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NOTE

Study of Activation Energy of Methoxy Acetic Acid in Different Solvents

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Dielectric measurements at 9.318 GHz on methoxy acetic acid are carried out at room temperature in three different solvents. These data are used to evaluate relaxation times of solute molecule in three solvents. The difference in activation energies for a pair of solvents is determined. The result is used to explain the difference of relaxation time of the same solute molecule in various solvents.

Key Words: Dielectrics, Activation energy, Dipole relaxation, Relaxation time.

Eyring *et al.*[1] treating relaxation as rate process expressed relaxation time as

$$\tau = \frac{h}{kT} e^{\left(\frac{E_\tau}{RT}\right)} \tag{1}$$

where E_τ is the activation energy for dipole orientation. This can be expressed as

$$\tau = \frac{h}{kT} e^{\left(\frac{\Delta F^*}{RT}\right)} \tag{2}$$

where ΔF^* = free energy of activation for dipole relaxation, R = gas constant, h = Planck's constant, k = Boltzman constant, T = absolute temperature.

By finding the relaxation times of same molecule in two solvents (τ_1 and τ_2) at the same temperature, the ratio $\frac{\tau_2}{\tau_1}$ will be

$$\frac{\tau_2}{\tau_1} = e^{\frac{\Delta F_2^* - \Delta F_1^*}{RT}} \tag{3}$$

The Debye[2] relation

$$\tau = \frac{4\pi\eta a^3}{kT} \tag{4}$$

fails to explain the reason for getting different values of τ for the same molecule in different solvents of same viscosity and at same temperature. But the equation (3) explains this phenomenon at the same temperature due to differing values of

ΔF^*, the activation energy, in different solvents though their viscosity values may be same. Any difference in ΔF^* values may be considered as a measure of hindrance to the rotation of solute dipole in a given solvent. Thus relaxation time measurements in different solvents are expected to give a useful clue for studying the solute-solvent interaction. Keeping the above considerations the dielectric measurements at 9.318 GHz on methoxy acetic acid are carried at room temperature using a set up similar to that of Heston *et al.*[3], in three solvents, namely, benzene, 1,4-dioxane and cyclohexane. The values of ε' and ε'' are calculated for several graded concentration dilute solutions. From these data using the microwave conductivity concept dipole moment and relaxation time are calculated[4]. Using these relaxation times and with the aid of equation (3) difference in activation energies for a pair of solvents is determined[5]. The results are given in Tables 1 and 2.

TABLE-1
DIPOLE MOMENT AND RELAXATION TIME OF METHOXY ACETIC ACID IN DIFFERENT SOLVENTS

Solevent	μ (Debyes)	τ (Pico-Sec)
Benzene	1.78 D	3.2
1,4-Dioxane	2.38 D	9.0
Cyclohexane	0.82 D	16.8

TABLE-2
RATIO OF RELAXATION TIME OF METHOXY ACETIC ACID IN A PAIR OF SOLVENTS

Solvents	$\left(\frac{\tau_2}{\tau_1}\right)$	$(\Delta F_2^* - \Delta F_1^*)$
Benzene-cyclohexane	5.25	988
Benzene-dioxane	2.81	616
Dioxane-cyclohexane	1.86	372

The relaxation time varies from benzene to cyclohexane through dioxane in the order 1 : 3 : 5 approximately. Hence activation energies ΔF^* should also increase in the same order of solvents. Therefore hindrance to rotation of solute dipole will be highest in cyclohexane and least in benzene while dioxane offers a hindrance intermediate between the two.

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