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THERMODYNAMIC PARAMETERS OF AN ULTRASOUND RELAXATION PROCESS IN 2-NITROBUTANOL-1

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Measurements of the velocity and absorption coefficient of ultrasound were carried out in 2-nitrobutanol-1 with respect to the frequency of the sound and the temperature. The relaxation process can be accounted for in terms of a rotation about the C–C bond. The relaxation parameters for the observed process have been determined.

1. Introduction

Disubstituted butane derivatives are very interesting for ultrasonic investigations because within this group of compounds the existence of relaxation effects connected with a restricted rotation about the C–C bond can be expected. As a result of this restricted rotation process, molecules of different conformational forms are present in the environment.

Investigation of the absorption frequency spectrum and the ultrasound velocity enables us to observe such effects and to determine the kinetic and thermodynamic parameters of the ultrasonic relaxation process.

The aim of this work was the investigation of the relaxation effects in 2-nitrobutanol-1, a representative of the β-nitroalcohols which have not previously been examined with acoustic methods.

The investigated substance was also of interest because its two polar groups $-OH$ and $-NO_2$ can form an intermolecular hydrogen bond, which constitutes an additional factor stabilizing one of conformational forms.

In our previous paper [1] results of measurements of the ultrasonic velocity and absorption coefficients for 2-nitrobutanol-1 have been presented. However, the frequency range was too narrow to permit a full description of the examined phenomenon.

The present studies, carried out over widened frequency and temperature ranges allow us to determine all the characteristic parameters of the ultrasonic relaxation process connected with the rotation of the 2-nitrobutanol-1 molecule about the C–C bound.

The measurements were made over the temperature range −55 to +80°C with an high frequency apparatus US-4, which has been described previously [2], and with an ultrasound spectrometer CSU-250 over frequency range 2.5-57 MHz. The ultrasound velocity in the same temperature range was determined with a modified pulsephase interferometer UI-14, over the frequency range 2.5-15 MHz.

2. Experimental part

As the ultrasonic attenuation of the investigated substance is of the order of 10^{-13}, it was necessary to make the measurements using very thin liquid films, of the order 100 μm. In order to achieve adequate accuracy in measuring this distance we used a modified Abbe cathetometer, made by Carl Zeiss Jena, which measured the distance to an accuracy of ±0,5 μm.

Accurate measurement of the temperature in the experimental vessel was achieved by using a compensating method and a resistance thermometer. The resistance thermometer was made of platinum and gave an accuracy of ±0.01°C, it has a very stable characteristic curve over long periods of use. For the investigations, 2-nitrobutanol-1 produced by the firm Fluka AG of Switzerland was used. The initial experiments were carried out over the temperature range 0° to 80°C. They showed a slight decrease in the ultrasonic attenuation with increasing temperature [1]. The results of these measurements showed the necessity of extending the investigated temperature range below 0°C. Absorption coefficients were measured for the following frequencies: 2.5, 5, 7.5, 10.0, 12.5, 13.4, 15.1, 17.9, 21.1, 35.9, 44.2 and 57.3 MHz over the temperature range −55 to +10°C. The velocity of ultrasound was determined for frequencies of 2.5, 5, 7.5, 10, 12.5 and 15 MHz. Within the investigated frequency range, dispersion of the velocity was not observed.

3. Discussion

The analysis of the curves of α/f^2 versus $\log f$ (Fig. 1) leads us to conclude that in 2-nitrobutanol-1, in these ranges of frequency and temperature, we can observe relaxation processes associated with conformational rearrangements of this compound. It may be described by the equation [3]

$$\alpha/f^2 = \frac{A}{1+(f/f_c)^2} + B, \tag{1}$$

where A and B are constants, and f_c is the specific relaxation frequency.

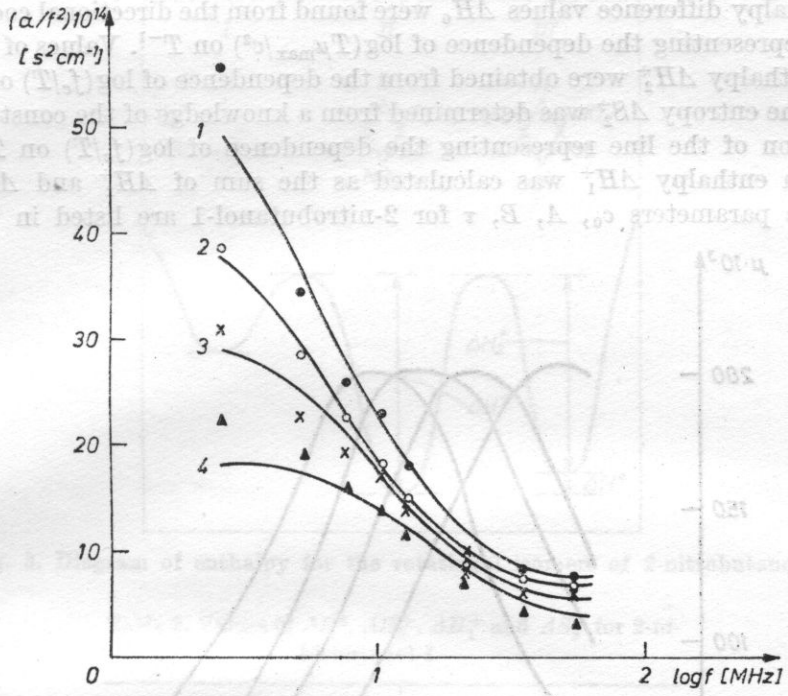

Fig. 1. The plot of α/f^2 vs. log$f$
1 – –50.0°C; *2* – –47.5°C; *3* – –45.0°C; *4* – –42.5°C

A coefficient of relaxation absorption per wave-length, μ, was calculated from equation

$$\mu = (\alpha/f^2 - B)c_0 f, \tag{2}$$

where c_0 is the velocity of sound at low frequencies and B is the limiting of α/f^2 for high frequencies (Table 1).

The values of μ are shown in Fig. 2. The relaxation terms (Table 1) were calculated from:

$$\tau = (2\pi f_c)^{-1}. \tag{3}$$

Table 1. Thermodynamic parameters A, B, τ and velocity c_0 for 2-nitrobutanol-1

T [°C]	A [10^{17} s^2·cm^{-1}]	B [10^{17} s^2·cm^{-1}]	c_0 [m/s]	$\tau \times 10^{-8}$ [s^{-1}]
–50.0	84 865	7000	1674	5.31
–47.5	35 057	6500	1668	2.27
–45.0	25 307	5000	1660	1.59
–42.5	15 448	3180	1652	0.96
–40.0	14 388	2500	1646	0.88
–37.5	12 256	1500	1638	0.76
–35.0	8570	500	1632	0.72

Enthalpy difference values ΔH_0 were found from the directional coefficients of lines representing the dependence of $\log(T\mu_{max}/c^2)$ on T^{-1}. Values of the activation enthalpy ΔH_2^+ were obtained from the dependence of $\log(f_c/T)$ on temperature. The entropy ΔS_2^+ was determined from a knowledge of the constant term in equation of the line representing the dependence of $\log(f_c/T)$ on T^{-1}. The activation enthalpy ΔH_1^+ was calculated as the sum of ΔH_2^+ and ΔH_0. The ultrasonic parameters c_0, A, B, τ for 2-nitrobutanol-1 are listed in Table 1.

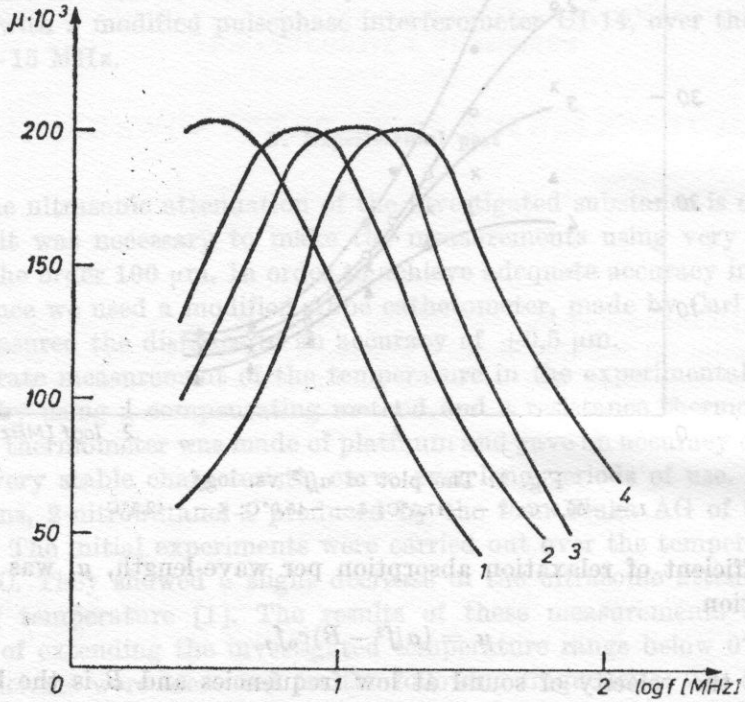

Fig. 2. The plot of μ vs. $\log f$
1 – −50°C; *2* – −47.5°C; *3* – −45.0°C; *4* – −42.5°C

The relaxation process which we observed in our sample is related to the rotation of the molecules around the C–C bond. Theoretically three different conformations are possible for 2-nitrobutanol-1 and are shown schematically in Fig. 3. Owing to the presence of NO_2, C_2H_5 and OH groups in the molecule of 2-nitrobutanol-1, the conformers have different energy levels. Of the three considered here the first seems to be the least stable (i.e. it has the highest energy level) because of the steric hindrance caused by the NO_2, C_2H_5 and OH groups. The second and third conformers have much lower energy levels, but the second will be probably the more preferred as the two polar groups, NO_2 and OH, may form hydrogen bonds [4, 5].

The values of activation enthalpy ΔH_2^+, ΔH_1^+, the enthalpy difference ΔH^0, and the entropy of activation ΔS_2^+ are collected in Table 2.

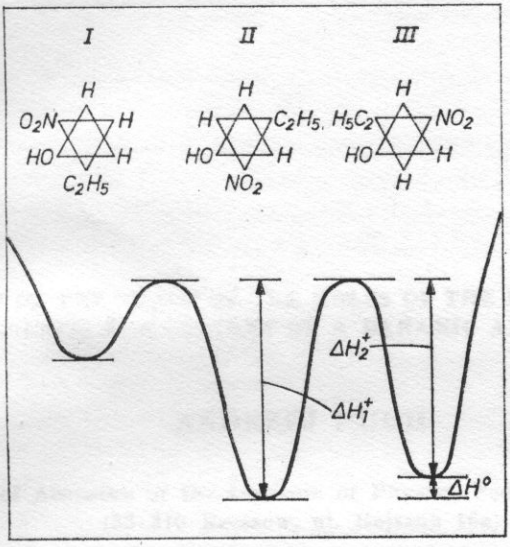

Fig. 3. Diagram of enthalpy for the rotational isomers of 2-nitrobutanol-1

Table 2. Values of ΔH^0, ΔH_2^+, ΔH_1^+ and ΔS_2^+ for 2-nitrobutanol-1

ΔH_0 [kcal/mol]	ΔH_2^+ [kcal/mol]	ΔH_1^+ [kcal/mol]	ΔS_2^+ [cal/mol]
1.05	15.22	16.27	−44.12

The high value of the activation enthalpy ΔH_2^+ indicates that the form II is present in a significant majority.

Mechnical energy introduced into our system by acoustic waves id absorbed in order to overcome the energy barrier involved in the transformation between the second and third conformers.

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