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THE ABSORPTION OF ULTRASONIC WAVES IN THE MIXTURES OF KNESER LIQUIDS

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Measurement of the absorption and velocity of ultrasonic waves in the mixtures of thiophene with m-. and p-xylenes were made by Eggers method of the frequencies between 0.3 and 5 MHz and temperature 293 K and carbon tetrachloride with o-, m- and p-xylenes by pulse method in the frequency range 20–30 MHz. The 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 the gases. In measured frequency range is any dispersion region.

1. Introduction

For many years I have been carrying the acoustical investigation of pure heterocyclic liquids [16, 17]. These results and the investigation of other authors [3, 21, 24] show that the absorption of propagating ultrasonic wave rapidly goes down when the liquid medium (benzene, pyridine, thiophene, furane, thiazole etc.) contains the other cyclic or heterocyclic liquids (xylenes, picolines, lutidines etc.). First group of compounds has a great acoustical absorption and long relaxation time. For the second one the absorption is much lower and the relaxation times is about ten times shorter.

Recently many researches have been engaged in the problem of energy migration between the vibrational levels of different molecule of two gases, and ultrasonic wave [2]. It leads to faster deactivation of acoustically active internal degrees of freedom.

The results obtained from my acoustical research (the structure of vibrational levels 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. 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 and B for which energies will be similar $E_A \approx E_B$.

It was observed ealier 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 [10] for gases and Pinkerton [21], Bauer [3] and Sette [24] for liquids at low frequency range.

2. Experimental methods and results

The acoustical measurements of velocity and attenuation coefficient were carried out by Eggers method which has been already described in earlier papers [9, 18] and pulse method for the frequency range from 20 to 30 MHz [29, 15]. The measurements were made at 293 K in the frequency range from 0.3 to 5 MHz for two mixture of thiophene with m- and p-xylenes and from 20 and 30 MHz for the mixtures of carbon tetrachloride (CCl_4) and o-, m- and p-xylenes. 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 [15]. The temperature of the solutions was controlled to within 0.1 K with ultra-cryostat MK 70.

The absorption of ultrasonic waves in the mixtures are presented in Figs. 1, 2, 3, 4 and 5. In all the cases there were a very rapid decrease 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 (Figs. 1, 2, 3, 4 and 5).

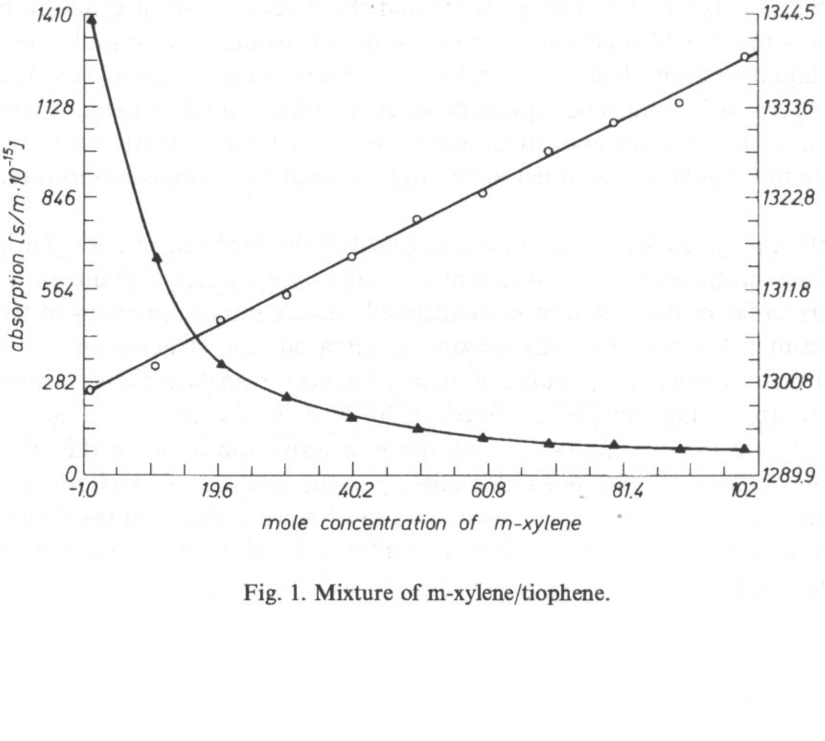

Fig. 1. Mixture of m-xylene/tiophene.

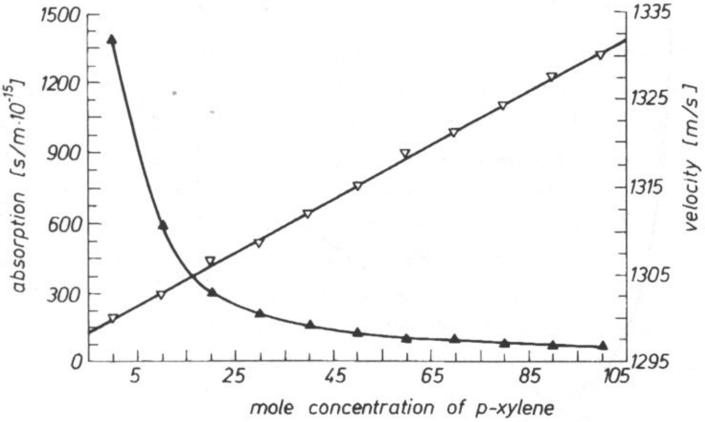

Fig. 2. Mixture of p-xylene/tiophene.

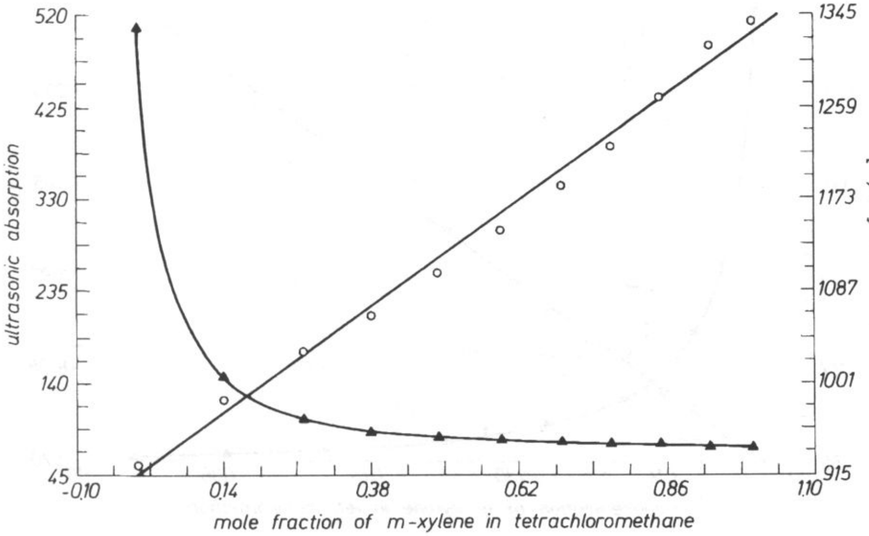

Fig. 3. The velocity and absorption versus concentration of m-xylene at the frequency of 30 MHz.

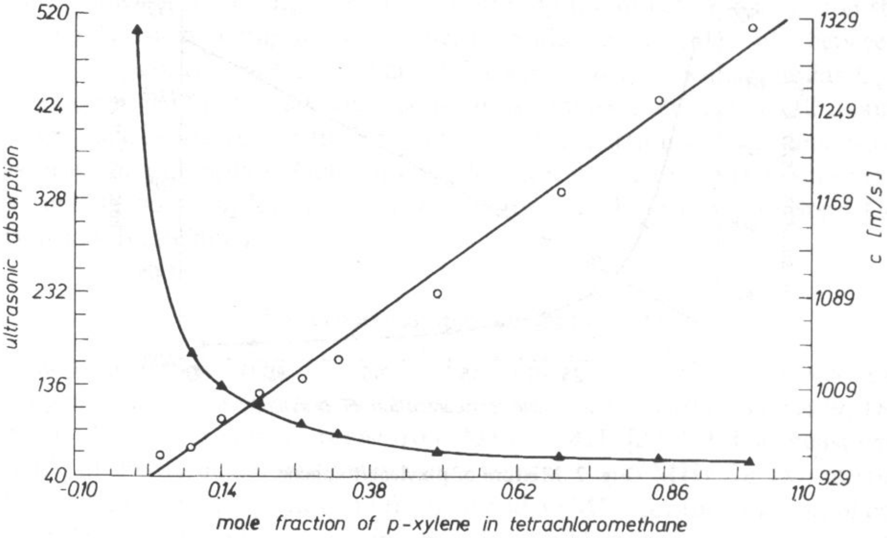

Fig. 4. The velocity and absorption versus mole fraction of p-xylene in tetrachloromethane at the frequency of 20 MHz.

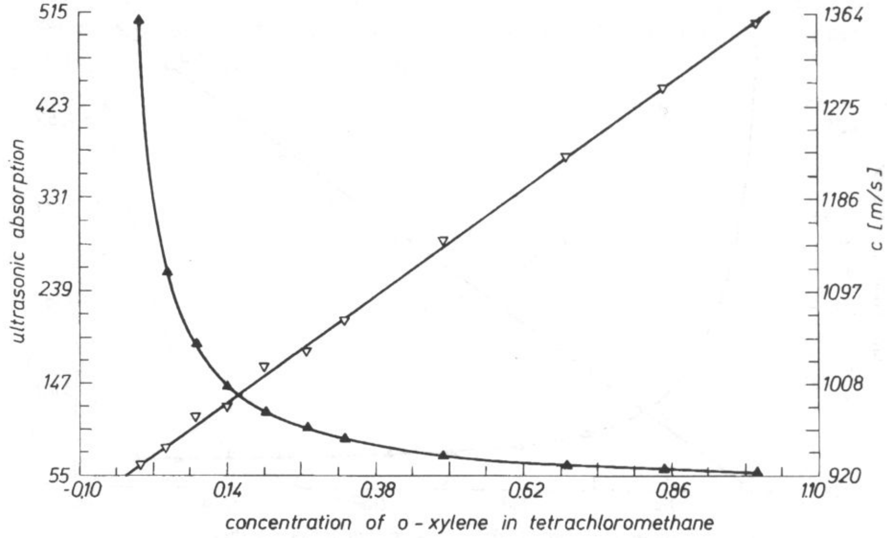

Fig. 5. The velocity and absorption versus mole fraction of o-xylene in tetrachloromethane at the frequency of 30 MHz.

3. Binary mixture of two Kneser liquids

It is already very well known that in case of gases small traces of impurities may have an extremely large effect on the absorption. A similar effect has been found in a number of liquids like carbon disulphide, benzene [11b], dichloromethane, [12] where the absorption falls very rapidly when a small quantity of a less absorbing liquid is added to one of high absorption. Pinkerton and Bauer has shown that this effect can be explained on a very simple relaxation picture. This basic ideas yield results which are in good agreement with experiment.

Let us consider the binary mixture: a mixture of liquids *A* (strongly absorbing) and B (other one) the equilibrium between the energies is associated with internal and external degrees of freedom is set up by collisions. „*A*" has a much smaller frequency than „*B*", so that an *A* molecule, once excited, has a much smaller chance of deexcitation than an excited *B* molecule. For simplicity in the analysis it will be assumed that only binary collision need be considered and that collision between

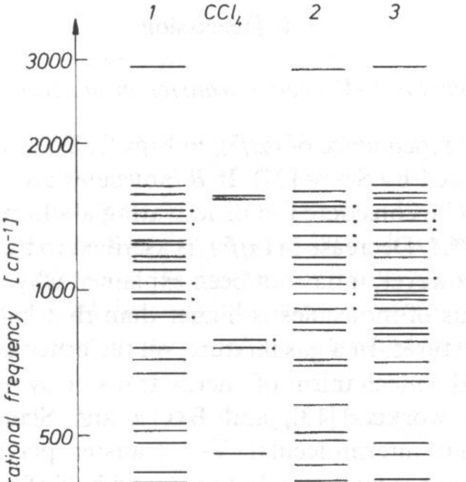

Fig. 6. Energy level diagram representing probably V-V and V-T relaxation process for vibrationally excitated CCl_4 in the mixture with o- (2), m- (1), and p-xylenes (3), as represented by eqs. a, b, c. The dots indicate double degeneracy. The arrows between levels indicate near resonant intermolecular V-V transfer [27], the arrows down-direction V-T transfer. $\tau_{CCl,\ V\text{-}T} = 126$ ps, $\tau_{1,\ V\text{-}T}$, $\tau_{2,\ V\text{-}T}$, $\tau_{3,\ V\text{-}T} < 20$ ps. The frequencies beyond 2000 cm^{-1} can be negligible and they are not presented in this figure.

excited molecules may be neglected. A and A^* represent an unexcited and excited A molecule respectively, and similary for B and B^*. In this mixture an (A, A^*) collision is much less efficient than $a(B, B^*)$ collision because τ_B is much shorter than τ_A. In such a mixture it is possible to define four relaxation times as follows: τ_{AA} and τ_{BB} are the relaxation times for collisions between similar molecules of type A and B respectively τ_{AB} is that for collision of excited type A with deexcited B, and τ_{BA} that for colisions of excited B with deexcited A. Since the absorption in A is much greater than in B we can assume $\tau_{AA} > \tau_{AB}$ and write $\tau_{AB} = \tau_{BA} = \tau_{BB}$. The reason for this is that if molecule of type B possess a stronger mutual interaction, the interaction between A and B molecules may well be of the same order as between two molecules of B, and may expected to be much greater that the mutual interaction between molecules of type A. Thus, as the concentration of B molecules increases, the net efficiency of all collision tands rapidly to the value corresponding to the liquid B, so that the absorption falls sharply, and we can see it in the Figs. 1 to 5.

4. Discussion

4.1. V-T and intermolecular V-V energy transfer in mixture

The concentration dependence of $(\alpha/f^2)_0$ in Figs. 1, 2, 3, 4 and 5 might be explained with the theory proposed by SETTE [24]: If B molecules are mixed with A molecules, the binary collision to be considered in deactivating a vibrationally excited molecule A^*A, A^*B, B^*B and B^*A. Decrease in $(\alpha/f^2)_0$ is ascribed to the high efficiencies of A^*B and B^*A collisions. However, it has not been explained why the efficiency of collision between different kinds of molecules is higher than that between the same kinds of molecules in liquid mixtures. In a gas mixture, on the other hand, many workers have investigated in detail the mechanism of energy transfer by molecular collisions [1, 7, 28]. LAMBERT and co-workers [13], and BAUER and SCHOTTER [4] showed using ultrasonic method that intermolecular V-V transfer plays an important role in vibrational relaxation in gas mixtures. In the second half of seventieth, intermolecular V-V transfer was observed with laser-excited vibrational relaxation study in gas [6] and liquid [5, 14] mixtures. These works shown that the energy transfer by the colision between different kinds of molecules involves two process: vibrational-translational (V-T) and intermolecular vibrational-vibrational (V-V) energy transfers. The interpret the decrease in absorption and relaxation frequency in mixture system, these two processes must be taken into account.

It is assumed that binary collision process is responsible for the vibrational energy transfer in liquid, as was made for the gases. This assumption has been verified experimentally by MADIGISKY and LITOVITZ [10], CALAWAY and EWING [5], and theoretically by DAVIS and OPPENHEIM [8]. Let A the highly-absorbing liquid (thiophene or carbon tatrachloride) and B the low-absorbing (xylenes), that is the relaxation frequency of A is lower than that of B. The possible processes for V-T transfer are:

a) $$A^*+A \underset{k'_{AA}}{\overset{k_{AA}}{\Leftarrow\Rightarrow}} A+A$$

b) $$A^*+B \underset{k'_{AB}}{\overset{k_{AB}}{\Leftarrow\Rightarrow}} A+B$$

c) $$B^*+B \underset{k'_{BB}}{\overset{k_{BB}}{\Leftarrow\Rightarrow}} B+B$$

d) $$B^*+A \underset{k'_{BA}}{\overset{k_{BA}}{\Leftarrow\Rightarrow}} B+A$$

where k_{AA} is the forward rate constant in A^*A collision and the other symbols have a similar meaning. In these processes, each molecule is assumed to have two vibrational states, ground state and excited one, which includes all the vibrational modes responsible for the relaxation. The process for intermolecular V-V transfer is:

e) $$A^*+B \underset{k'_{v}}{\overset{k_{v}}{\Leftarrow\Rightarrow}} A+B^*$$

If the vibrational quanta in the two molecules are not equal, the energy different is exchanged with translational energy. In pure liquid of A, the relaxation frequency is proportional to the rate constant k_{AA}. In mixtures, the increase in relaxation frequency of A indicates that process (b) or (e) is faster than (a). Process (c) and (d) are indirectly related through (e) to the relaxation frequency of A.

Herzfeld and Litovitz [11a] discussed the concentrations dependence of relaxation frequency of A using processes (a) — (e) and obtained the equation for small X:

$$f_r=\frac{1}{2\pi}\{k_{AA}(1-X)+k_{AB}X+[k_v k_{BA}X+k_v(k_{BB}-k_{BA})X^2]^* \tag{4.1}$$

$$^*[k'_v+k_{BA}-(k'_v+k_{BA}-k_{BB})X]^{-1}\}$$

Here X is the mole fraction of B molecules, and f_r is the relaxation frequency for specific heat. A. Monkevicz [20] applied Eq. (4.1) to methane-water mixtures in vapour to get the rate constant k. The equation can also be applied to liquid mixtures as for the binary collision theory is valid.

5. CONCLUSION

The results of acoustical measurements of absorption coefficient as a function of mole fraction show that that transfer energy (the deexcitation of a molecule) is more probable between two different molecules than with molecules of the same species. It is possible that transfer of energy happens during the collision between the vibrationally excited molecule of thiophene and not excited of a xylene one. From the table of vibrational degree of freedom [25], (Table 1) it is possible to conclude that here, may occur a rapid near resonant vibration-vibration transfer [26] between the lowest fundamental mode of thiophene ($\nu_1=452$ cm^{-1}) and the made ($\nu_6=495$ cm^{-1}) of p-xylene for thiophene — p-xylene mixture and between the made ($\nu_1=452$ cm^{-1}) of thiophene and ($\nu_5=421$ cm^{-1}) of m-xylene for thiophene — m-xylene mixture.

Table 1. Several main vibrational frequencies of thiophene, p- and m-xylenes [25]

p-xylene	Thiophene	m-xylene
(1) 170	(1) 452	(1) 205
(2) 290	(2) 567	(2) 230
(3) 313	(3) 606	(3) 279
(4) 386	(4) 690	(4) 404
(5) 405	(5) 712	(5) 421
(6) 495	(6) 749	(6) 484
(7) 489	(7) 834	(7) 517
(8) 645	(9) 868	(8) 538
(9) 671	(10) 905	(9) 679
(10) 702	(11) 1021	(10) 726
(11) 793	(12) 1032	(11) 770
(12) 810	(13) 1082	(12) 882
(13) 829	(14) 1253	(14) 910
(14) 936	(15) 1358	(15) 970

Table 2. Main vibrational frequencies of CCl_4 and several f_V for o-xylene [23]

CCl_4	o-xylene
(1) 218	(1) 179
(2) 314	(2) 211
(3) 459	(3) 257
(4) 762	(4) 406
(5) 768	(5) 434
(6) 790	(6) 486
(7) 797	(7) 506
(8) 1539	(8) 582
(9) 1550	(9) 700

From the acoustical results and spectroscopic data, Table 2. [23] and Fig. 6 it is possible to conclude that for the mixtures of CCl_4 and three isomers of xylenes the most probable transfer energy V-V could realise via $\nu_{1\mathrm{CCl}}\rightarrow\nu_{2-\mathrm{oX}}$; $\nu_{1\mathrm{CCl}}\rightarrow\nu_{1-\mathrm{mX}}$ and $\nu_{2\mathrm{CCl}}\rightarrow\nu_{3-\mathrm{pX}}$.

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 [15]). The intermolecular V-V transferr in series from e.g. 495 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 (a), (b), and the intermolecular V-V transfer (e) followed by the V-T transfers (c), (d). The latter path would be much faster than the former one. Similar situation is for the second mixture of thiophene as well as for carbon tetrachloride and xylenes mixture.

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 CCl is 126 ps [22], and the thiophene's one even 500 ps [27], but the times of xylenes are less than 20 ps, [15]) 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 components is shown to be caused by the intermolecular V-V energy transfer. In binary mixtures than 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 [6]. From this research we can see that it is so important to have 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 for which the characteristic relaxation frequency will be in the range of measurement frequency.

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