BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (7), 2225 (1975)

Dielectric Relaxation and Molecular Structure. XVI. Dielectric Behavior of Tertiary Alcohols

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(Received April 2, 1975)

Synopsis. The relaxation time and the activation energy of the principal dispersion of tertiary alcohols do not increase but *decrease* with increase in the number of the carbon atoms in the molecule. This observation seems to be in accord with a hypothesis that the principal dispersion is associated with the size of the hydrogen-bonded cluster of alcohols.

It is well known for *n*-alkyl bromides[1] and alkyl acetates,[2,3] that the relaxation time and the activation energy regularly increase with increase in the number of carbon atoms in the molecular chain. The same trend has been found also in normal primary alcohols.[4] The purpose of this note is to report that an exception to this general tendency is found in the case of tertiary alcohols.

Recently, the dielectric behavior of 2-methyl-2-butanol and 3-methyl-3-pentanol have been studied by the method described before.[5] The relaxation times, τ, of these tertiary alcohols and 2-methyl-2-propanol[6] are plotted, in Fig. 1, against the carbon number of the alcohol. It will be seen that the τ curve in the full line decreases with increase in the number of carbon atoms; it exhibits a striking contrast to the broken curve for normal primary alcohols.[4] Moreover, the curves for the reduced relaxation time, τ/η,[7] against the number of carbon atoms also show a downward slope for tertiary alcohols. The activation enthalpies, ΔH^*, of these tertiary alcohols[8] are plotted in Fig. 2 together with those of normal primary alcohols.[4] The ΔH^* *vs.* carbon number curve shows a decrease for the tertiary alcohols, while that for normal alcohols increases. For tertiary alcohols treated here, the larger the molecule becomes, the smaller are the τ and ΔH^* values. This indicates that the principal dispersion of these alcohols is not determined by the molecular size; that is, their relaxation is not a property of a monomer. Since the steric hindrance around the OH group increases with increase in the carbon number, the size of clusters by hydrogen bonds would become smaller possibly in the order of 2-methyl-2-propanol>2-methyl-2-butanol>3-methyl-3-pentanol. The above statement seems to be in accordance with the hypothesis that the principal dispersion is associated with the size of the hydrogen-bonded cluster of alcohols.[8]

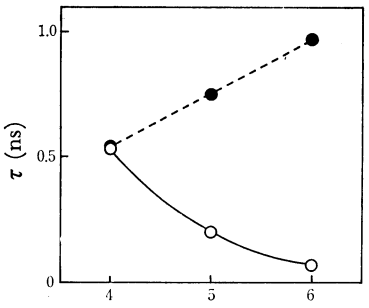

Fig. 1. Relaxation time, τ, *vs.* the number of carbon atoms of the alcohol at 25 °C.
○: tertiary alcohols, ●: normal alcohols.[4]

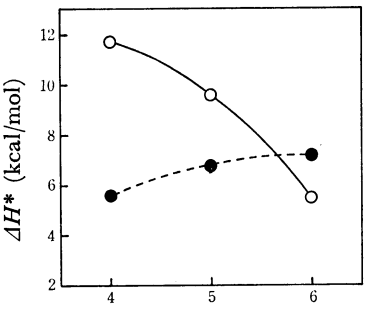

Fig. 2. Activation enthalpy, ΔH^*, *vs.* the number of carbon atoms of the alcohol.
○: tertiary alcohols, ●: normal alcohols.[4]

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