

## Theoretical evaluation of relaxation times of some aromatic esters using different methods

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Theoretical evaluation of relaxation times by five different methods namely Debye's  $\tau_1$  (Debye 1929), modified Debye's  $\tau_B$  (Fischer 1939), Wirtz *et al*'s  $\tau_B$  (Wirtz *et al* 1953), Murty's  $\tau_4$  (Murty 1959) and Syamalamba and Premaswarup's  $\tau_B$  (Syamalamba and Premaswarup 1966) equations have been employed to make theoretical predictions and to compare these with the experimental results for the four systems containing methyl isonicotinate, ethyl nicotinate, ethyl isonicotinate and benzyl nicotinate for which experimental values were available (Sharma and Gandhi 1990) at 9.94 GHz in six different non-polar solvents at 40°C. It has been found that Murty's equation is a better representation of the phenomenon of relaxation than the other equations.

The relaxation times calculated from five different equations are given in Table 1 alongwith the experimental values reported by Sharma and Gandhi (1990). A comparison of experimental and calculated values of  $\tau$  given in Table 1 shows that Debye's equation gives values of  $\tau$ , 3–44 times those of experimental values. It is obvious that for all the four aromatic esters in all the six solvents, the predictions of  $\tau_1$  by the Debye's equation are many folds of the actual experimental relaxation time values. The Debye's equation therefore cannot be employed for the present systems. This is as expected since the four aromatic esters under study do not have spherical molecular shapes, while the Debye's equation is applicable to the spherical molecules.

The same table shows  $\tau$  values obtained by replacing  $\eta_1$  by 0.36  $\eta_1$  in Debye's equation as suggested by Fischer (1939), the deviations of the predicted relaxation times from the experimental values are considerably reduced. However, these theoretically predicted values are also many times higher than the experimental ones. The modified Debye's equation is therefore, certainly an improvement over the Debye's equation but it still remains totally inadequate to represent the relaxation behaviour of compounds under the present investigations.

This is again as expected because in this equation, although the viscosity of the medium has been modified to have a better representation of the resistance of the internal viscosity to the rotation of the polar molecules, but no account of the deviation from the spherical shape of the molecules has been taken. Similar type of behaviour was observed by Khatri *et al* (1990).

**Table I.** Experimental relaxation time  $\tau_n$ , and theoretical relaxation time  $\tau_1, \tau_2, \tau_3, \tau_4$  and  $\tau_5$  values in Ps for the four aromatic esters in different non-polar solvents at 40°C.

Solvent	$\tau_0$	$\tau_1$	$\tau_2$	$\tau_3$	$\tau_4$	$\tau_5$
Solute : Methyl isonicotinate						
<i>n</i> -Heptane	7.6	48.1	17.3	5.6	5.5	6.3
Benzene	5.7	69.7	25.1	9.4	7.3	9.7
Cyclohexane	14.0	97.2	35.1	16.4	10.8	13.4
Carbon-tetrachloride	34.1	108.5	39.1	18.6	11.5	16.1
1,4-Dioxane	10.1	128.8	46.4	17.7	13.6	19.1
Decalin	12.1	255.2	91.9	29.0	27.3	37.3
Solute : Ethyl nicotinate						
<i>n</i> -Heptane	12.6	53.2	19.2	8.5	6.1	7.0
Benzene	3.6	77.0	27.7	10.8	8.0	10.7
Cyclohexane	9.4	107.5	38.7	14.2	11.9	14.8
Carbon-tetrachloride	41.1	120.0	43.2	20.6	12.6	17.8
1,4-Dioxane	12.2	142.4	51.3	20.3	15.1	21.1
Decalin	42.0	282.0	101.5	33.3	30.1	41.2
Solute : Ethyl isonicotinate						
<i>n</i> -Heptane	11.8	50.6	18.2	8.1	5.9	6.6
Benzene	4.7	73.3	26.4	12.8	7.8	10.2
Cyclohexane	26.6	102.3	36.8	17.2	11.4	14.1
Carbon-tetrachloride	32.9	114.2	41.1	19.6	12.3	17.0
1,4-Dioxane	3.1	135.5	48.8	23.8	14.6	20.1
Decalin	33.9	268.4	96.6	42.7	29.2	39.3
Solute : Benzyl nicotinate						
<i>n</i> -Heptane	15.5	71.1	25.6	11.3	9.0	9.3
Benzene	4.7	103.0	37.1	18.2	11.9	14.4
Cyclohexane	11.5	143.7	51.7	24.4	17.7	19.8
Carbon-tetrachloride	15.8	160.3	57.7	27.9	18.7	17.0
1,4-Dioxane	14.2	190.3	68.5	34.1	22.3	28.2
Decalin	30.1	377.0	135.7	59.2	44.6	55.1

The Table 1 shows that the values of  $\tau$  calculated using equations given by Wirtz *et al* (1953) and Syamalamba and Premaswarup (1966), are found to be nearer to the experimental values. These results indicate that the equations of Wirtz *et al* (1953) and the Syamalamba and Premaswarup (1966) can predict the relaxation

time values far better than those of Debye (1929) and the modified Debye (Fischer 1939). The discrepancies are still large and can be supposed to be due to (i) the large deviations of the molecular shape from the spherical shape and (ii) the existence of internal rotations which have not been considered in the development of both of these equations. However, the values of  $\tau$  obtained from Murty's equation are in good agreement with the experimental values. Therefore, it is concluded that Murty's equation (Murty 1959) is a better representation of the relaxation phenomenon for the systems considered in the present note.

The discrepancy between the experimental values and those calculated by different equations may be due to the internal rotation in the molecule concerned which is not taken into account in these equations. All these equations are concerned with overall molecular volume and do not account for the difference in volume swept out in rotation round different axes.

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