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INFLUENCE OF THE MOLECULAR STRUCTURE ON ACOUSTIC ABSORPTION IN THE GROUP OF SATURATED KETONES

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The results of acoustic investigation into some heterocyclic liquids showed very close relation between ultrasonic absorption and structure of chemical molecules [1, 2, 3].

1. Introduction

Many authors (Bergmann and Jeansch, Parthasaraty, Rao, Lagemann, Schaaffs and Sette) very accurately determined relations between the velocity of ultrasonic waves and liquid molecules structure, but there are no systematic papers concerned with the relationship between the absorption and molecular structure. Three authors only have clasified liquids in relation to the attenuation quantity: Pinkerton, Michajłow and Verma. These approches are not based on the dependences between sound attenuation and molecule structure.

The results of acoustic investigation in many heterocyclic liquids showed very close relation between ultrasonic absorption and the structure of chemical compounds and it was presented in the papers published in Archives of Acoustics [2, 3].

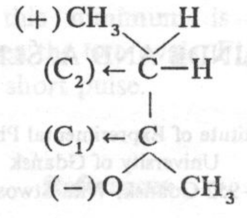
On the basis of own investigation, concerning absorption in cyclic compounds with a carbonyl group, certain strict relation between acoustic absorption and the structure of molecule was also established. In this paper we tried to explain relation as a result of isomeric relaxation.

2. Experiment

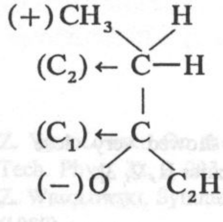
The ultrasonic absorption spectra were measured by the ultrasonic pulse method from 10 to 180 MHz [4] and the ultrasonic velocity was obtained using an ultrasonic pulse-phase interferometer UI-12 [4]. Additional measurements of the viscosity by means of the ultrasound viscosimeter UNIPAN 505 A were performed in order to calculate the classical absorption coefficient. All acoustic measurements were performed in the temperature range from 253 to 313 K with the accuracy of 0.05 K. The temperature was stabilized by a U — 10 ultrathermostat.

The estimated errors of determining the absorption coefficient are contained in the range from 3.5 to 5%.

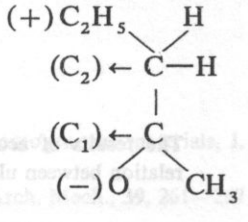
3. Results and discussion



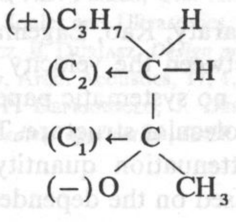
1. Methyl – ethyl ketone



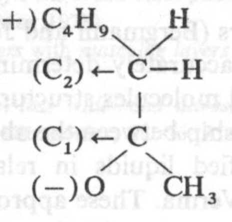
2. Dietyl ketone



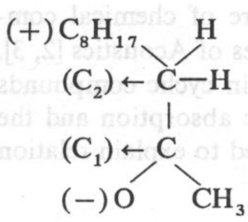
3. Methyl – propyl ketone



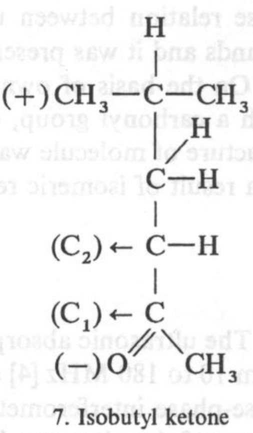
4. Methyl – butyl ketone



5. Methyl – pentyl ketone



6. Methyl – nonyl ketone



7. Isobutyl ketone

Fig. 1. Chemical structures of the measured ketones.

Seven different ketones have been subject to ultrasonic investigations, volume viscosity, classical absorption and thermal coefficients of absorption and ultrasonic velocity of the ketones have been calculated (Table 1 and 2)

$$\left(\frac{\alpha}{f^2}\right)_{kl} = \frac{8\pi^2\eta_s}{3\rho c^3} \qquad \eta_v = \frac{4}{3}\eta_s \frac{\dfrac{\alpha}{f^2} - \left(\dfrac{\alpha}{f^2}\right)_{kl}}{\left(\dfrac{\alpha}{f^2}\right)_{kl}}. \tag{3.1}$$

Table 1

Ketone	$\frac{\alpha}{f^2}\,10^{-15}\,[s^2m^{-1}]$	$\frac{\Delta v}{\Delta T}[ms^{-1}K^{-1}]$	$\frac{\Delta\alpha}{f^2\Delta T}\,[s^2m^{-1}K^{-1}]$	$C[ms^{-1}]$
1	29,0	−5,4	−0,2	1193,6
2	31,9	—	—	1235,5
3	33,0	−3,97	−0,25	1238,1
4	35,4	—	—	1248,5
5	41,6	−4,22	−0,41	1284,4
6	66,0	−2,1	−1,06	1379,6
7	68,2	—	—	1211,4

No relaxation region in all the liquids considered in the measured frequency range exists. The dependence of ultrasonic absorption on the frequency can be described by a linear relation

$$y = ax + b \qquad \text{with } a = 0 \tag{3.2}$$

However, the calculated classical absorption coefficients and volume viscosities (Table 2) suggest that in all compounds the relaxation process should exist [5, 6, 7]. The experimental absorption coefficients are several times higher than the classical ones, and shear viscosity of the ketones are 3 to 8 times lower than the volume viscosity (Table 2).

It is evident that the relaxation times of these processes in the liquids are shorter than 10^{-9} s.

In this group of compounds the relationship between the ultrasonic absorption and the structure of molecules is visible. The absorption increases with increasing the

Table 2

$\left(\frac{\alpha}{f^2}\right) \times 10^{15}\,[s^2m^{-1}]$	Methyl-propyl ketone	Methyl-pentyl ketone
	33.0	41.6
$\left(\frac{\alpha}{f^2}\right)_{kl} \times 10^{15}\,[s^2m^{-1}]$	10.5	5.2
$\rho \times 10^3\,[\mathrm{kG}\,m^{-3}]$	0.809	0.815
$\eta_s \times 10^{-2}\,[P]$	0.62	1.23
$\eta_v \times 10^{-2}\,[P]$	1.77	9.28
$\frac{\eta_v}{\eta_s}$	2.8	7.6

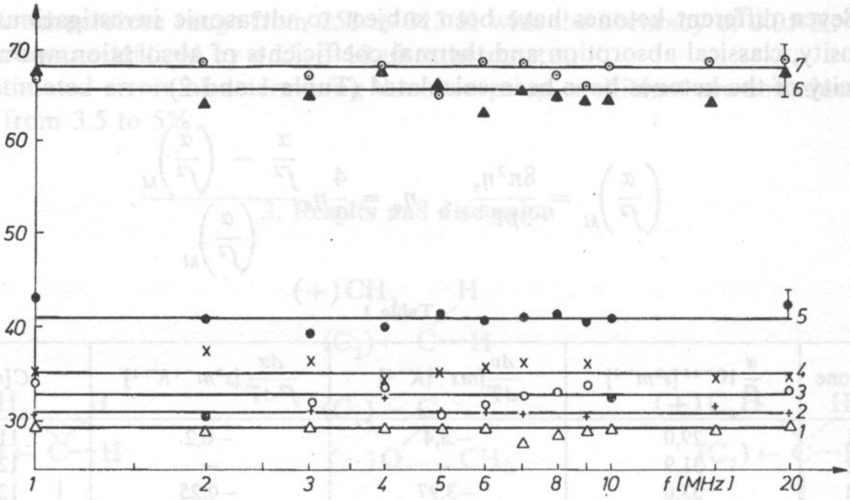


Fig. 2. Ultrasonic attenuation in the group of ketones absorption at 293 K. The numbering of the curves is the same as in Fig. 1.

chain-length of the ketones. This relation is opposite to that observed in heterocyclic compounds (Fig. 2).

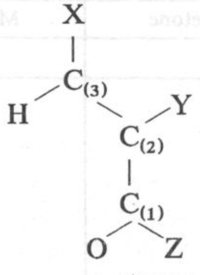
It is not possible to explain the relation in the same way. It means that the absorption is not caused by Kneser processes, and that the Herzfeld formula

$$\left(\frac{\alpha}{f^2}\right)_{\text{rel}} = \frac{\alpha}{f^2} - \left(\frac{\alpha}{f^2}\right)_{kl} = \frac{2\pi^2\tau}{c}\,\frac{C_i\,(C_p - C_v)}{C_p\,C_v} = A \tag{3.3}$$

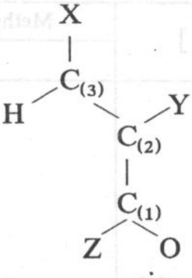
in not useful in that case.

The calculated thermal coefficients of absorption are negative (Table 1), what suggests that the rotational isomerism is responsible for the absorption [6, 8], and for such compounds as it was predicted by Young and Petrauskas [9], the contributions of absorption due to shear viscosity, heat conduction etc. are negligible when compared to the absorption due to rotation of molecules.

In saturated ketones



— trans



— cis

there are no electrical forces and charge-conjugation between π-electrons of double bonds, then rotational barrier around the $C_{(1)}$—$C_{(2)}$ bound is not high. Acoustic absorption is then small and relaxation time shorter than that in unsaturated ketones. The relaxation region is possible in higher frequency range or at lower temperature.

In such compounds as ketones there are effects of electrical attraction between the partially negatively charged oxygen and the partially positively charged $C_{(3)}$. In these compounds the cis-conformation is favoured. The exchange of methyl group for propyl-, etc. grows the quantity of protons (positive charge) close to $C_{(3)}$ and should strengthen the conjugation of the $C_{(1)}$—$C_{(2)}$ bond and hence increase the rotational barrier and acoustic absorption as well what has appeared in the experiment.

4. Conclusion

All the relations founded in saturated ketones are similar for unsaturate ones [6], but because the conjuction is absent, in saturated ketones, the relaxation time is much shorter and the absorption lower for frequency range. These relations for saturated compounds do not manifest so clearly thus it is much more difficult to notice their presence.

References

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