

Ultrasonic velocity dispersion in methylcyclohexane

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Abstract. Ultrasonic velocity dispersion in methylcyclohexane was studied in the frequency range of 0.5 to 5.0 MHz at 60°, 65°, 70°, 75° and 80° C using a variable path interferometer. Necessary corrections for the diffraction of the ultrasonic beam were applied. The velocity data were used to evaluate the relaxation parameters pertaining to the interconversion of the axial and equatorial isomers. The value of the difference in enthalpy, difference in entropy and the activation energy are 11.2 ± 4.0 kJ mole⁻¹, 28.0 ± 8.0 J mole⁻¹K⁻¹ and 43.7 ± 4.0 kJ mole⁻¹ respectively. These values are in good agreement with values derived by Piercy and Subrahmanyam from their ultrasonic absorption measurements.

Keywords. Ultrasonic relaxation, methylcyclohexane.

1. Introduction

The skeletal structure of methylcyclohexane takes mainly a chair configuration and the substituent atom an equatorial position. This isomer is believed to be in equilibrium with another having chair configuration and an axial substituent atom (figure 1), the two isomers being rapidly interconvertible by distortion of the skeletal structure. Passage of sound waves of appropriate frequency disturbs this equilibrium leading to relaxational behaviour. Relaxation parameters could be determined from a study of ultrasonic absorption or velocity as a function of frequency at different temperatures.

Ultrasonic absorption in methylcyclohexane was previously studied by a number of workers (see Piercy and Subrahmanyam 1965). While all these studies excepting

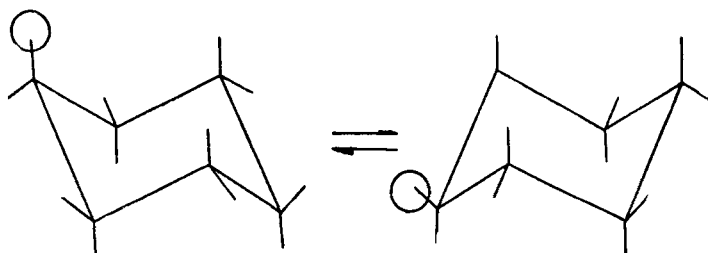


Figure 1. The skeletal structure of the chair isomers of methylcyclohexane shown in perspective. The long lines represent carbon-carbon bonds, the short lines carbon-hydrogen bonds and the circle the methyl group.

those of Hall (1969) indicate single relaxational behaviour, there is no agreement between different workers regarding the numerical values of the thermodynamic parameters. Hall, on the other hand, observed that some of his absorption measurements did not have the frequency dependence characteristic of a single relaxation process.

In view of the difference in the reported relaxation parameters we took up the study of ultrasonic velocity dispersion in this liquid.

In the present work, ultrasonic velocity dispersion in the frequency range 0.5 to 5.0 MHz was studied at 60°, 65°, 70°, 75° and 80° C using a variable path interferometer developed for such studies (Subrahmanyam and Hyder Khan 1972, 1973).

2. Evaluation of relaxation parameters

For a given temperature and pressure the frequency dependence of ultrasonic velocity due to a single relaxation process may be represented by the standard formula (Subrahmanyam and Piercy 1965).

$$\frac{u_{\infty}^2 - u^2}{u_{\infty}^2 - u_0^2} = \frac{1}{1 + (f/f_r)^2} \quad (1)$$

for the usual case of small $u_{\infty}^2 - u_0^2$, where u_{∞} and u_0 are the velocities corresponding to very high frequency ($f \gg f_r$) and very low frequency ($f \ll f_r$) respectively; f_r is the relaxation frequency and u is the velocity at the frequency f . According to equation (1) the shape of the plot of $\log(u_{\infty}^2 - u^2)$ versus $\log f$ is independent of the magnitude of the relaxation parameters. Hence, a template of the theoretical curve can be used to fit the velocities and evaluate the relaxation frequency. However, it is essential to know u_{∞} values for this purpose. Direct determination of velocity at very high frequency is not possible with the present method. Hence u_{∞} was evaluated using the velocity data at 1, 3 and 5 MHz (u_1 , u_3 and u_5) via the relation

$$u_{\infty}^2 = \frac{2u_5^2u_3^2 - 3u_5^2u_1^2 + u_1^2u_3^2}{3u_3^2 - 2u_1^2 - u_5^2} \quad (2)$$

The above equation yields accurate values of u_{∞} when u_{∞} is not far removed from u_5 . For methylcyclohexane, this condition is satisfied at all the five temperatures studied.

The kinetic parameters of the relaxation process are related to f_r via [Mason (1965)].

$$f_r = A \exp(-\Delta E_a/RT) \quad (3)$$

where A is frequency factor and ΔE_a is activation energy of the backward reaction and is independent of temperature. The slope of $\log f_r$ versus reciprocal of absolute temperature curve yields ΔE_a .

The equilibrium parameters ΔH_0 and ΔS_0 the difference in enthalpy and that of entropy respectively between the two isomers in their standard states are related to the velocity dispersion via the relation [Mason (1965), Hyder Khan *et al* (1973)]

$$\frac{2}{M} \frac{(C_{p0})^2}{\alpha} \left(\frac{u_\infty - u_0}{u_0^2 u_1^2} \right) \approx \frac{B}{T} \left[\exp \left(\frac{\Delta H_0}{RT} \right) \exp \left(\frac{\Delta S_0}{R} \right) \right] \quad (4)$$

where C_{p0} is the heat capacity at constant pressure, M the molecular weight, α the thermal expansion coefficient and $u_1 = (u_\infty + u_0)/2$. Assuming ΔS_0 to be independent of temperature, the slope of the plot of $\log \left[T \frac{u_\infty - u_0}{u_0^2 u_1^2} \right]$ versus $1/T$ leads to the values of ΔH_0 . Using the value of ΔH_0 , one can evaluate ΔS_0 via equation (4) and ΔG_0 using the standard thermodynamic relation

Table 1. Velocity dispersion in methylcyclohexane

| Frequency (MHz) | Expt | Ultrasonic velocity, ms ⁻¹ | | Estimated error |
|--------------------|--------|---------------------------------------|-----------------------|--------------------|
| | | Diffraction correction | Corrected velocity | |
| 60° C | | | | |
| 0.5 | 1061.7 | 4.9 | 1056.8 | ±0.4 |
| 1.0 | 1061.7 | 1.4 | 1060.3 | ±0.2 |
| 1.5 | 1061.8 | 0.9 | 1060.9 | ±0.2 |
| 3.0 | 1063.0 | 0.2 | 1062.8 | ±0.3 |
| 65° C | | | | |
| 0.5 | 1042.0 | 4.8 | 1037.2 | ±0.4 |
| 1.0 | 1041.4 | 1.3 | 1040.1 | ±0.2 |
| 1.5 | 1041.9 | 0.8 | 1041.1 | ±0.2 |
| 3.0 | 1042.8 | 0.2 | 1042.6 | ±0.2 |
| 5.0 | 1043.2 | 0.1 | 1043.1 | ±0.3 |
| 70° C | | | | |
| 0.5 | 1021.7 | 4.7 | 1017.0 | ±0.4 |
| 1.0 | 1020.9 | 1.3 | 1019.6 | ±0.2 |
| 1.5 | 1021.8 | 0.8 | 1021.0 | ±0.2 |
| 3.0 | 1022.4 | 0.2 | 1022.2 | ±0.2 |
| 5.0 | 1023.3 | 0.1 | 1023.2 | ±0.3 |
| 75° C | | | | |
| 0.5 | 1000.8 | 4.6 | 996.2 | ±0.4 |
| 1.0 | 999.3 | 1.2 | 998.1 | ±0.2 |
| 1.5 | 999.7 | 0.7 | 999.0 | ±0.2 |
| 3.0 | 1001.2 | 0.2 | 1001.0 | ±0.2 |
| 5.0 | 1002.2 | 0.1 | 1002.1 | ±0.3 |
| 80° C | | | | |
| 0.5 | 977.4 | 4.5 | 972.9 | ±0.4 |
| 1.0 | 974.8 | 1.2 | 973.6 | ±0.2 |
| 1.5 | 976.8 | 0.7 | 975.1 | ±0.2 |
| 3.0 | 977.9 | 0.2 | 977.7 | ±0.2 |
| 5.0 | 978.9 | 0.1 | 978.8 | ±0.3 |

$$\Delta G_0 = \Delta H_0 - T\Delta S_0 \quad (5)$$

3. Experimental

Ultrasonic velocities in purified methylcyclohexane were measured at five frequencies (0.5, 1.0, 1.5, 3.0, 5.0 MHz) using a variable path interferometer developed for this purpose. (Subrahmanyam and Hyder Khan 1972, 1973).

The errors associated with the diffraction of the ultrasonic beam were estimated from a series of measurements on non-relaxing liquids of different absorption values, following the method described by Subrahmanyam *et al* (1969) and Hyder Khan (1972). Measurements were made at a distance of 3 cm from the source and the diameter of the source is 1.95 cm. The diffraction corrected velocities were used in evaluating the relaxation parameters.

4. Results and discussion

Ultrasonic velocity data obtained in the present work are shown in table 1. The error limits indicated in the table include uncertainties introduced in the evaluation of diffraction correction and in the measurement of ultrasonic velocity. Plots of $\log(u_\infty^2 - u^2)$ versus $\log f$ at 60°, 65°, 70°, 75° and 80° C are shown in figure 2.

The relaxation frequency f_r and the factor $(u_\infty^2 - u_0^2)$ were evaluated by fitting the results to the theoretical template. Relaxation parameters so evaluated are shown in table 2.

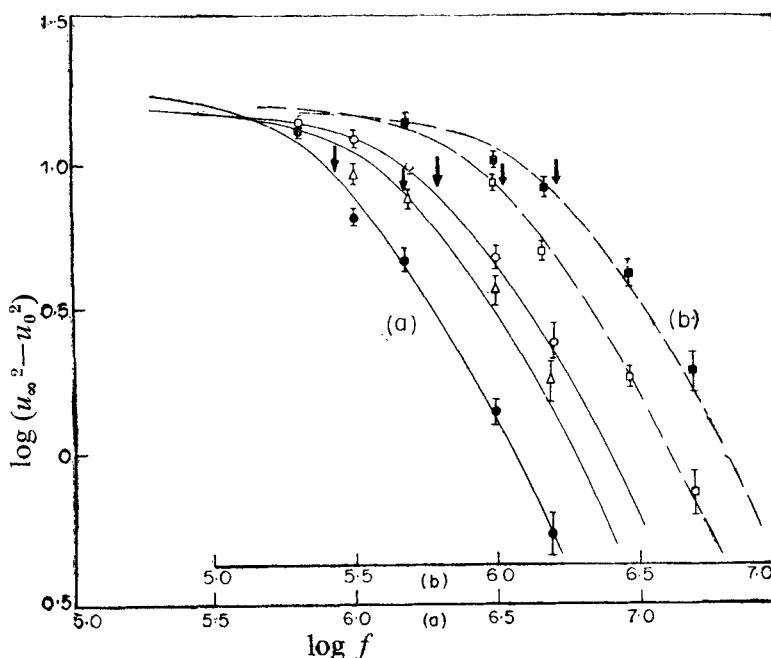


Figure 2. Velocity dispersion in methylcyclohexane; $\log(u_\infty^2 - u^2)$ as a function of $\log f$, \bullet at 60° C, \square 65° C, \triangle 70° C, \blacksquare 75° C, \circ 80° C. The curve represents the template fit and arrow head the relaxation frequency.

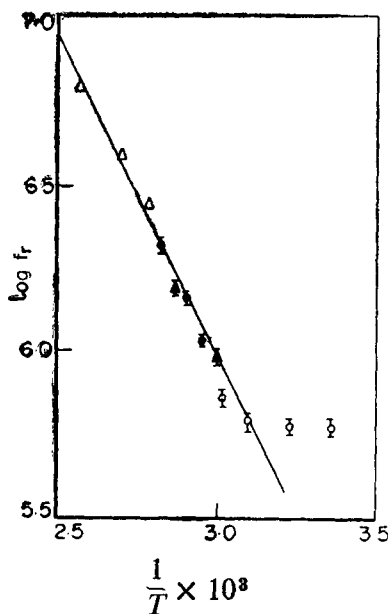


Figure 3. Variation of $\log f_r$ as a function of $1/T$: The solid line represents the straight line fit of the results of this work (\bullet), Piercy and Subrahmanyam (Δ), and Pedinoff (\circ).

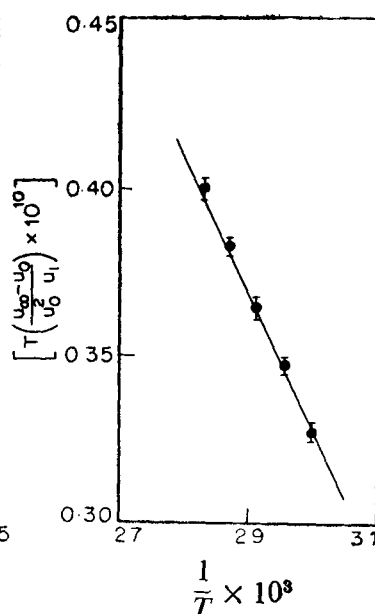


Figure 4. Variation of $\log [T(u_\infty - u_0) \times 10^{10}/u_0^2 u_i]$ as a function of $1/T$; The solid line represents the straight line fit of the results of this work.

The temperature dependence of the relaxation frequencies is shown in figure 3. These values are in good agreement with those reported by Piercy and Subrahmanyam (1965). The values reported previously in the literature are also recorded in this figure. The low temperature data of Pedinoff (1962) and Karpovich (1954) do not fall in line with other data. As pointed out by Piercy and Subrahmanyam (1965) the data of the above workers may be considered qualitative. Hence the data of the present work, that of Piercy and Subrahmanyam (1965) and the higher temperature points of Pedinoff (1962) were fitted to a straight line in figure 3. The slope yields a value of 44.0 ± 4.0 kJ mole⁻¹ for the activation energy. This is

Table 2. Relaxation parameters of methylcyclohexane.

| Temp. °C | f_r (MHz) | u_∞ (ms ⁻¹) | $u_\infty - u_0$ (ms ⁻¹) | u_0 (ms ⁻¹) |
|-------------|----------------|-----------------------------------|-----------------------------------------|------------------------------|
| 60 | 0.84 ± 0.1 | 1063.4 | 7.6 | 1055.8 |
| 65 | 1.05 ± 0.1 | 1043.4 | 7.3 | 1036.1 |
| 70 | 1.45 ± 0.1 | 1024.0 | 7.1 | 1016.9 |
| 75 | 1.75 ± 0.1 | 1003.0 | 6.9 | 996.1 |
| 80 | 2.01 ± 0.2 | 979.9 | 6.6 | 973.3 |

in good agreement with the value of $43.1 \text{ kJ mole}^{-1}$ reported previously by Piercy and Subrahmanyam using absorption data. Indirect spectroscopic evidence (Jenson *et al* 1962; Harris and Sheppard 1961; Reeves and Stromme 1960) indicates activation energy in the range 37.7 to $48.1 \text{ kJ mole}^{-1}$ for molecules of this type (example: cyclohexane and chlorocyclohexane).

The variation of $\log [T(u_{\infty} - u_0)/u_0^2 u_1]$ with the reciprocal of the absolute temperature is shown in figure 4.

The slope of the plot leads to a value of $13.1 \pm 4.0 \text{ kJ mole}^{-1}$ for the difference in enthalpy, ΔH_0 . This is in reasonable agreement with the value of $14.6 \pm 2.9 \text{ kJ mole}^{-1}$ reported by Piercy (1961) from absorption measurements on solutions of methylcyclohexane in xylene and with the value of $12.14 \pm 2.1 \text{ kJ mole}^{-1}$ reported by Piercy and Subrahmanyam (1965) based on absorption data in pure methylcyclohexane. This value is slightly higher than the value of 6.7 to $10.0 \text{ kJ mole}^{-1}$ evaluated by Beckett *et al* (1947) using the specific heat data of gaseous methylcyclohexane. Under these conditions, no agreement better than that obtained need be expected.

The difference in entropy between one mole of axial and equatorial isomers of methylcyclohexane works out to be $19.8 \pm 8.0 \text{ J mole}^{-1}\text{K}^{-1}$. This is in reasonable agreement with the value of $13.4 \pm 2.5 \text{ J mole}^{-1}\text{K}^{-1}$ reported earlier by Piercy and Subrahmanyam. Both these values are higher than the zero value predicted by Pitzer *et al* (1947) theoretically. Since one can effectively rule out the possibility of experimental errors, it is worthwhile studying the theoretical model of Beckett *et al* in detail. However, the authors are not in a position, at present, to offer specific suggestion to effect changes in the model.

The change in free energy ΔG_0 , evaluated using equation (5) is $6.2 \pm 2.0 \text{ kJ mole}^{-1}$. This is in every good agreement with the values of $7.7 \pm 1.0 \text{ kJ mole}^{-1}$ evaluated by Piercy and Subrahmanyam (1965) and the theoretical value of 6.7 kJ mole^{-1} predicted theoretically by Beckett *et al* (1947).

5. Conclusions

Ultrasonic velocity dispersion measurements indicate single relaxation in the frequency range studied for methylcyclohexane. The relaxation parameters derived are in good agreement with those evaluated by Piercy and his coworkers using the ultrasonic absorption measurements.

The present measurements reveal interferometer as a convenient and accurate tool in the study of relaxation phenomena.

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