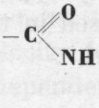
ARCHIVES OF ACOUSTICS
8, 2, 113-118 (1983)

ULTRASONIC INVESTIGATIONS OF THE RELAXATION PROCESSES RELATED TO THE PRESENCE OF THE GROUP $-\mathrm{C}\langle^{\mathrm{O}}_{\mathrm{NH}}$ IN MOLECULES



$-\mathrm{C}\langle^{\mathrm{O}}_{\mathrm{NH}}$

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Measurements of the velocity and the absorption coefficient of ultrasound were taken in monosubstituted amides as a function of temperature and frequency. It was found that a single relaxation process related to rotation of molecules around the C−N bond occurs over the temperature and frequency range investigated. Termodynamic parameters which characterize the process observed were determined.

1. Introduction

Measurements of the velocity and absorption of ultrasound as a function of temperature and frequency are a valuable tool in the investigations of the structure of the substance and permit the determination of the parameters characteristic of the processes which occur in the given medium.

The aim of the present investigation is to determine the relaxation parameters characteristic of the process of hindered rotation in monosubstituted amides. The investigations of dipole moments [1], dielectric constants [2], infrared and Raman spectra [3] and NMR investigations [4-6] showed the existence of two conformation states which occur as a result of hindered rotation around the C−N bond.

The present paper is an attempt to explain the processes of ultrasonic relaxation in this group of compounds on the basis of acoustic investigations of amides with different length of hydrocarbon chains which occur within a molecule.

2. Experimental part

The absorption coefficient α/f^2 was determined on the basis of measurements taken with a US-4 set and a high-frequency CSU-250 system. This equipment permitted measurements of the absorption coefficient α/f^2 over the frequency range 10-74 MHz. The velocity was measured using a pulse-phase UI-14 interferometer.

The measurement method was described in previous papers [7, 8]. N-propylformamide, N-propylacetamide, N-propylpropionamide and N-butylpropionamide were used in the investigations. All these reagents were synthesized by the authors.

3. Results and conclusions

As an example, Fig. 1 shows the dependence of α/f^2 on frequency (at 50°C) for N-propylacetamide, N-propylpropionamide and N-butylpropionamide.

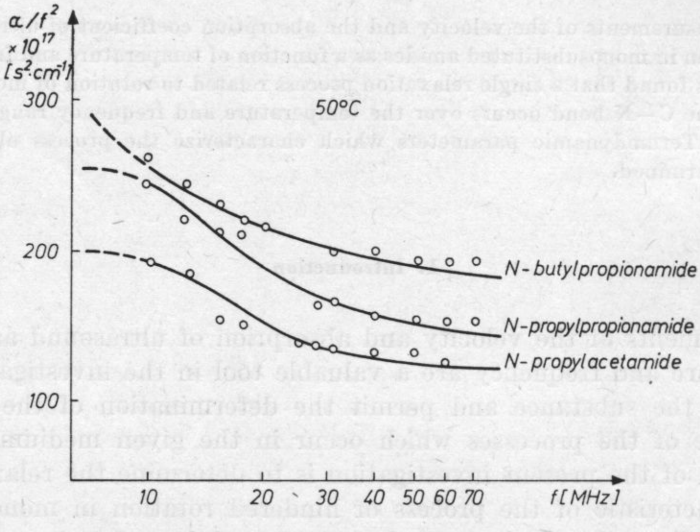


Fig. 1. The dependence of α/f^2 on $\log f$ (temp. 50°C) for N-butylpropionamide, N-propylpropionamide and N-propylacetamide

In the compounds under investigation, except N-propylformamide, there occurs a relaxation process which is characterized by a single relaxation time. In the case of N-propylformamide no dispersion of the absorption coefficient was observed over the whole frequency and temperature range. For the other substances the dependence of the absorption coefficient α/f^2 on frequency is given by the relaxation equation

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

where A is the relaxation parameter depending on the equilibrium characteristic and B represents the contribution of the classical absorption and other relaxation processes with characteristic frequency much greater than f_c.

On the basis of the expression

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

the values of the coefficients a/f^2 served to determine the excess absorption coefficients μ per wavelength. c_0 is the sound velocity for low frequencies at which no dispersion is observed. Fig. 2 shows the dependence of μ on frequency at a temperature of 50°C. Tables 1-3 give the values of the velocity c_0, the coefficients A, B and μ and the relaxation frequency f_c.

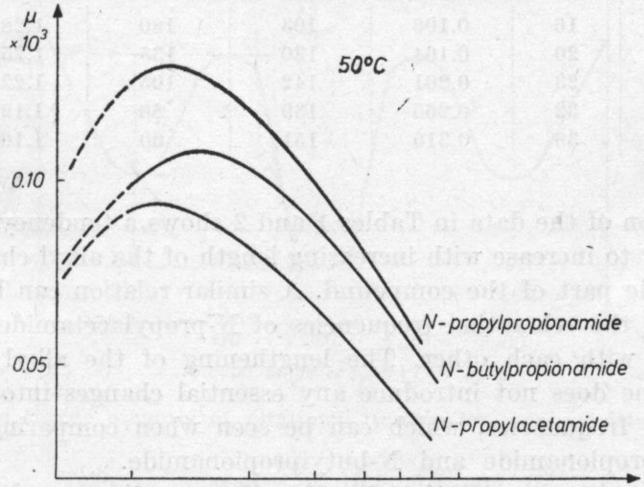


Fig. 2. The dependence of the excess absorption coefficient μ on log f (temp. 50°C) for N-butylpropionamide, N-propylpropionamide and N-propylacetamide

Table 1. The values of the relaxation parameters for N-propylacetamide

T [°C]	f_c [MHz]	$\mu_{\max} \cdot 10^3$	$A \cdot 10^{17}$ [cm$^2 \cdot$s^{-1}]	$B \cdot 10^{17}$ [cm$^2 \cdot$s^{-1}]	$c_0 \cdot 10^5$ [cm$\cdot$s^{-1}]
40	11	0.66	87	173	1.388
50	12	0.92	117	122	1.305
60	18	0.80	69	110	1.275
70	22	0.84	62	84	1.240
80	30	0.89	49	72	1.205

Table 2. The values of the relaxation parameters for N-propylpropionamide

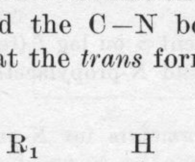
T [°C]	f_c [MHz]	$\mu_{\max}\cdot 10^3$	$A\cdot 10^{17}$ [$cm^2\cdot s^{-1}$]	$B\cdot 10^{17}$ [$cm^2\cdot s^{-1}$]	$c_0\cdot 10^5$ [$cm\cdot s^{-1}$]
40	10	1.129	170	184	1.330
50	13	1.283	153	148	1.290
60	21	1.402	106	126	1.260
70	25	1.345	88	95	1.220
80	39	1.301	56	86	1.185
90	42	1.601	67	73	1.150

Table 3. The values of the relaxation parameters for N-butylpropionamide

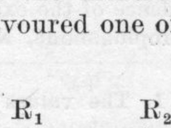
T [°C]	f_c [MHz]	$\mu_{\max}\cdot 10^3$	$A\cdot 10^{17}$ [$cm^2\cdot s^{-1}$]	$B\cdot 10^{17}$ [$cm^2\cdot s^{-1}$]	$c_0\cdot 10^5$ [$cm\cdot s^{-1}$]
50	16	0.106	103	180	1.286
60	20	0.164	130	135	1.254
70	23	0.201	142	105	1.224
80	32	0.265	139	80	1.192
90	36	0.316	151	60	1.160

Comparison of the data in Tables 1 and 2 shows a tendency of the relaxation frequency to increase with increasing length of the alkyl chain originating from the amide part of the compound. A similar relation can be observed in comparison of the relaxation frequencies of N-propylacetamide and N-butylpropionamide with each other. The lengthening of the alkyl chain coming from the amine does not introduce any essential changes into the values of the relaxation frequencies, which can be seen when comparing these values for N-propylpropionamide and N-butylpropionamide.

The ultrasonic relaxation in monosubstituted amides results from limited rotation around the C$-$N bond. The results of the hitherto investigations have shown that the *trans* form (I) is the more favoured one of the two possibilities.



trans (I)



cis (II)

Changes in the enthalpy ΔH for this type of conformation transformation can be illustrated with a diagram.

The value of the energy barrier ΔH_2^+ which a molecule has to overcome in its transition from a state of higher energy to the primary state and the values of the enthalpy difference ΔH_0 were determined for all the compounds investigated. Table 4 gives the values of ΔH_2^+, ΔH_0 and $\Delta H_1^+ = \Delta H_2^+ + \Delta H_0$.

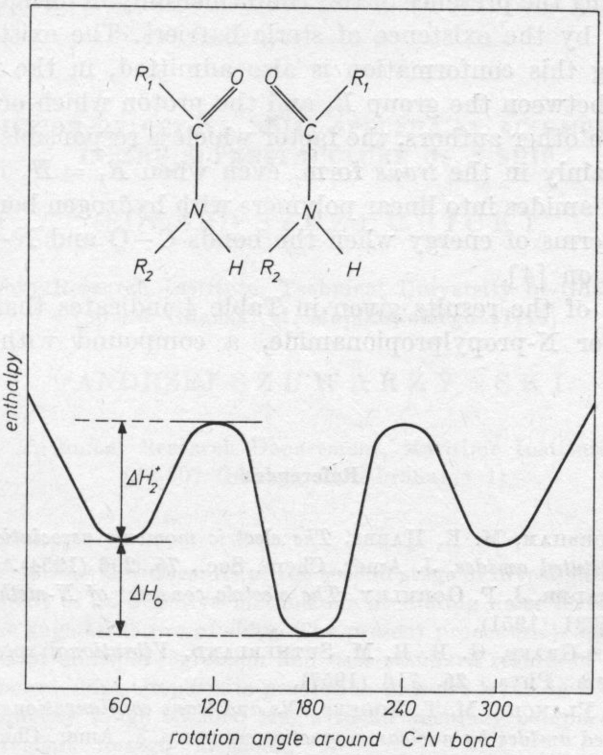


Fig. 3. The energy diagram of rotational isomers for monosubstitud amides

Table 4. The values of ΔH_2^+, ΔH_0 and ΔH_1^+ for N-propylacetamide, N-propylpropionamide and N-butylpropionamide

	ΔH_0	ΔH_2^+	ΔH_1^+
N-propylacetamide	3.3	5.1	8.4
N-propylpropionamide	3.8	6.2	10.0
N-butylpropionamide	8.2	4.2	12.4

ΔH_2^+ takes its lowest value for N-butylpropionamide. This is caused by the relatively large volumes of alkyl groups, which causes an increase in steric interaction between the alkyl substituent at nitrogen and the alkyl substituent which comes from the amide. The durability of the *cis* configuration decreases, and accordingly there is an decrease in the value of the energy ΔH_2^+. The result of this is the parallel increase in the value of the enthalpy difference ΔH_0 between forms I and II. The enthalpy difference ΔH_0 increases as the sums R_1 and R_2 increase, which indicates that the *trans* form stabilizes as the alkyl groups enlarge.

The NMR investigations [4] exclude the existence of the *cis* configuration in amides, allowing the presence of this conformer only in formamides ($R_1 = H$). This is justified by the existence of steric barriers. The existence of another factor stabilizing this conformation is also admitted, in the form of a weak hydrogen bond between the group R_1 and the proton which occurs at nitrogen [9]. According to other authors, the factor which is responsible for maintaining the molecule mainly in the *trans* form, even when $R_1 = H$, is the possibility of association of amides into linear polymers with hydrogen bonds. This process is favoured in terms of energy when the bonds C–O and N–H occur in the *trans* configuration [4].

Comparison of the results given in Table 4 indicates that ΔH_2^{+} takes its highest value for N-propylpropionamide, a compound with a symmetrical structure.

References

[1] J. E. Worsham, M. E. Habbs, *The electric moments association and structure of some N-mono-substituted amides*, J. Amer. Chem. Soc., **76**, 206 (1954).

[2] G. R. Leader, J. F. Gormley, *The electric constant of N-methylamides*, J. Amer. Chem. Soc., **73**, 5731 (1951).

[3] D. E. De Graff, G. B. B. M. Sutherland, *Vibrational spectrum of N-methylformamide*, J. Chem. Phys., **26**, 716 (1957).

[4] L. A. La Planche, M. T. Rogers, *Cis and trans configurations of the peptide bond in N-monosubstituted amides by nuclear magnetic resonance*, J. Amer. Chem. Soc., **86**, 1, 337 (1964).

[5] T. Drakenberg, K. J. Dahlgvist, S. J. Forsen, *The barrier to internal rotation in amides. IV. N. N-dimethylamides, substituent and solvent effects*, Phys. Chem., **76**, 15, 2178 (1972).

[6] W. Doepke, B. Bartholme, T. Gross, *Studies on rotationally hindered systems*, Z. Chem., **16**, 8, 327 (1976).

[7] B. Zapiór, A. Juszkiewicz, Z. Bartynowska, *Investigation of the relaxation processes in 2-nitrobutanol-1 using acoustic methods*, Zeszyty Nauk. UJ, Prac. Chem., **21**, 191 (1976).

[8] A. Juszkiewicz, *System for measurements of the ultrasonic absorption coefficient at 10-60 MHz over the temperature range $-60°C - +200°C$* (in Polish), Zeszyty Nauk. UJ, Prac. Chem., **21**, 257 (1976).

[9] R. A. Nyquist, *The structural configuration of some a-substituted secondary acetamides in dilute CCl_4 solution*, Spectrochim. Acta, **19**, 509 (1963).

Received on May 6, 1982.