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ROTATIONAL RELAXATION STUDIES FROM RAYLEIGH SCATTERING II CYCLOHEXANE DERIVATIVES

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The Rayleigh scattering band profiles were recorded for cyclohexanol, cyclohexanone and methylcyclohexane using a He-Ne laser excitation and a Ramanor HG2S instrument. The profiles were analysed by splitting them into a low frequency (10-25cm^{-1}) and a high frequency (25–60^{-1}) region. An average rotational relaxation time and diffusion constant were obtained using the low frequency profile. The rotational relaxation times are smaller than those for benzene derivatives.

Key Words : Rotational Relaxation; Rayleigh Scattering; Cyclohexanol; Cyclohexanone; Methylcyclohexane; He–Ne Laser Excitation; Ramanor HG2S

INTRODUCTION

IN their previous paper[1] (hereafter referred to as I), the authors demonstrated the usefulness of depolarised Rayleigh scattering spectroscopy as a technique for studying rotational motion in pure liquids of mono-substituted benzene derivatives.

In this paper, the authors present the depolarized Rayleigh scattering for pure liquids of cyclohexanol, cyclohexanone and methylcyclohexane. As it has been shown in *I*, the intensity of the scattered light $I(\omega)$ as a function of frequency for the low frequency part (10 to 25cm^{-1}) is given by :

$$I(\omega) \propto \tau_r \left\{ \left[1 - \left(\frac{I}{4kT} \right) \omega^2 \right]^2 + \omega^2 \tau_r^2 \right\}^{-1} \qquad ...(1)$$

The scattered intensity in the high frequency part 26 to 50cm^{-1} or more is given by :

$$I(\omega) \propto \omega^{12/7} \exp\left(- \frac{\omega}{\omega_0} \right) \qquad ...(2)$$

τ_r, the rotational relaxation times of cyclohexanol, cyclohexanone and methylclyclohexane have been calculated from the plots of $I(\omega) - I(\omega_0)/I(\omega)$ versus ω^2 using the equation

$$[I(\omega_0) - I(\omega)]/I(\omega) = \tau_r^2 \omega^2 \qquad ...(3)$$

which gives a straight line of slope τ_r^2.

EXPERIMENTAL

All Rayleigh recordings were obtained using the apparatus described in *I*, in the region 10cm^{-1} to 60cm^{-1}.

The liquids used for study, after distillation, were :—
cyclohexanol, cyclohexanone and methylcyclohexane.

Results and Observations

(i) The recordings of the Rayleigh wings of the cyclohexane derivatives are given in Fig. 1(*b*). It may be noted that the low frequency part (10 to 25cm^{-1}) falls off rapidly, but the high frequency part beyond 25cm^{-1} extends over a longer region than the case in the benzene derivatives, Fig. 1(*a*).

(ii) The plots of $I(\omega_0) - I(\omega)/I(\omega)$ *vs.* ω^2 are given for those liquids in Fig. 2 for the low frequency region and in Fig. 3 for the high frequency region. These

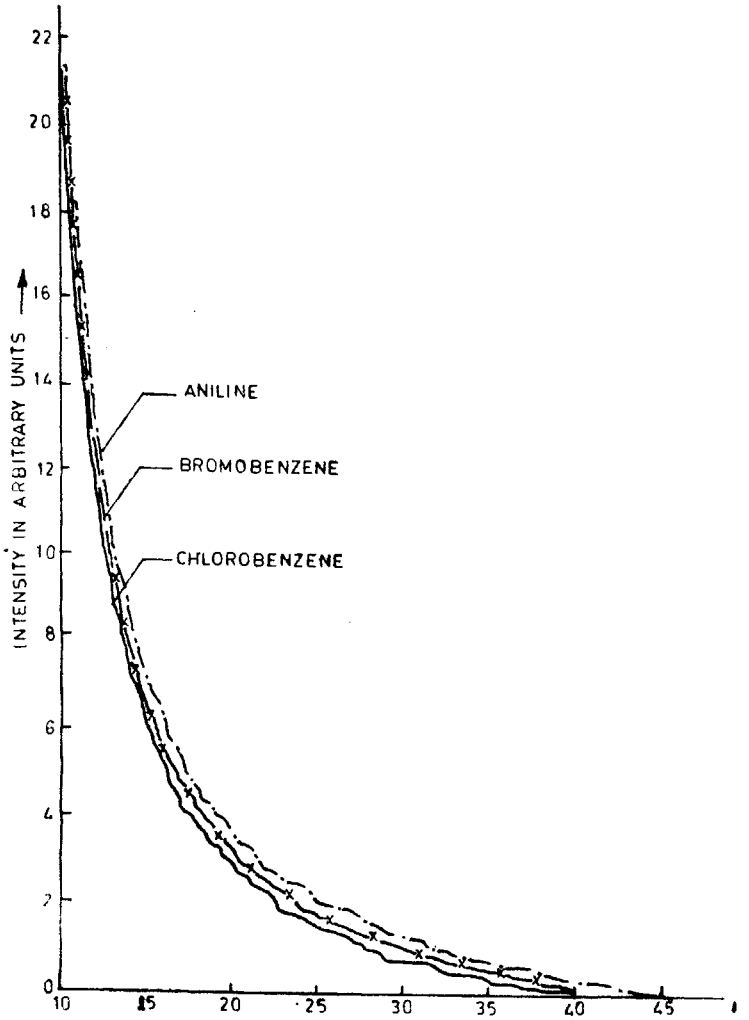

FIG 1 (*a*) RAYLEIGH wing frequencies in cm^{-1} from the centre

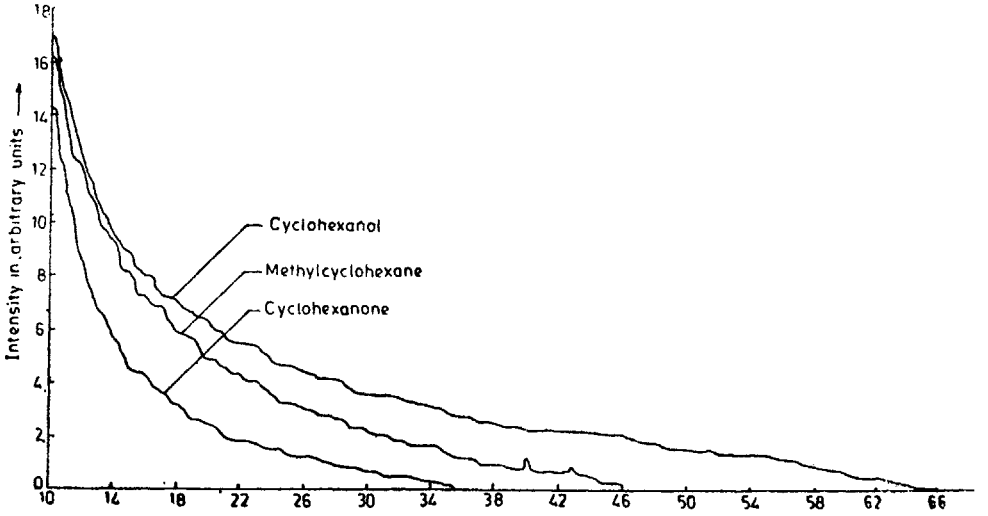

FIG 1 (*b*) Rayleigh wing frequencies in cm^{-1} from the centre

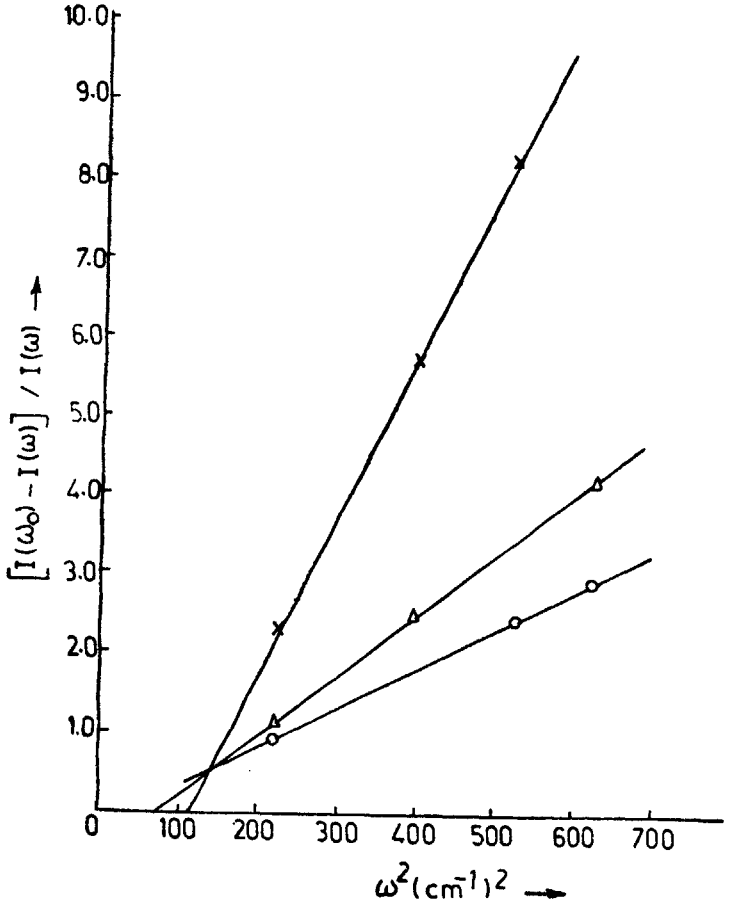

FIG 2 A plot of $[I(\omega_0) - I(\omega)]/I(\omega)$ *vs* ω^2 for cyclohexanone ×, methylcyclohexane Δ, and cyclohexanol o (10 to 25 cm^{-1})

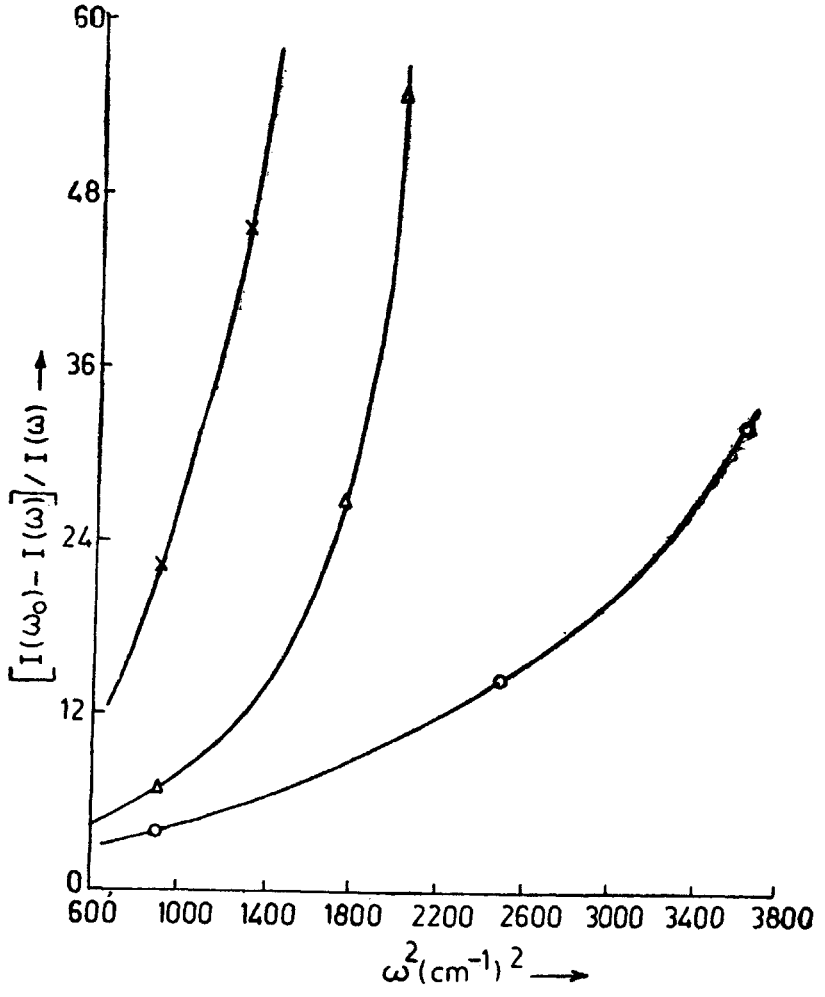

FIG 3 A plot of $[I(\omega_0) - I(\omega)]/I(\omega)$ *vs* ω^2 for cyclohexanone ×, methylcyclohexane △, and cyclohexanol o (26 to 61 cm^{-1})

are straight lines for the low frequency region but show upward curvature for the high frequency region.

(iii) The plots of log $[I(\omega).\omega^{-12/7}]$ *vs.* ω are given for the high frequency region in Fig. 4. These are straight lines as per eq. 2.

(iv) The rotational relaxation times obtained from the slopes of the graphs of the low frequency region are given in Table I. The values of the average rotational diffusion constant are also given in the same Table. The Table also contains the viscosity data of the liquid.

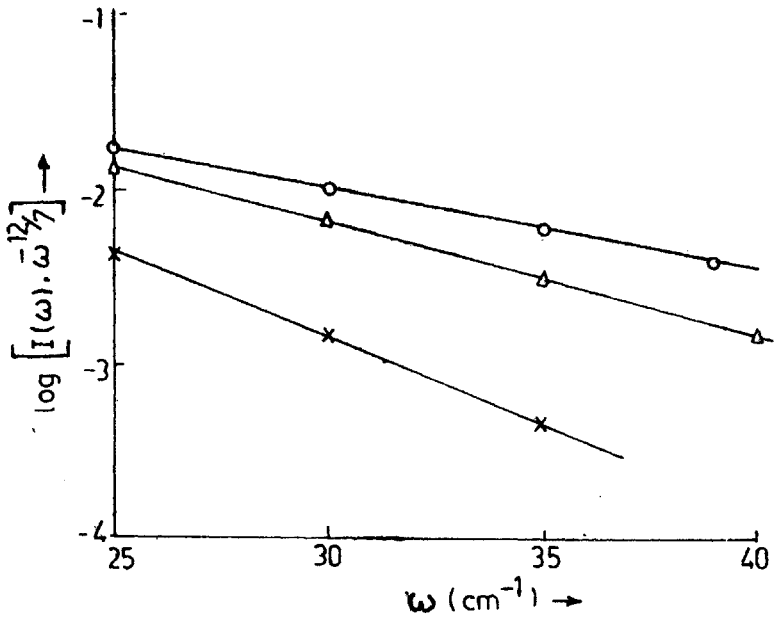

FIG 4 Plots of log $[I(\omega).\omega^{-12/7}]$ *vs* ω for cyclohexanol o, methylcyclohexane Δ, and cyclohexanone $\times$

TABLE I

Correlation times in units of 10^{-12}*s at 22 °C for cyclohexane derivatives*

S. No.	Liquid	Viscosity[2] (cp)	τ_r	Diffusion constant D $\times 10^{12} S^{-1}$
1	Cyclohexanol	41.07	2.34	0.0712
2	Cyclohexanone	1.803	4.70	0.0355
3	Methylcyclohexane	0.685	2.94	0.0567

CONCLUSIONS

No values of τ_r are available in the literature for the cyclohexane derivatives, which can be compared. The average values of τ_r are lower than the values obtained for benzene derivatives in *I*, indicating a faster rotation of these molecules.

REFERENCES

1 H A Ahmed and G Thyagarajan *Proc Indian natn Sci Acad* 55A (4) (1989) 661–669
2 *Lange's Handbook of Chemistry* (*Ed* J A Dean) McGraw Hill (1985) 10–103