THE ABSORPTION AND VELOCITY OF ULTRASONIC WAVES IN CYCLIC COMPOUNDS AND THEIR MIXTURES

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ABSTRACT

In this paper there is presented the results of acoustic research of velocity and absorption in three pure liquids: thiophene, p-, and m-xylenes and the mixtures of these liquids and CCl_4 with xylenes. The measurements for the mixtures of thiophene were provided by Eggers method at the frequencies between 0.3 and 5 MHz and pure liquids by pulse method in the frequency range between 10 MHz and 10 GHz, all at the temperature of 293.15 K, but for tiophene at 281 & 333 K.

The result of absorption in both thiophene and CCl_4 shows that in the observed relaxation processes, caused by Kneser processes, take part all vibrational degrees of freedom. The process can be described as a vibrationa relaxation with one relaxation time. In the mixtures absorption decreased with increasing the quantity of xylenes, as is predicted by theory for gases and these results suggest that the absorption is probably due to the same phenomenon as in gases.

INTRODUCTION

For many years the authors have been carrying the acoustical investigation of pure heterocyclic liquids [1 – 3]. These results as the investigation of other authors [4 – 6] show that the absorption of propagating ultrasonic wave rapidly goes down when the liquid medium (benzene, pyridine, furane, thiazole etc.) contains the other cyclic or heterocyclic liquids (toluene, picolines, lutidines etc.). First group of compounds has a great acoustical absorption and a long relaxation time. For the second one the absorption is much lower and the relaxation times about ten times shorter.

Many researches have been engaged in the problem of energy migration between the vibrational levels of different molecule of two gases [7, 8], as well as for liquids [9 – 11], and ultrasonic wave. It leads to faster deactivation of acoustically active internal degrees of freedom.

The results obtained from the acoustic research, the structure of vibrational levels of the molecules and their activity in exchange of energy between translational-vibrational and vibrational- vibrational degrees of freedom as well as the results of gas mixture research, suggest the possibility of observation a transition between the vibrational levels of two different liquid molecules existing in the mixture of two liquids, and the propagating ultrasonic waves.

This way we can observe changes in the deactivation process of acoustically active vibrational degrees of freedom and it is possible to notice shortening of the acoustical relaxation time caused by taking the energy from liquid molecules, which have a longer relaxation time by the molecule having the shorter one. Certainly, such a migration of energy could be possible only between the vibrational levels of two molecules A & B for which energies will be similar $E_A \approx E_B$.

It was observed earlier that some substances, admixed even in small quantities, have a very marked effect on the absorption and dispersion of ultrasonic waves as well as in gases and liquids. General consideration of such an effect were made by Eucken and Becker [12] for gases and Pinkerton [5], Bauer [4] and Sette [10] for liquids at low frequency range.

EXPERIMENTAL METHODS AND RESULTS

The acoustical measurements velocity and attenuation coefficient, in low frequency range 0,3 to 5 MHz, were carried out by Eggers method which has been already described in earlier papers [13] and pulse method for the frequency range from 20 to 30MHz for the measurement of mixtures and from 10 MHz to 10 GHz for pure liquids [2, 14]. The measurements were made at 293 K for two mixtures of thiophene with m- & p-xylenes and in the range of 280 – 333K for pure liquids. The accuracy for the velocity measurements was 0.1 percent and for the absorption 5 percent for the method of Eggers and 0.05% and 3% for pulse method. The temperature of the solutions was controlled to within 0.1 K with ultra-cryostat MK 70.
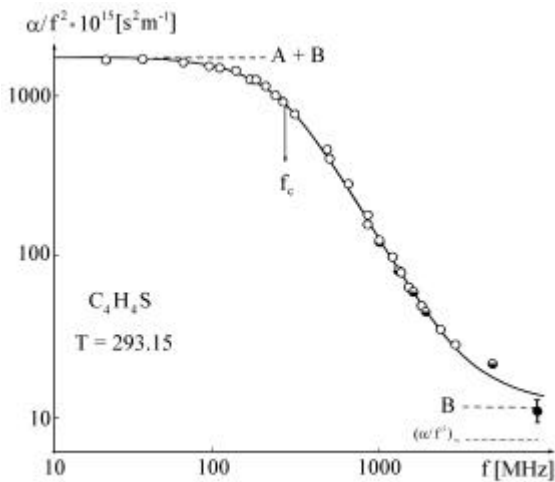
The results of the investigation are presented in Figs. 1. – 2. The first correspond to pure liquids and shows typical relaxation curve.

The dependence of absorption of ultrasonic waves in function of mole fraction in the mixtures is presented in fig. 1. In all the cases there were a very rapid decrease of in α as the proportion of the less absorbing liquid was increased. Further increases in the proportion of the later had progressively less effect. The acoustical velocity in function of concentration has a linear dependence (Fig. 2).
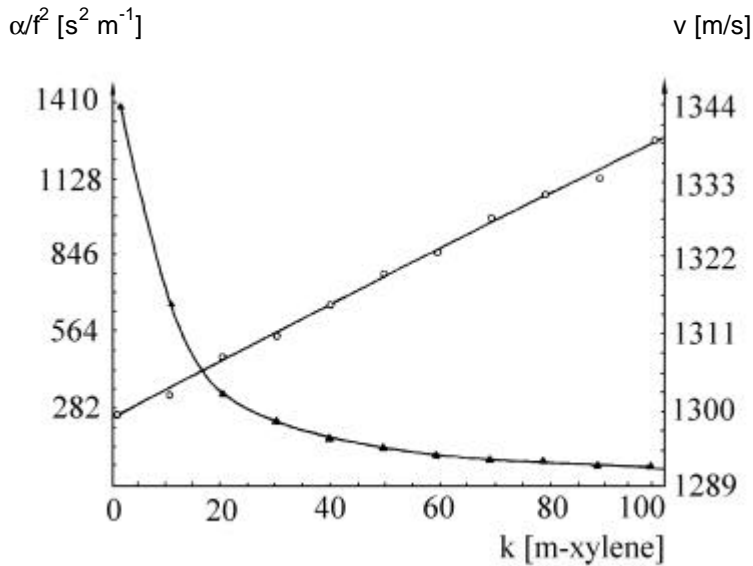

Fig. 1. Curves representing acoustic relaxation process in carbon disulphide at 293,15 K.

α/f² [s² m⁻¹]   v [m/s]

$\alpha/f^2\ [s^2\ m^{-1}]$ $v\ [m/s]$

Fig. 2.
Dependence of ultrasound absorption and velocity on mole concentration of m-xylene in thiophene.

RELAXATION PROCESS

In the case of acoustic relaxation $\alpha/f^2(f)$ absorption curve can be described as follows:

$$\frac{\alpha}{f^2} = \frac{A}{1+\omega^2\tau'^2} + B \qquad (1)$$

where:

A & B are constants (shown in the Fig.1.).

For Kneser relaxation process, e.g. exchange of energy between transaltional and vibrational degrees of freedom, equation (1) has the form [15]:

$$\frac{\alpha}{f^2} \approx \frac{2\pi^2}{c_o} \frac{R'C_i}{C_v(C_p - C_i)} \frac{\tau'}{1+\omega^2\tau'^2} \qquad (2)$$

where:

C_v & C_p – specific heats at constant volume and pressure, C_i - specific heat of vibrational degrees of freedom, c_0 – ultrasonic velocity for low frequency and $\tau' = \tau\,(C_p - C_i)/C_{p,}$.

In the low frequency range it can be rearranged giving:

$$A \approx \frac{2\delta^2}{c_o} \frac{(C_p - C_v)\,C_i}{C_vC_p}\,\hat{o} \qquad \& \qquad C_{i\,acoust.} \approx \frac{Ac_0}{2\pi^2} \frac{C_p\,C_v}{C_p - C_v}\,\hat{o}_{acoust.} \qquad (3.a,b)$$

But, the contribution of molecules vibration to the specific heat may be calculated from the vibrational energies distribution (frequencies ν_i) using Planck – Einstein formula:

$$C_{i\,opt} = R \sum_i g_i \left(\frac{h\nu_i}{kT}\right) \frac{\exp(-h\nu_i/kT)}{[1-\exp(-h\nu_i/kT)]^2} \qquad (4)$$

where:

      g - degree of degeneration, ν_i - frequency of the "i" vibration mode, T - temperature,

      h - Planck's constant, k - Bolzmann's constant

Comparison of the values $C_{i\,opt}$ and $C_{i,\,acoust.}$ calculated from Herzfeld formula (3) gives a possibility to decide which vibrational degrees of freedom take part at the observed relaxation process.

DISCUSSION

From the relaxation curve presented in the Fig. 1 it is possible to determine the relaxation time. The relaxation is caused by energy transfer between translational and vibrational degrees of freedom, and all these degrees take part in the process observed. The values of calculated specific heats $C_{i\,acoust.}$ and $C_{i\,opt.}$ For different temperatures as well as the temperature dependence of absorption and relaxation time are the evidence of the conclusion that it is Kneser process (energy transfer between translational and vibrational degrees of freedom).

Theoretical calculations of the probability of the vibrational-translational (VT) transition in multiatomic liquids have till now presented quite a lot difficulties. Nonetheless, the character of this dependence upon temperature can serve as an indirect argument for the concept of vibrational relaxation presented in many papers [15 – 17].

The concentration dependence of $(\alpha/f^2)_O$ in Fig.2 might be explained with the theory proposed by Sette [10]:

CONCLUSION

The observed acoustic relaxation process is caused by TV processes and can be described by one relaxation time and in this process take part all vibrational degrees of freedom. The result is in contrary to this obtained by Takagi at all. [6] who decided that observed process posses two relaxation times. The apparatus they have used had a possibility to measure to 400 MHz only, and probably the frequency range was to narrow to obtain correct value of the time.

The results of acoustical measurements of absorption coefficient as a function of mole fraction show that the transfer of energy (de-excitation of a molecule) is more probable between two different molecules than with a molecules of the same species.

From this experimental results it can be concluded that transfer of energy happens during the collision between the vibrationally excited molecule of thiophene and not excited of a xylene one. From values of vibrational degree of freedom it is possible to conclude that here, may occur a rapid near resonant vibration-vibration transfer [9] between the lowest fundamental

mode of thiophene (ν_1 = 452 cm^{-1}) and the mode (ν_6 = 459 cm^{-1}) of p-xylene for thiophene - p-xylene mixture and between the mode (ν_1 = 452 cm^{-1}) of thiophene and (ν_5 = 421 cm^{-1}) of m-xylene for thiophene - m - xylene mixture.

Fig.3.

Energy level diagram representing probably V-V & V-T relaxation process for vibrationally excited thiophene in the mixture with m- and p – xylenes. The stars indicate double degeneracy. The arrows between levels indicate near resonant intermolecular V-V transfer [27], the arrows down-direction V-T transfer: $\tau_{thiophene}$ = 620 ps, $\tau_{m,V-T}$ and $\tau_{p,V-T}$ < 20 ps. The frequencies beyond 2000 cm^{-1} can be negligible and they are not presented in this figure.
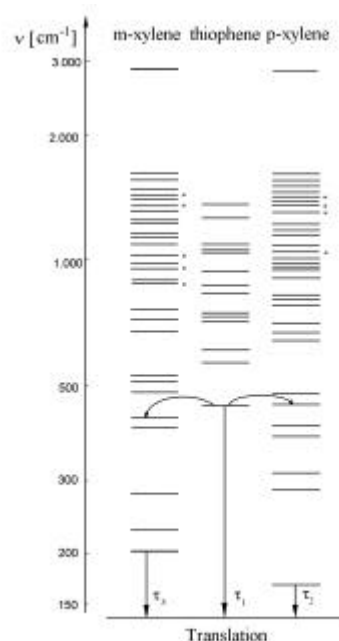
Intermolecular V - V transfer between higher modes would be negligible, since higher modes have smaller contribution to vibrational specific heat, it can be calculated theoretically from Einstein Planck formula (4).

The intramolecular V -V transfers in series from e.g. 459 cm^{-1} mode to the lowest mode of p-xylene (170 cm^{-1}) are expected to occur very quickly compared with the V-T transfer of the lowest modes of thiophene. Consequently, the vibrational energy of thiophene transferred to translational energy via two path: the V-T transfers, and the intermolecular V-V transfer followed by the V-T transfers. The latter path would be much faster than the former Fig.3. Similar situation is for the second mixture of thiophene as well as for CCL4 and xylenes mixture [11].

In the other case, if there is no such a transfer, the relaxation time of this acoustical process will be longer (the relaxation time of thiophene is 500 ps), but the times of xylenes are less than 20 ps, [2] and the absorption coefficient much higher, and there would not be so big influence of the impurities for the acoustical absorption.

Decrease in absorption - equivalent to relaxation frequency decreasing - shortening of the relaxation time - of highly-absorbing component is shown to be caused by the intermolecular V-V energy transfer. In binary mixtures then of highly-absorbing and low-absorbing fluids, in general, the decrease in absorption coefficient with the addition of low-absorbing liquids would be explained by intermolecular V-V energy transfer in the collision process between two different molecules. Similar results were obtained in the investigation of shortening of phosphorescence time in some binary mixtures [18]. From this research we can see that it is not so important to have the mixture of two cyclic or heterocyclic compounds or the other, but it is important to take the liquids with absorption caused mainly by Kneser effect.

For more clear interpretation it is necessary to provide acoustical investigation for higher frequency range which the characteristic relaxation frequency will be in the range of measurement frequency, for all mixtures.

ACKNOWLEDGEMENTS

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