hydrogen-bonded

clusters. If this argument be correct, the large ΔH^* and ΔS^* values in benzene would point to the large clusters, and the small values in pyridine the small clusters. The addition of pyridine to primary alcohols would tend to destroy the alcohol clusters, while non-hydrogen-bonding benzene would be unable to do so.

The situation in the tertiary alcohols is different. Hydrogen bonds formed by neighbouring alcohol molecules must be weak on account of the large steric hindrance. For this reason, benzene would be able to destroy the loosely bounded clusters of tertiary alcohols and, hence, ΔH^* of 2-methyl-2-propanol would show a decrease on dilution with benzene. However, the principal relaxation cannot be explained only by over-all rotation of the clusters. This seems to be evident since 2-methyl-2-propanol has a larger ΔH^* [2,3,11] and a smaller τ/η [12] than 1-butanol.

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(Received March 14, 1975)