THERMAL RELAXATION PROCESSES IN SOME ORGANIC LIQUIDS

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Measurements of propagation velocity and absorption coefficient of acoustic waves in some organic liquids have been made for frequencies between 10^6 Hz and 5×10^9 Hz at 20°C. On the basis of the data obtained the problem of thermal relaxation in liquids examined has been discussed. It was found that this process cannot be described by the relaxation time, which means that at a given frequency only some of internal degrees of freedom undergo excitation. Tests have been undertaken aimed at estimating which of the said degrees of freedom take an active part in the process of energy exchange.

Amongst many relaxation processes which occur during the propagation of an acoustic wave an essential role is played by that of thermal relaxation. While considering this process the assumption is very frequently made that it is characterized by one time of relaxation, which means that all external degrees of freedom undergo excitation simultaneously. This, however, is only a rough approximation.

In this paper, on the basis of the measurement of the propagation velocity of ultra- and hypersonic waves, the problem of thermal relaxation in some organic liquids will be discussed.

The following considerations will be true in the case when only one thermal relaxation occurs in the liquid.

It is assumed that the relaxation process is related to the energy exchange between the internal and external degrees of freedom. Assuming only one relaxation time it can be shown [2] that

$$\tau = \frac{2a_{\eta'} v_0 c_p (c_v - c')}{c'(c_p - c_v)} \tag{1}$$

and

$$\left(\frac{v_\infty}{v_0}\right)^2 = \frac{\varkappa_\infty}{\varkappa_0}, \tag{2}$$

where τ means the time of relaxation, $a_{\eta'}$ — absorption coefficient due to shear viscosity, v_0, v_∞ — velocities of acoustic wave, correspondingly to very low and very high frequencies,

$$\varkappa_\infty = \frac{c_p - c'}{c_v - c'}; \quad \varkappa_0 = \frac{c_p}{c_v},$$

c_p — molecular heat at constant pressure, c_v — molecular heat at constant volume, c' — molecular heat relative to internal degrees of freedom.

In addition, the relaxation time can be determined by experimental methods from measurements of the dispersion of the sound velocity. Namely [4]

$$\tau = \frac{A + (A^2 - 4\omega^2)^{1/2}}{2\omega^2}, \tag{3}$$

where $A = (\omega^2 \eta_0')/(v^2 - v_0^2)$, η_0' means static coefficient of volume viscosity, $\omega/2\pi$ — frequency of acoustic wave.

Measurements of the propagation velocity and absorption coefficient of hypersonic waves were made using the Mandelsztam-Brillouin dispersion effect. The measuring accuracy is 0.5%; absorption coefficient — approx. 20%. Within the ultrasonic range the measurements were made with the aid of an ultrasonic interferometer UI-10.

The results of measurements and calculations for the liquids examined are shown in Table 1. The $\varkappa_\infty/\varkappa_0$ values of specific heats necessary for the

Table 1. Calculated and measured values of the ratio v_∞/v_0 and relaxation times τ

Substance	c_p $\left[\dfrac{J}{\text{mol deg}}\right]$	c_v $\left[\dfrac{J}{\text{mol deg}}\right]$	c' $\left[\dfrac{J}{\text{mol deg}}\right]$	$\dfrac{\varkappa_\infty}{\varkappa_0}$	$\left(\dfrac{v_\infty}{v_0}\right)^2$	$\tau_0 \times 10^{10}$ [s]	$\tau_T \times 10^{10}$ [s]
Benzene	134.9	93.0	51.7	1.40	1.21	2.72	1.38
Carbon tetrachloride	129.0	87.1	49.7	1.42	1.24	0.78	0.57
Chloroform	83.8	77.5	32.7	1.25	1.09	2.27	0.61
Toluene	155.0	113.2	71.3	1.46	1.07	0.69	0.11
Methylene chloride	101.0	65.3	18.0	1.13	1.03	17.1	5.0
Methylene bromide	98.5	71.2	22.2	1.15	1.22	1.1	1.5
Chlorobenzene	161.3	118.0	66.6	1.33	1.12	0.68	0.26
Bromobenzene	155.2	117.2	64.5	1.30	1.10	0.84	0.14

calculation of this ratio are taken from [5]. Specific values of the internal degrees of freedom are evaluated from the formula

$$c_i' = d_i \frac{R\left(\dfrac{h v_i}{kT}\right)^2}{e^{\frac{h v_i}{kT}}\left(1 - e^{-\frac{h v_i}{kT}}\right)^2}, \tag{4}$$

where d_i means multiplication factor of degeneration at given frequency, ν_i — vibration frequency of degree i of freedom, R — gas constant, h — Planck constant, k — Boltzmann constant, T — absolute temperature.

Column 6 contains the experimental value of the ratio v_∞/v_0. In column 7 the relaxation time τ_0 as is given evaluated from the measurement of the dispersion of the sound velocity, while in column 8 the relaxation time τ_D calculated on the basis of formula (1). A considerable divergency between the times of relaxation τ_D and τ_T as well as the ratio $(v_\infty/v_0)^2$ and $\varkappa_\infty/\varkappa_0$ is evident.

Except for methylene bromide the experimental value v_∞/v_0 is in all cases smaller than the theoretical one. Hence, it can be concluded that within the examined frequency range of the acoustic wave only some of internal degrees of freedom participate in the energy exchange process with internal degrees of freedom or, to put it in another way, the relaxation times of various internal degrees of freedom are different.

It is expected that, first of all, the excitation affects the degrees of freedom with lowest frequency since the likelihood of their excitation is the highest. With very low frequency of acoustic wave the state of equilibrium is established. All internal degrees of freedom participate in the energy exchange process with external degrees of freedom. Namely, the time of equilibrium stabilization is shorter than the acoustic wave period. For higher frequencies of the acoustic wave the state of equilibrium can be achieved only for those external degrees of freedom, for which the time necessary to produce the oscillatory quantum and the time within which it is again transformed into the translating energy; thus the relaxation time is smaller than the acoustic wave period. This condition can be satisfied primarily for those internal degrees of freedom for which the least amount of energy for excitation is necessary, whereas the remaining degrees of freedom, if they undergo excitation at all, will not manage to transfer their energy into the translatory motional energy.

For higher acoustic wave frequencies the internal degrees of freedom, commencing from those for which the excitation energy is the largest, undergo «freezing», since the time necessary for their excitation is longer than the acoustic wave period. When the latter becomes very small, that is, when we go on to very high frequencies, all degrees of freedom undergo «freezing» and the specific heat of the substance is reduced. Having this in mind tests have been performed to ascertain which of degrees of freedom participate in the energy exchange process.

Thus, if v_∞ and v_0 are measured, c' can be evaluated from the formula

$$\left(\frac{v_\infty}{v_0}\right)^2 = \frac{(c_p - c')c_v}{(c_v - c')c_p},$$

c' will be designated in the following text as c_{ak}, since it can differ from the specific heat of internal degrees of freedom calculated from spectroscopic data.

The velocity v_0 measured at the frequency 10^6 Hz, the velocity v_∞ — at the frequency 5×10^9 Hz. Evaluating c_{ak} we have

$$c_{ak} = \frac{\left[1 - \left(\dfrac{v_0}{v_\infty}\right)^2\right] c_p}{\varkappa_0 - \dfrac{v_0^2}{v_\infty^2}}. \tag{5}$$

It can be seen from Table 2 that for all liquids except for methylene bromide the value of the molar heat calculated from spectroscopic data is higher than that of the molar heat obtained from acoustic measurements. It only supports the earlier suggestion that the relaxation times of various internal degrees of freedom are different, which means that at a given frequency of the hypersonic wave only some of the internal degrees of freedom participate in the process of energy exchange.

Table 2. Values of specific heats c_{ak} and c' for examined liquids

Substance	c_{ak} $\left[\dfrac{J}{mol\,deg}\right]$	c' $\left[\dfrac{J}{mol\,deg}\right]$
Benzene	37.5	51.7
Carbon tetrachloride	37.0	49.7
Chloroform	15.9	32.7
Toluene	23.1	71.3
Methylene chloride	11.3	18.0
Methylene bromide	27.2	22.2
Bromobenzene	33.5	64.5
Chlorobenzene	37.7	66.6
Nitrobenzene	37.7	65.7

To have more insight into the problem, let us consider in greater detail the vibration of molecules. Table 3 contains frequencies and corresponding specific heats of internal degrees of freedom of the benzene molecule. The values of vibration frequencies are taken in all cases from papers [1, 3].

The comparatively best agreement with experiment is obtained when vibrations belonging to the same class of symmetry are grouped. Vibrations v_1, v_3, v_5, v_7, v_{10}, v_{11}, v_{14}, v_{15}, v_{16}, v_{17}, and v_{20} belong to the class type E. The value of specific heat of these internal degrees of freedom is 36.45 J/mol deg. Vibrations v_2, v_6, v_9, v_{12} and v_{18} belong to the symmetry class type B, while vibrations v_4, v_8, v_{13} and v_{19} to the symmetry class type A. Corresponding values of specific heats are 9.95 J/mol deg and 5.57 J/mol deg, respectively.

If we assume that the calculated relaxation time $\tau = 2.7 \times 10^{-10}$ s is related to the excitation of vibrations belonging to the symmetry class type E, then the value $c_{ak} = 37.5$ J/mol deg is very close to that of the specific heat for these

Table 3. Values of vibration frequencies v_i and specific heats c_i' of internal degrees of freedom for benzene

v	$v_i \times 10^{-12}$ [s^{-1}]	d_i	c_i' $\left[\dfrac{J}{\text{mol deg}}\right]$	v	$v_i \times 10^{-12}$ [s^{-1}]	d_i	c_i' $\left[\dfrac{J}{\text{mol deg}}\right]$
v_1	12.11	2	12.24	v_{11}	35.46	2	1.72
v_2	15.08	1	5.15	v_{12}	39.55	1	0.55
v_3	18.17	2	8.38	v_{13}	42.05	1	0.42
v_4	20.19	1	3.61	v_{14}	44.52	2	0.59
v_5	20.74	2	6.54	v_{15}	47.58	2	0.42
v_6	23.45	1	2.77	v_{16}	55.59	1	0.08
v_7	25.56	2	4.61	v_{17}	91.52	2	—
v_8	29.78	1	1.55	v_{18}	91.71	1	—
v_9	30.09	1	1.47	v_{19}	91.82	1	—
v_{10}	31.07	2	2.68	v_{20}	93.03	2	—

degrees of freedom. On the other hand the time of relaxation related to the excitation of vibrations belonging to the symmetry class types A and B differs greatly from the period of the hypersonic wave under consideration.

It is also possible to achieve a satisfactory agreement with experiment, if we assume that the relaxation time is related to the excitation of internal degrees of freedom with lowest frequencies: $v_1, v_2, v_3, v_4, v_5, v_6$. Specific heat of these internal degrees of freedom is 38.65 J/mol deg which is very close to $c_{ak} = 37.5$ J/mol deg. The remaining internal degrees of freedom with frequencies from v_7 to v_{20} at the given frequency of the acoustic wave do not undergo excitation since in this case a selective excitation of vibrations is encountered to which reference has already been made. The time required for their excitation is higher than the acoustic wave period.

Table 4. Values of vibration frequencies v_i and specific heats c_i' of internal degrees of freedom for carbon tetrachloride

v	$v_i \times 10^{-12}$ [s^{-1}]	d_i	c_i' $\left[\dfrac{J}{\text{mol} \times \text{deg}}\right]$
v_1	6.54	2	15.10
v_2	9.41	3	20.69
v_3	13.75	1	5.52
v_4	23.14	3	8.40

Table 4 contains frequencies and specific heats of internal degrees of freedom of carbon tetrachloride. The best agreement with the experimental value c_{ak} will be obtained if we assume that vibrations v_2, v_3 and v_4 account for the relaxation processes within the examined frequency range.

The relaxation time connected with the excitation of the vibration v_1 is considerable shorter. This seems to be justified, since the likelihood of the excitation of the vibration with lowest energy is the highest. Consequently, it very quickly undergoes excitation, while at the tested frequency of the hypersonic wave, $f = 4 \times 10^9$ s^{-1}, transfer of energy to the internal degrees of freedom will occur and the state of equilibrium will be established. The value of the specific heat $c_{2,3,4}' = 34.61$ J/mol deg differs from c_{ak}, but it seems that such

a possibility is the most probable, particularly the case of CCl_4 where the Fermi resonance is likely to result, since $\nu_2 + \nu_3 \simeq \nu_4$ and vibrations $\nu_2 + \nu_3$ and ν_4 belong to the same symmetry class.

The situation is similar in the case of methylene chloride. Table 5 contains vibration frequencies of the of internal degrees of freedom and their specific heats.

Table 5. Values of vibration frequencies ν_i and of specific heats c_i' of internal degrees of freedom for methylene chloride

ν	$\nu_i \times 10^{-12}$ $[s^{-1}]$	d_i	c_i' $\left[\dfrac{J}{mol\,deg}\right]$
ν_1	8.50	1	7.13
ν_2	21.23	1	3.44
ν_3	22.18	1	3.18
ν_4	27.07	1	2.10
ν_5	34.62	1	1.05
ν_6	37.84	1	0.67
ν_7	42.99	1	0.42
ν_8	89.52	1	—
ν_9	90.03	1	—

Table 6. Values of vibration frequencies ν_i and specific heats c_i' of internal degrees of freedom for chloroform

ν	$\nu_i \times 10^{-12}$ $[s^{-1}]$	d_i	c_i' $\left[\dfrac{J}{mol\,deg}\right]$
ν_1	7.75	2	14.80
ν_2	11.09	1	6.41
ν_3	20.08	1	3.68
ν_4	22.81	2	6.05
ν_5	36.42	2	1.72
ν_6	90.01	1	—

If we assume that vibrations with the lowest frequency ν_1 participate in the energy exchange process with the external degrees of freedom, which means that their relaxation time is considerably shorter than the hypersonic wave period, then the specific heat of the remaining internal degrees of freedom is $c' = \sum\limits_{i=2}^{9} c_i' = 10.86$ J/mol deg which is in satisfactory agreement with the value $c_{ak} = 11.3$ J/mol deg. Thus, the calculated relaxation time $\tau = 1.71 \times 10^9$s would be connected with these eight internal degrees of freedom.

Another possibility is that the above mentioned relaxation time is related to vibrations ν_1, ν_2, ν_7, and ν_8 which belong to the same symmetry class. The value of the specific heat $c_{1,2,7,8}'$ is 10.99 J/mol deg which is very close to the value c_{ak}.

From the foregoing it can be seen that it is not possible to determine unequivocally which of the internal degrees of freedom participates in the energy exchange process with external degrees of freedom during the propagation of an acoustic wave even though a suitable value of specific heat is obtained.

Even more complex is the problem in the case of chloroform for which the frequency of internal vibrational degrees of freedom and corresponding specific heats are stated in Table 6. This could be expected since the previously calculated values of the relaxation times from the half-width of spectral lines of dispersed light and from sound velocity dispersion differ greatly.

If we group vibrations in the same symmetry class, thus ν_1, ν_4, ν_5 as well as ν_2, ν_3 and ν_6, then the corresponding values of specific heats are respectively: $c'_{1,4,5} = 22.57$ J/moldeg and $c'_{2,3,6} = 10.09$ J/moldeg. However, if we assume that the calculated relaxation time $\tau = 2.27 \times 10^{-10}$ is related to the excitation of internal degrees of freedom from ν_2 to ν_6, then the value of specific heat $c'_{2,3,4,5,6}$ is 17.86 J/moldeg. Both this value and the previous ones differ essentially from the value of specific heat calculated from acoustic data, $c_{ak} = 15.9$ J/moldeg. It should be concluded that in the case of chloroform there occurs a superposition of several relaxation processes the times of which are only approximate.

Methylene bromide is the only one of the examined liquids for which $(v_\infty/v_0)^2 > \varkappa_\infty/\varkappa_0$, and this leads to the calculated c_{ak} being higher than c'. It should be concluded that in this case it is predominately other processes which cause an additional dispersion of sound velocity.

Because of a large number of internal degrees of freedom a very complex problem is encountered in the cases of chlorobenzene, bromobenzene and nitrobenzene. However, the data obtained permit the following conclusions pertaining to chlorobenzene to be derived. A good agreement with the experimental is achieved if one assumes that the relaxation time of the internal degrees of freedom with frequencies from 5.91×10^{12} s^{-1} to 9.17×10^{12} s^{-1} is shorter than $\tau = 0.84 \times 10^{-10}$s. This time would correspond to the excitation of internal degrees of freedom with frequencies from 20.02×10^{12} s^{-1} to 91.18×10^{12} s^{-1}.

Equally good agreement with the value c_{ak} is obtained on the assumption that the calculated relaxation time $\tau = 0.84 \times 10^{-10}$ s is connected with the excitation of vibrations from 5.91×10^{12} s^{-1} to 30.41×10^{12} s^{-1}. The specific heat corresponding to these internal degrees of freedom is 37.6 J/moldeg and this is in very good agreement with the value $c_{ak} = 37.7$ J/moldeg. The remaining internal degrees of freedom are no longer active in the energy exchange process with the external degrees of freedom.

The relaxation time of bromobenzene for the processes connected with the excitation of internal degrees of freedom with frequencies from 5.94×10^{12} s^{-1} to 10.79×10^{12} s^{-1} is shorter than 0.68×10^{-10} s whereas vibrations with frequencies from 18.38×10^{12} s^{-1} to 91.72×10^{12} s^{-1} account for the relaxation processes within the examined frequency range.

For nitrobenzene the best agreement with experiment is achieved on the assumption that the relaxation time of vibrations with frequencies varying from 5.27×10^{12} s^{-1} to 10.73×10^{12} s^{-1} is shorter than 0.5×10^{-10} s.

From the examples given it can be concluded that the process of thermal relaxation is complex and cannot be described by only one relaxation time. At a given frequency of the acoustic wave usually only some of the internal degrees of freedom participate in the energy exchange process. However it is not possible to predict how this process will proceed.

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