Ultrasound Absorption in Trifluoroacetic Acid and its Equimolar Mixture with Acetic Acid

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Ultrasound absorption has been measured in pure trifluoroacetic acid and its approximately equimolar mixture with acetic acid (51.5 mole% of acetic acid) at 20, 30, 40, and 50 °C and atmospheric pressure over the frequency range 3–57 MHz. The absorption curve of trifluoroacetic acid could be fiitted by a single relaxation step (relaxation frequency 3.5–11 MHz, low frequency absorption about one tenth of that of acetic acid), whereas the equimolar mixture followed a two step relaxation curve (lower relaxation frequency 1.5–3 MHz, absorption correspondingly higher than in pure trifluoroacetic acid, higher relaxation frequency 12.5–39 MHz, absorption about 3% of the low frequency absorption).

I. Introduction

Determination of the frequency and temperature dependence of ultrasonic absorption provides information about the kinetics and thermodynamics of chemical reactions [1, 2], if it is clear what reactions are responsible for the ultrasonic relaxation, and what the activities of the reactants are [3]. For association reactions, cyclic associates have in general relatively long lifetimes, so that cyclic associates can be favourably studied by ultrasonic relaxation [4].

In the present paper we present first qualitative information on the relaxation behaviour of trifluoroacetic acid and its equimolar mixture with acetic acid. We were interested to compare the behaviour of the trifluoroacetic acid dimer and of the trifluoroacetic acid – acetic acid heterodimer with that of acetic acid in the light of other investigations [5].

II. Experimental

The linear amplitude absorption coefficient has been measured by a pulse technique apparatus [6]. X-cut quartzes with eigenfrequencies of about 1 and 5 MHz were excited in their odd harmonics, so that the frequency range 3 – 57 MHz could be covered. For the low frequencies (3 – 7 MHz) a diffraction correction was necessary. For this correction the sound velocity was determined approximately (±10%).

Temperature was kept constant within ±0.05 °C. The error in the frequency was ±1% for 3 MHz and less than 0.02 MHz for all higher frequencies. The absorption coefficients were calculated by a least squares-program for different pathlengths of the pulse at each frequency, with a standard deviation of ±3 – 5%; the smallest deviations were in the frequency range 15 – 35 MHz.

The substances were purified as described elsewhere [7], and stored in dark in vapour phase contact with $Mg(ClO_4)_2$. Melting point of trifluoroacetic acid was −15.9 °C, of acetic acid 16.43 °C.

III. Results

For pure trifluoroacetic acid the results are compatible with a single step relaxation function [Eq. (1) with $A_2 = 0$]:

$$y = \frac{\alpha}{f^2} = \frac{A_1}{1 + (f/f_{r1})^2} + \frac{A_2}{1 + (f/f_{r2})^2} + B. \quad (1)$$

Here α is the absorption coefficient, f the frequency, A_1, A_2, f_{r1}, and f_{r2} the characteristic parameters of two relaxation steps, and B the high frequency absorption. The fitted constants A_1 and f_{r1} for the trifluoroacetic acid relaxation are presented in Table 1.

For the mixture of trifluoroacetic acid and acetic acid (51.51 mole % of acetic acid) it was necessary to include a second relaxation step ($A_2 \neq 0$) in order to avoid systematic deviations between calculated and experimental relaxation curves (Figure 1). The parameters of the two step function are listed in

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Table 2. Error limits are running up to 20% for the parameters A_1 and f_{r1}, and up to 50% for the parameters A_2 and f_{r2}.

Table 1. Pure trifluoroacetic acid. Single relaxation data with standard deviations, and approximate sound velocities c.

T/°C	$A \cdot 10^{17}$ / cm^{-1} s^2	f_r/MHz	$B \cdot 10^{17}$ / cm^{-1} s^2	c / m s^{-1}
19.9	11470 ± 8%	3.52 ± 5%	252 ± 3%	—
29.8	9265 ± 4%	5.27 ± 3%	242 ± 2%	676
38.9	7625 ± 3%	7.46 ± 3%	245 ± 4%	634
49.0	5938 ± 1%	10.97 ± 3%	258 ± 6%	626

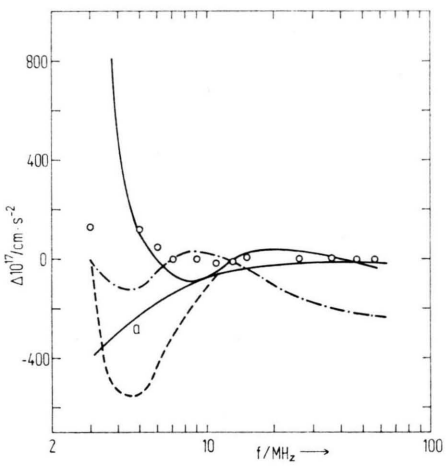

Fig. 1. Plot of $\Delta = y_{exp} - y_{calc}$ [cf. Eq. (1)] for the equimolar mixture of trifluoroacetic acid + acetic acid at 19.9 °C versus the frequency. Points correspond to a fitting by two relaxation steps, curves give Δ fitted by a single relaxation step in such a way that $\Delta = 0$ for three experimental points. Here a systematic trend of Δ is obvious. Line a gives the approximate experimental error (the symmetric line for positive Δ is omitted).

Table 2. Mixture trifluoroacetic acid + acetic acid of 51.51 mole % acetic acid. Two step relaxation data [cf. Eq. (1)] and approximate sound velocities c.

T/°C	$A_1 \cdot 10^{17}$ / cm^{-1} s^2	f_{r1}/MHz	c/m s^{-1}
19.9	22420	1.56	865
29.9	19976	2.05	855
39.3	18570	2.55	835
49.0	17940	3.0	804
T/°C	$A_2 \cdot 10^{17}$ / cm^{-1} s^2	f_{r2}/MHz	$B \cdot 10^{17}$ / cm^{-1} s^2
19.9	841	12.5	128
29.8	617	20.6	103
39.3	555	25.2	113
49.0	577	39.1	64

IV. Discussion

For pure trifluoroacetic acid, Sano et al. [8] have given relaxation parameters which are shown in Table 3. The disagreement to our values might be due to the fact that Sano et al. used commercial trifluoroacetic acid without further purification, and that small polar impurities can have an extreme influence on the relaxation behaviour [9].

Table 3. Ultrasound absorption data for trifluoroacetic acid on the basis of a single relaxation step according to Sano et al. [8].

T/°C	$A \cdot 10^{17}$/cm^{-1}	$B \cdot 10^{17}$/cm^{-1}	f_r/MHz
15	5733	276	6.5
20	5263	253	7.3
25	4881	253	8.1
30	4942	189	9.0

Comparison with the relaxation parameters of acetic acid [3] (for 20 and 40 °C: $A_1/10^{-17}$ cm^{-1} s^2 = 150000 and 74000, f_{r1}/MHz = 0.58 and 1.50, resp.) shows the shorter lifetime of the trifluoroacetic acid homodimer, which is in line with the smaller association constants as determined in gas phase and in dilute solutions [10].

In the equimolar mixture with acetic acid the heterodimer occurs in much higher concentration than the homodimers, as the heteroassociation of trifluoroacetic acid and acetic acid is strongly preferred [11] (a model calculation [12] yielded for the mole fraction of the heterodimer 0.83, for the mole fraction of the acetic acid homodimer 0.07, and for the mole fraction of the trifluoroacetic acid homodimer 0.06). Therefore, it is believed that both relaxation steps are caused by the heteroassociation, though the possibility cannot be completely excluded that the second relaxation step is caused by the homoassociation of acetic acid. Here it would be necessary to follow the concentration dependence of each relaxation step.

Comparing the relaxation of the equimolar mixture with the relaxation of the pure acids, it can be said that the results are by no means extraordinary. However, it has to be kept in mind that quantitative comparisons are impossible for two reasons: (1) It would be necessary to transform the complicated multistep reaction scheme into independent reaction coordinates, and (2) it is impossible to get the

heterodimer free of the presence of the homodimers, which act as impurities and may alter the relaxation parameters appreciably. Therefore, it can only be stated in a sloppy way that the lifetime of the heterodimer is in between the lifetime of the homodimers, and that its lifetime decreases slower with increasing temperature than those of the homodimers.

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