EFFECT OF TEMPERATURE ON ULTRASONIC ABSORPTION IN ACETIC ACID

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ABSTRACT.—The theory of ultrasonic absorption based on the structural changes in the quasi-crystalline structure of the liquid state has been applied to acetic acid. Variation of maximum absorption frequency with the variation of temperature (20°C to 65°C), as observed by Lamb and Pinkerton, has been explained by this theroy.

In the previous paper (Ghosh and Varma, 1949) we have calculated the values of absorption frequencies in the various unassociated liquids on the assumption of quasi-crystalline structure of the liquid state. The work function A was deduced on the basis of 'hole theory' of viscosity. All the values refer to 300°K. The value 4.87 Mcs. obtained in the case of acetic acid is high because here we had neglected the effect of temperature *viz.*, the value of $\left(\frac{\alpha}{N^2} \times 10^{17}\right)$ sec^2 cm^{-1} = 12,000 which we have taken is a low value for 27°C and moreover dispersion in velocity with temperature was also neglected

It may be pointed out that the work function A given as

$$A = R \frac{TT'}{T'-T} \log \frac{\eta T'}{\eta' T}$$

which depends upon the values of viscosity (η) of the liquid at two temperatures varies with temperature. As defined previously A is the work function required to remove N molecules from the interior of the body to infinite distance. Fig. 1 shows the plot of viscosity (η) against temperature and Table I gives the value of A at the various temperatures ranging from 25°C to 65°C. Fig. 2 shows the plot of work function A (cals/mole) against temperature.

It may be observed from the Fig. 2 that A at first decreases slowly with temperature and a minimum is obtained near about 55°C and it again rises sharply to high values. The variation of A with temperature is represented by $A = A_0 + \gamma (T - T')^2$ where A_0 is the minimum value of A at the corresponding temperature T' and on either side it increases. A_0 = 3228 cals/mole. The rate of increment with regard to the square of the temperature difference, *viz.* γ, is of the order 2 cals/mole per degree centigrade, for temperatures below T'°C and for temperatures above T'°C it

is of the order 2.6 cals/mole to 5 cals/mole per degree centigrade. Further dA/dT is of the order of 9 cals/mole per degree centigrade.

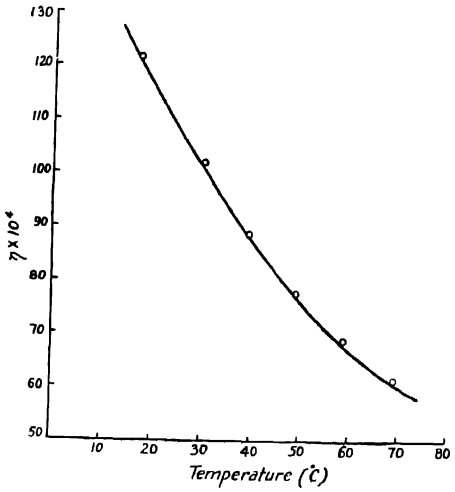

FIG. 1

$\eta \times 10^4$ (Viscosity) plotted against temperature for Acetic Acid. Range of Temp. 20°C–70°C Values of viscosity have been taken from Physical Chemical Constants by Kaye and Laby

TABLE I

S NO	temperature	A cals/mole	C cal deg^{-1} mole^{-1}
1	25°C	3402	2034
2	30°C	3365	·2359
3	35°C	3331	2531
4	40°C	3286	2831
5	45°C	3246	3095
6	50°C	3336	3234
7	55°C	3228	·3414
8	60°C	3295	·3550
9	65°C	3422	·3459

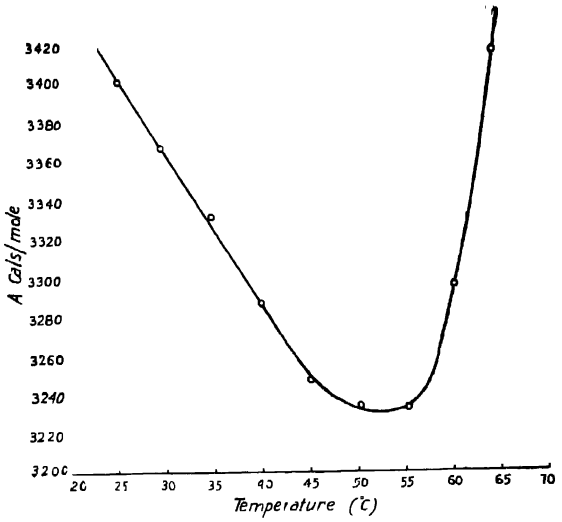

FIG. 2

Work function A cals/mole plotted against Temp for Acetic Acid (20°C 70°C)

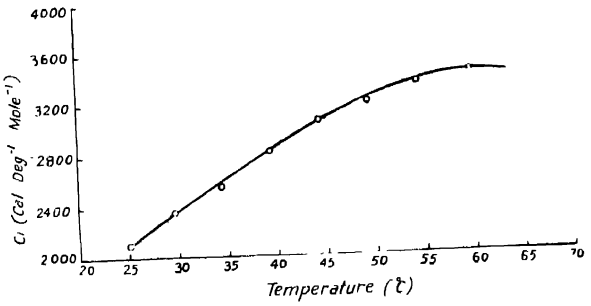

FIG. 3

The corresponding values of internal structural specific heat Ci calculated from the formula $Ci=R\left[\frac{A}{RT}\right]^2 e^{-A/RT}$ where R is the gas constant for the different temperatures are also given in Table I. Fig. 3 shows the plot of C_i against temperature.

The minima of A at 55° C indicates that most of the molecules at this particular temperature are in their equilibrium positions. This will at first sight appear to be wholly inappropriate in the case of a liquid with their characteristic fluidity. But it may be pointed out that the equilibrium positions of the molecule in the liquid body are not absolutely permanent, but have a temporary character for a given molecule After performing more or less large no of oscillations about the same equilibrium position during a certain time T, each molecule can jump to a new equilibrium position. If the time T is large compared with the vibration period, this sporadic change of the equilibrium position cannot affect the magnitude of the specific heat, which is evident from Fig 3 where a plot of C_i against temperature is given in the neighbourhood of 55°C

It may be observed from Fig. 3 that Ci at first increases linearly with temperature and then becomes flat, horizontal near about 60°C, the temperature where minima in A is observed The values of the maximum absorption per wavelength (μ_m) at the absorption frequency (N_m) have been calculated as described in the previous paper. The values of $[\alpha/N^2]$ $N << N_m$ for the various temperatures ranging from 25°C to 60°C have been taken from Pinkerton's paper (1949) Here the dispersion of the velocity with temperature has also been taken into account.

TABLE II

S NO	Temperature	$(\alpha/N^2 \times 10^{17}) N << N_m$ sec^2 cm^{-1}	$C \times 10^5$ cm/spec	$2\mu_m$	N_m(Mcs)
1	25°C	132,000	1.12	.061	13
2	30°C	107,000	1.10	.071	61
3	35°C	88,700	1.08	.076	.80
4	40°C	72,900	1.065	.086	1.10
5	45°C	58,800	1.05	.093	1.51
6	50°C	48,400	1.035	.098	1.94
7	55°C	41,100	1.02	.103	2.00
8	60°C	33,800	.99	.107	3.20
9	65°C	25,000	.97	.104	4.30

Column four in Table 2 gives the values of velocity at different temperatures These have been taken from Lamb and Pinkerton's graph showing the plot of velocity against temperature. The values of the absorption frequencies at the various temperatures are given in the last column. The value for $(\alpha/N^2 \times 10^{17})$ for 65°C is the extrapolated one.

Fig. 4 shows the plot of $\log_{10} Nm$ against temperature reciprocal.

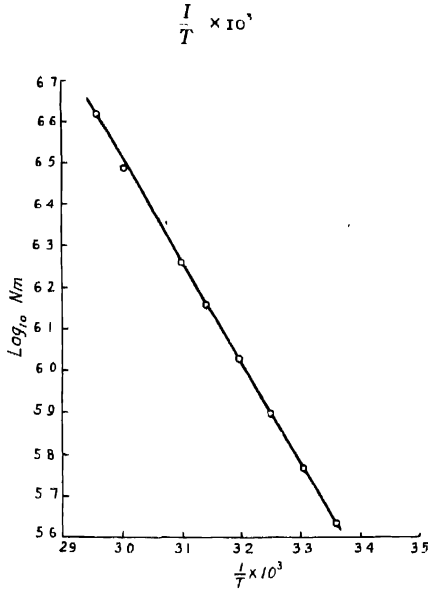

FIG 4

Dependence of $\log_{10} Nm$ against $1/T$, N_m being the absorption frequency

As it is evident from the graph that $\log_{10} N_m$ is a linear function of $1/T$, that is N_m (absorption frequency) is proportional to the factor $e^{-\Delta E/RT}$ where ΔE is the energy required for the creation of extra holes when ultrasonic waves pass through the medium. From the slope of graph of $\log_{10} N_m$ and $1/T$ we find that the value of ΔE comes out to be 8.69 kilocalories. This coincides with the activation energy obtained by Pinkerton.

Thus our theory of ultrasonic absorption in liquids "that the mechanism of absorption in the case of liquids is not entirely due to vibration of atoms, but that the structural changes in the quasi-crystalline state of the liquid molecules play an important part in the absorption of ultrasonic waves and that the phenomenon of absorption and viscosity are all related ones and both can be described in terms of 'hole theory' of liquid state" which has not only been able to explain the absorption and predict the absorption frequencies in most of the liquids successfully but also explains the temperature effect on the absorption frequency as well as on the maximum absorp-

tion per wavelength experimentally obtained by Lamb and Pinkerton in the case of acetic acid.

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