ARCHIVES OF ACOUSTICS
14, 1-2, 61-65 (1989)

PROBLEM OF ACOUSTICAL RELAXATION OF LUTIDINE 3–4

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In this paper the results of acoustical absorption measurements in frequency range from 300 kHz to 9 GHz for lutidine 3–4 are presented. An acoustical relaxation process in the low frequency range between 0.3–10 MHz was observed. The relaxation process which has been noticed can be explain as a phenomenon of association and dislocation of sandwich molecules.

W pracy przedstawiono wyniki pomiarów absorpcji akustycznej w 3–4 lutydynie w zakresie częstotliwości od 300 kHz do 9 GHz. Obserwowano proces relaksacji akustycznej w zakresie niskich częstotliwości od 0,3 do 10 MHz. Proces ten można wytłumaczyć jako zjawisko asocjacji i dysocjacji cząsteczek sandwiczowych.

1. Introduction and experimental setup

The ultrasound investigations in many organic liquids indicate that it is necessary to use a set-up which gives a possibility of acoustical absorption measurements in very wide frequency range to obtain the complete information about relaxation processes in such liquids. Usually it is rather difficult.

In this paper we present the ultrasound measurements performed by four different methods. They allowed to cover five decades of frequencies. The frequency range was divided into four intervals and the following methods were applied: 0.3 MHz–3 MHz – the statistical reverberation method [4], 10–180 MHz – the pulse method [10], 0.4–1.3 GHz – the pulse method using the lithium niobate crystal

excited in the resonance cavity [1, 2], and in the highest GHz range for two 6 and 9 GHz(1) – Mandelstam Brillouin scattering method.

2. Investigations and results

The previous results of the measurements of ultrasound velocity as a function of temperature [8] in benzene derivatives liquids suggest the existence of the phase transition that could be due to breaking of the sandwich structures (Fig. 1) as it was assumed by authors conducting NMR investigations [7].

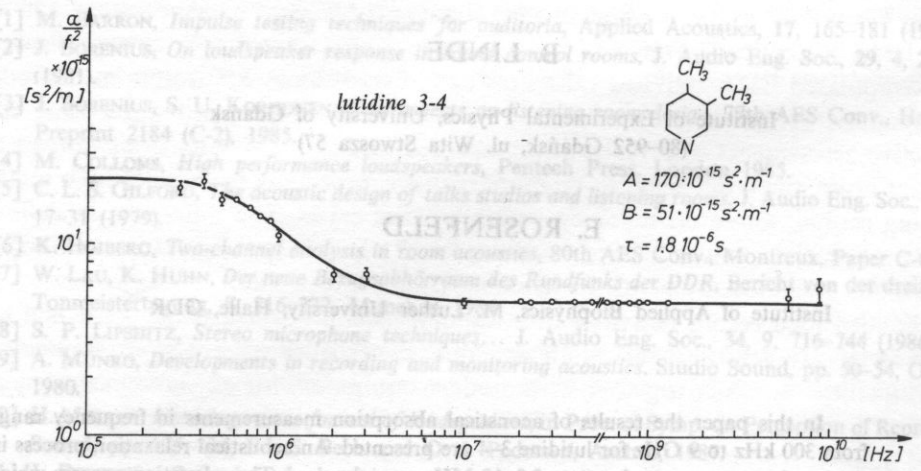

FIG. 1. Sandwich associates

The following investigations of the absorption as a function of frequency (10 MHz–1.3 GHz) [9, 12] showed us that there was no relaxation processes in this frequency range.

However the classical absorption coefficient (defined by expression [6]) is almost five times lower than experimental one (α_{exp}) (Table 1).

Table 1

$\frac{\alpha_{class}}{f^2}\left[\frac{s^2}{m}\cdot 10^{-15}\right]$	$\varrho\left[\frac{kg}{m^3}\cdot 10^3\right]$	η_s[cP]	$c\left[\frac{m}{s}\right]$	$\frac{\alpha_{exp}}{\alpha_{class}}$	$\frac{\alpha_{exp}}{f^2}\left[\frac{s^2}{m}\cdot 10^{-15}\right]$
10.4	0.9625	1.248	1487.9	4.9	51.0

$$\frac{\alpha_{class}}{f^2} = \frac{8\pi^2}{3\varrho c^3}\eta_s, \tag{1}$$

(1) The measurements for these highest frequencies were carried out by T. Pelous and M. Bassier from Laboratoire de Spectrometrie Rayleigh-Brillouin, University of Montpellier.

where c is the velocity of ultrasound waves, ϱ the density and η_s the coefficient of shear viscosity. This result is probably due to the relaxation process (Kneser relaxation [11]) for higher frequency above 10 GHz. Furthermore, the relaxation time calculated from Herzfeld equation [5] (2) is also of order of 10^{-10} s.

$$\tau = \frac{cA}{2\pi^2} \cdot \frac{C_p C_V}{C_i (C_p - C_V)} \tag{2}$$

where A is the acoustical absorption for low frequency, C_p, C_V and C_i specific heats at constant pressure, volume and vibrational specific heat (Table 2). It is possible to

Table 2

Substance	$C_i\left[\frac{\mathrm{J}}{\mathrm{mol\,K}}\right]$	$\frac{\alpha_{exp}}{f^2} - \frac{\alpha_{class}}{f^2} \approx A\left[\frac{\mathrm{s}^2}{\mathrm{m}} \cdot 10^{-15}\right]$	$\tau[\mathrm{s} \cdot 10^{-11}]$
3–4 lutidine	68.6	40.6	1.0

calculate the value of C_i from Planck-Einstein relation (3) using the frequencies of fundamental vibration ν_i determined from infrared or Raman spectra [3].

$$C_i = R \sum_i \frac{\left(\frac{h\nu_i}{kT}\right)^2}{\exp\left(\frac{h\nu_i}{kT}\right) \cdot \left[1 - \exp\left(\frac{h\nu_i}{kT}\right)\right]^2}, \tag{3}$$

where R is the gas constant, h – Planck constant, k – Boltzman constant and T – temperature.

The extension of the measurement frequency range up to 9 GHz (Table 3) did not confirm the existence of the relaxation process. There are two possible ways of

Table 3

f[MHz]	$\frac{\alpha}{f^2}$	f	$\frac{\alpha}{f^2}$	f	$\frac{\alpha}{f^2}$	f	$\frac{\alpha}{f^2}$
0.3	196.0	2.0	70.0	70.0	51.6	700.0	50.7
0.4	214.0	3.0	72.0	80.0	52.0	800.0	51.8
0.5	160.0	10.0	51.1	90.0	50.8	900.0	51.9
0.6	173.0	20.0	50.9	100.0	51.9	1000.0	50.6
0.7	155.0	30.0	51.7	180.0	51.6	1150.0	51.9
0.8	141.0	40.0	50.7	410.0	51.3	1250.0	51.1
0.9	133.0	50.0	50.2	500.0	51.1	6600.0	63 ± 6
1.0	112.0	60.0	51.2	600.0	51.9	9000.0	55 ± 10

explanation: the first one is, that the vibrational spectrum for lutidine 3 4 given in the paper by GREEN et al. [3] is not complete; and the other that the assumption (4) should not be used in calculation of the relaxation time. (Such assumption are usually adopted [5, 11] when the values of C_p and C_v are not accessible.)

$$C_p - C_i \approx 10R \quad \text{and} \quad C_p - C_V \approx 5R. \tag{4}$$

In this case the value of the relaxation time is given by the formula (5)

$$\tau = \frac{A \cdot c}{2\pi^2} \cdot \left(5 + \frac{C_i}{R}\right) \cdot \left(10 + \frac{C_i}{R}\right) \cdot \left(5 \frac{C_i}{R}\right)^{-1}. \tag{5}$$

In the lowest frequency range we have found a typical relaxation region (Fig. 2). The experimental curve α/f^2 can be well described by the relaxation equation (6) [7] with a single relaxation time τ.

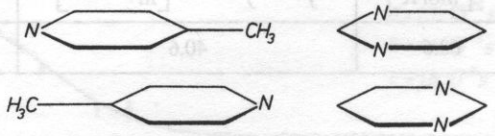

FIG. 2. Absorption coefficient α/f^2 in function of frequency (f) for lutidine 3–4 (for 293 K)

$$\frac{\alpha}{f^2} = \frac{A}{1 + (\omega\tau)^2} + B. \tag{6}$$

Similar relaxation process was found by MOKHTAR et al. [13] for toluene.

3. Conclusion

Acoustical relaxation which was observed in this low frequency range is probably in close connection with process which was mentioned above – association and dissociation of sandwich aggregates. This problem certainly needs further clasification and it is necessary to carry out the temperature investigations to obtain more precise explanation. These investigations give a possibility to calculate the activation energies of the relaxation process and allow to identify molecular process, presented in Fig. 1.

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Received on December 14, 1987.