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The Relaxation Strength and the Computed Relaxation Spectra of the H-Bond Association of Amides

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The ultrasonic relaxation strength of the H-bond association of *N*-methyl acetamide dissolved in carbon tetrachloride is shown to be a product of two factors, Q and Z. Q depends on the thermodynamic properties of the entire system, while Z depends on the properties of the self association of solute. The concentration dependence of Q is investigated by measuring the ultrasonic velocity (at 3.5 Mc) and the density of *N*-methyl acetamide dissolved in carbon tetrachloride at 20°C in the concentration range 0.0 – 0.5 M. The measurements show that Q can be considered as being constant. The concentration dependence of Z is investigated by computing the entire relaxation spectrum for the H-bond polymerization mechanism. Z is shown to increase with increasing amide concentration. The consequences of these observations for the previously presented interpretation of the relaxation spectra of *N*-methyl acetamide dissolved in carbon tetrachloride are discussed. Finally the agreement between the computed relaxation spectra and the previously published ultrasonic absorption data is verified.

The ultrasonic absorption technique has proved to be useful in investigating the kinetics of fast reactions in solution. Several reactions in which hydrogen bonds are formed have been investigated and rate constants for the hydrogen bond forming and breaking have been obtained.[1–2] The evaluation of all the rate constants from the experimentally obtained relaxation spectra can be made only for H-bonding systems for which the reaction mechanism is assumed to be a single, elementary reaction step in which a hydrogen bonded dimer is formed. If the reaction mechanism is more complicated, for instance if the dimer is doubly bonded and consequently must be formed by two elementary reaction steps, the kinetic analysis is complicated and the evaluation of the rate constants requires a knowledge of the various equilibrium constants involved.[3] The consequences which may arise if the relaxation spectra are interpreted in terms of a reaction mechanism which is simpler than the mechanism which actually causes the relaxation have recently been demonstrated on the basis of simulation experiments.[4]

Recently attempts have been made to interpret the relaxation spectra of systems in which a hydrogen bond polymerization occurs and consequently a multistep reaction mechanism is involved. Thus the relaxation spectra of benzyl alcohol and tertiary butyl alcohol dissolved in cyclohexane,[5-6] *N*-methyl acetamide dissolved in dimethyl acetamide,[7] and *N*-methyl acetamide dissolved in carbon tetrachloride [8] have been interpreted in terms of the multistep association mechanism generally used to describe the equilibrium properties of the systems.[9-11] The interpretation is based on the fact that only one relaxation time is observed although a wide frequency and concentration range has been investigated. Similar observations have been reported, however, for other types of multistep mechanisms.[12] The multistep mechanism for the above mentioned compounds is used with the assumption that all the reverse rate constants are equal and that the observed relaxation is associated mainly with the smallest of the individual relaxation times involved. This treatment results in approximate values of the reverse rate constants for the polymerization mechanism. The mechanism successfully describes all the systems investigated so far up to solute concentrations of about 0.1 M. Above this concentration the measured values of the relaxation time are smaller than the values predicted from this mechanism. In the same concentration range the calculated relaxation strength decreases with increasing solute concentration. This is attributed to a change in the thermodynamic properties of the system caused by the increase of the solute concentration.

In this paper the change in the thermodynamic properties caused by the increasing solute concentration is investigated by measuring the sound velocity and the density for different solutions of *N*-methyl acetamide (NMA) in carbon tetrachloride. The effect of this change on the relaxation strength is calculated. Furthermore the above mentioned assumption that the measured relaxation time is associated with the smallest of the individual relaxation times of the mechanism is checked by constructing the entire relaxation spectrum for the polymerization model. The observed discrepancies between the results predicted from the above mentioned assumption and the experiments performed at high solute concentrations are explained on the basis of the constructed relaxation spectra.

THEORY

The ultrasonic absorption caused by the relaxation of a multistep reaction mechanism is given by

$$\frac{\alpha}{\nu_2} = \sum_{i=1}^{i=n} \frac{A}{1+(2\pi\tau_i\nu)^2} + B \qquad (1)$$

where α is the absorption coefficient of sound, ν is the frequency of sound, A_i is a relaxation strength, τ_i is a relaxation time, and B is the background absorption, *i.e.* the value of α/ν^2 at frequencies high enough for the first term in eqn. (1) to be negligible. The number of elementary reaction steps involved in the mechanism is denoted n.

The analysis of an observed relaxation results in values of i, A_i, τ_i, and B. If the relaxation times are closely spaced the minimum value of i which is

required for eqn. (1) to describe the data is very often smaller than the number of elementary reaction steps involved in the mechanism. A numerical criterion for deciding when a single term does not suffice to describe the data within experimental error has recently been developed on the basis of simulation experiments.[3] A further interpretation of the relaxation parameters requires a knowledge of the detailed mechanism of the reaction which actually causes the relaxation. The procedure is first to develop the theoretical expressions for the relaxation times and the relaxation strengths for the mechanism in question. Then the concentration dependence predicted from these expressions is compared with the concentration dependence which has been measured.

The theoretical expressions of the relaxation times consist of rate constants and solute concentrations only while the theoretical expressions of the relaxation strengths also contains thermodynamic parameters of the solute/solvent mixture. The actual value of τ obtained by the analysis of the relaxation spectrum depends on the actual value of A involved. Consequently the concentration dependence predicted from the theoretical expressions of τ can be correlated with the actually measured concentration dependence only for a limited concentration range. The size of this range is determined by the concentration dependence of the thermodynamic functions on which A depends.

For a reaction mechanism which consists of a single elementary reaction in which a dimer is formed with a negligible volume change, the relaxation strength is given by the following expression [13]

$$A = Q\,Z \tag{2}$$

where

$$Q = \frac{2\pi^2 V(C_p - C_v)}{U\,R\,T^2\,C_p C_v} \tag{3}$$

and

$$Z = (\Delta H^\circ)^2 \frac{1 + 4KC - \sqrt{1+8KC}}{8k_{12}(1+8KC)} \tag{4}$$

where R is the gas constant, U is the sound velocity, C_p and C_v are the heat capacities of the entire system, V is the molar volume, ΔH° is the standard enthalpy of reaction, K is the association equilibrium constant, k_{12} is the association rate constant, and C is the overall concentration of solute calculated as monomers. It is seen that Z depends on the properties of the self association of solute only while Q depends on the thermodynamic properties of the entire system. By taking the derivative of Z with respect to C the following expression is obtained

$$\dot{Z} = \frac{\sqrt{1+8KC} - 1}{2k_{21}(1+8KC)^2} \tag{5}$$

From eqn. (4) and eqn. (5) it appears that Z and $\dot{Z}$ are positive for $C > 0$. Consequently Z is a monotonically increasing function of the solute concentration. If the measured value of the relaxation strength for a simple dimerization at a certain solute concentration has a maximum, this must be attributed to

a decrease in Q and consequently the basic requirement for using the concentration dependence of the relaxation time is not fulfilled any more.

The hydrogen bond association of NMA dissolved in carbon tetrachloride is described by the following model

$$\begin{array}{l} N_1+N_1 \rightleftharpoons N_2 \\ N_1+N_2 \rightleftharpoons N_3 \\ N_1+N_3 \rightleftharpoons N_4 \\ \cdot \quad \cdot \quad \cdot \\ \cdot \quad \cdot \quad \cdot \\ \cdot \quad \cdot \quad \cdot \\ N_1+N_i \rightleftharpoons N_{i+1} \\ \cdot \quad \cdot \quad \cdot \\ \cdot \quad \cdot \quad \cdot \\ N_1+N_n \rightleftharpoons N_{n+1} \end{array} \tag{6}$$

It is generally accepted [9–11] that the equilibrium constant for the dimerization step, K_1, is different from that of subsequent steps, K_n, and that the latter may be taken as independent of n, the number of reaction steps involved in the mechanism. The total relaxation strength, A, for the polymerization mechanism is defined as

$$A=\lim_{\nu\to 0}\frac{\alpha}{\nu^2} \quad -B=\sum_{i=1}^{i=n} A_i \tag{7}$$

By comparing eqn. (7) with eqns. (2), (3), and (4) it seems likely that eqn. (7) can be rewritten as

$$A=Q\,Z \tag{8}$$

where Q is defined by eqn. (3) and Z is a function which depends on properties of self association only. The proof of eqn. (8) is given later in this paper. The effect on the relaxation strength of the polymerization caused by increasing solute concentration can be calculated if the concentration dependence of Q and Z is known. By introducing

$$U^2=\frac{C_p}{C_v\varrho\beta_T} \tag{9}$$

where β_T is the isothermal compressibility and ϱ is the density, Q can be expressed in the following way

$$Q=\frac{2\pi^2 V}{RT^2C_pU}\left(\beta_T\varrho U^2-1\right) \tag{10}$$

Since the actual values of the parameters in eqn. (10) do not change very much for very small concentration variations, the sensitivity of Q to the concentration variation depends on how close the value of $\beta_T\varrho U^2$ is to unity for the solvent used. In this paper the concentration dependence of ϱU^2 is used to estimate the concentration dependence of Q for NMA dissolved in carbon tetrachloride.

In order to evaluate the concentration dependence of the kinetic part of the relaxation strength an exact espression of Z is required. This implicitly involves an expression for the entire relaxation spectrum of the polymerization model. The individual relaxation times are given by

$$\frac{1}{\tau_i} = |\lambda_i| \tag{11}$$

where λ_i is the eigenvalue No. i in the coefficient matrix of the differential equations which describe the kinetics of the system when it is perturbed by the ultra sound. Combination of eqn. (1) and eqn. (11) gives the following expression of the relaxation spectrum

$$\frac{\alpha}{\nu^2} = \sum_{i=1}^{i=n} \frac{A_i \lambda_i^2}{\lambda_i^2 + 4\pi^2\nu^2} + B \tag{12}$$

The possibility of calculating the individual relaxation times for the polymerization model has recently been discussed.[5,8] The construction of the entire relaxation spectrum, however, requires furthermore a knowledge of A_i. Although the theoretical principles for calculating A_i for a multistep mechanism are wellknown they have only recently been developed into a form which directly permits a computation of the entire relaxation spectrum for a given multistep mechanism. Thus it can be shown [15] that eqn. (12) can be written as

$$\frac{\alpha}{\nu^2} = Q \sum_{i=1}^{i=n} \frac{\psi_i^2}{\lambda_i^2 + 4\pi^2\nu^2} + B \tag{13}$$

provided that the volume change involved is negligible. Q is given by eqn. (3) and ψ_i is the component No. i in a vector given by

$$\psi = \mathbf{M}\,\mathbf{G}\,\mathbf{H} \tag{14}$$

where $\mathbf{H}$ is a vector with the elements

$$\mathbf{H} = \Delta H_1^\circ, \Delta H_2^\circ, \Delta H_3^\circ, \ldots \tag{15}$$

and $\mathbf{G}$ is a diagonal matrix given by

$$\mathrm{Diag}\{\mathbf{G}\} = (k_1 \prod_{k=1}^{n} C_k^{\nu_{1k}^+})^{\frac{1}{2}},\ (k_2 \prod_{k=1}^{n} C_k^{\nu_{2k}^+})^{\frac{1}{2}}, \ldots \tag{16}$$

where k_i is the forward rate constant of the reaction step No. i, C_k is the molar concentration of component No. k, and ν_{ik}^+ is the stoichiometric coefficient for component No. k on the left hand side of the equilibrium in reaction step No. i. ν_{ik}^- is the corresponding stoichiometric coefficient on the right hand side. $\mathbf{M}$ is a matrix defined by

$$\mathbf{M}\,\mathbf{A}\,\mathbf{M}^{-1} = \Lambda \tag{17}$$

where Λ is a diagonal matrix. $\mathbf{A}$ is a matrix given by

$$\mathbf{A} = \mathbf{G}\,\mathbf{N}\,\mathbf{C}^{-1}\,\mathbf{N}^{\mathrm{T}}\,\mathbf{G} \tag{18}$$

where $\mathbf{N}$ is a matrix with the elements

$$\{\mathbf{N}\} = \{\nu_{ij}^{-} - \nu_{ij}^{+}\} \tag{19}$$

and $\mathbf{C}$ is a diagonal matrix with the elements

$$\mathbf{C} = C_1, C_2, C_3, \cdots \tag{20}$$

It appears from eqns. 13 – 20 that the total relaxation strength for the polymerization mechanism is given by eqn. (8) in which

$$Z = \sum_{i=1}^{i=n} \frac{\psi_i^2}{\lambda_i^2} \tag{21}$$

Z is seen to be a function of the parameters which describe the self association of amide only.

In order to construct the entire relaxation spectrum for the polymerization mechanism given by eqn. (6) the following approximations are introduced:

$$k_1 + k_2 = k_3 = \cdots = k_n \tag{22}$$

$$k_{-1} = k_{-2} = k_{-3} = \cdots = k_{-n} \tag{23}$$

$$\Delta H_1^\circ = \Delta H_2^\circ = \Delta H_3^\circ = \cdots = \Delta H_n \tag{24}$$

Since the reaction mechanism in principle consists of an infinite number of reaction steps, the matrices and vectors in eqns. (14) – (20) have an infinite number of elements. In order to calculate ψ_i and λ_i a finite number of reaction steps has to be introduced. A reasonable choise may be obtained by considering the distribution of NMA over the different polymeric species present in the solution. This distribution is given by

$$\phi(i) = \frac{C_i}{\sum_j C_j} \tag{25}$$

or

$$\phi(1) = \frac{C_1}{\sum_j C_j} \tag{26}$$

and

$$\phi(i) = \frac{K_1 (K_n C_1)^i}{K_n^2 \sum_j C_j} \qquad \text{for } i > 1 \tag{27}$$

where $\phi(i)$ is the fraction of the total number of chains which exist as i-mers. The finite number of reaction steps, n, used in the calculations at a given overall concentration is calculated from

$$\sum_i^n \phi(i) \geqslant 0.99 \tag{28}$$

This means that less than 1 % of the chains exists as polymers with more than n units. For a given value of Q the relaxation spectrum can be calculated if the values of B, K_1, K_n, k_{-n}, ΔH_n, and C_i are known. In this paper the relaxation spectra are computed for the overall concentrations of NMA used in the experiments which are reported in a previous paper.[8]

EXPERIMENTAL

The NMA used was fractionally recrystallized at room temperature. The NMA as well as the carbon tetrachloride was dried by passing it through a column with molecular sieves (Linde 4 A). The sound velocity of the solutions was measured at 20.0 ± 0.05°C by means of a NUS Model 6105 Laboratory Velocimeter, which works after the sing around principle. The sound wave used had the frequency 3.5 Mc. The densities of the solutions were measured by means of a Digital Precision Densitometer type DMA 02 produced by Anton Paar K. G., Austria. For the computation of the relaxation spectra a GIER computer was used. The computing time for a relaxation spectrum is about 900 sec.

RESULTS

The ratios of the sound velocity of different NMA/carbon tetrachloride mixtures and the sound velocity in pure carbon tetrachloride at 20°C are given in Table 1. The ratios of the density of different NMA/carbon tetra-

Table 1. The ratios U/U_0 and ϱ/ϱ_0 for different concentrations of NMA dissolved in carbon tetrachloride. U and ϱ are the sound velocity and the density, respectively, of the different solutions. U_0 and ϱ_0 are the values for pure carbon tetrachloride.

C M	0.0530	0.0849	0.1650	0.2095	0.2605	0.3196	0.5093
U/U_0	0.9999	1.0002	1.0014	1.0024	1.0033	1.0046	1.0089
ϱ/ϱ_0	0.9983	0.9974	0.9949	0.9933	0.9918	0.9900	0.9840

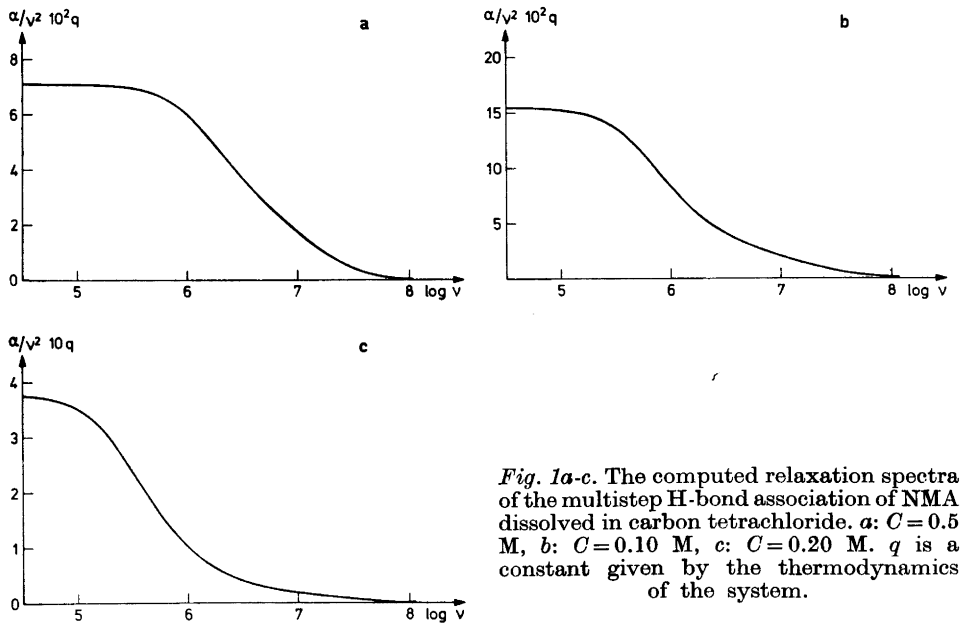

Fig. 1a-c. The computed relaxation spectra of the multistep H-bond association of NMA dissolved in carbon tetrachloride. *a*: $C = 0.5$ M, *b*: $C = 0.10$ M, *c*: $C = 0.20$ M. q is a constant given by the thermodynamics of the system.

chloride mixtures and the density of pure carbon tetrachloride are also given in Table 1. It appears that the change in the velocity and in the density is smaller than 1 % in the concentration range 0.0 – 0.5 M. For the carbon tetrachloride $\beta_T = 10.34 \times 10^{-11}$ cm²/dyne,[16] $\varrho = 1.594$ g/cm³,[16] and $U = 9.38 \times 10^4$ cm/sec.[16] Consequently the value of $\beta_T \varrho U^2$ is equal to 1.46. A 1 % change in $\beta_T \varrho U^2$ thus causes a change of 3 % in Q. Since the concentration dependence of ϱU^2 is very small it seems reasonable to conclude that Q can be considered as being constant at least up to NMA concentrations of about 0.5 M.

Fig. 1 a, b, and c show the constructed relaxation spectra for the polymerization mechanism with $B = 0, K_1 = 4.5\ \mathrm{M}^{-1}, K_n = 45\ \mathrm{M}^{-1}, \Delta H_n^\circ = -5$ kcal/mol, $k_{-n} = 4 \times 10^7\ \mathrm{sec}^{-1}$, the value reported in the previous work,[8] and $C_t = 0.05$ M, 0.10 M, and 0.20 M, respectively. From these spectra the concentration dependence of Z is calculated. Fig. 2 shows the result, obtained for 6 different

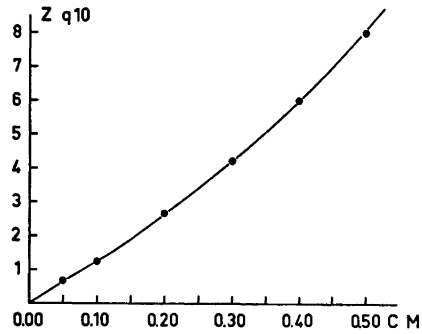

Fig. 2. The dependence of the kinetic part of the relaxation strength, Z, on the overall concentration.

concentrations in the range 0.05 – 0.5 M. As we might have expected, comparing with the result in the simpler case, Z turns out to be an increasing function of the overall concentration of NMA.

DISCUSSION

The sound velocity and the density measurements indicate that the thermodynamic factor in the relaxation strength does not change noticeably in the concentration range 0.0 – 0.5 M for NMA dissolved in carbon tetrachloride. Furthermore the computed relaxation spectra show that the kinetic factor, Z, increases with increasing amide concentration. Consequently the relaxation strength increases with increasing concentration of NMA. Since the measured value of the relaxation strength reported in the previous paper [8] decreases with about 25 % when the concentration increases from 0.08 M to 0.2 M it becomes clear that either the observed relaxation cannot be attributed to the hydrogen bond association of NMA described by mechanism (6) with the approximation given by eqns. 22 – 24 or the value of the relaxation strength actually measured is not equal to A but may be sort of an intermediate A-value connected with the high frequency part of the relaxation spectrum.

The individual relaxation times for the polymerization mechanism, calculated from the values of λ_i, cover a larger frequency range than the one investigated in the previous work.[8] The facts that the experimental results are described by one relaxation time and that the value of α/ν^2 at the high frequencies are very close to the values of the pure solvent lead to the approximation that the largest eigenvalue, λ_1, is associated with the largest relaxation strength and consequently is the one which is responsible for the observed relaxation. Although this approximation is exact in the limit $C \rightarrow 0$, it is seen from Fig. 1 a that already at 0.05 M the largest eigenvalue is not the only one which is responsible for the relaxation. Thus the computed spectrum predicts a considerable increase in α/ν^2 at lower frequencies at which the ultrasonic absorption technique does not permit measurements to be made yet. Instead of fitting the data to eqn. (1) with $i = 1$ it would presumably be a better approximation to consider the measured relaxation as being the upper part of the entire relaxation spectrum. Consequently a fit of the data to eqn. (13) is to prefer. As mentioned above the value of α/ν^2 at a given frequency can be calculated from eqn. (13) if B, Q, K_1, K_n, k_{-n}, ΔH_n, and C_t are known. A fit of the data to eqn. (13) is thus a 6-parameter fit. The values of K_1, K_n, and ΔH_n, however, are estimated from other types of experiments.[9-11] If these values are introduced the data fit turns out to be a 3-parameter fit giving the values of Q, B, and k_{-n}. Fig. 3 shows the best theoretical curves obtained by fitting the data to eqn.

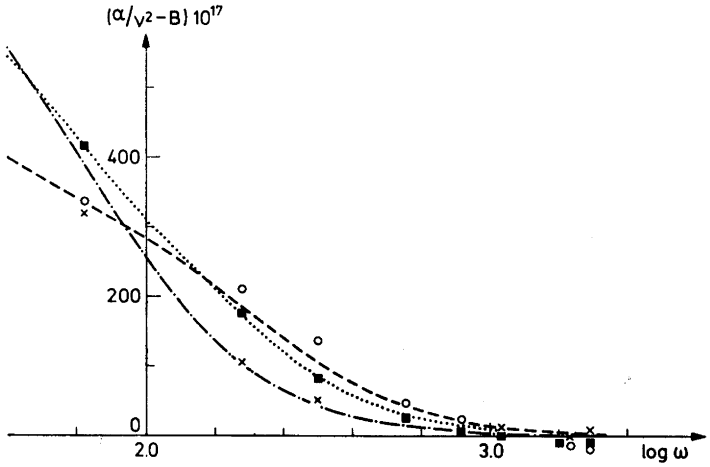

Fig. 3. The best theoretical curves obtained by fitting the experimental data to eqn. (13) by means of a least square fitting procedure. × (— · —): 0.0406 M; ■ (···): 0.0801 M; ○ (— — —): 0.2316 M.

(13) by means of a least square fitting procedure [17] with the above given values of K_1, K_n, and ΔH_n involved. Although the agreement between these curves and the actual measured values of α/ν^2 is not within experimental error ($\pm$ 2 %) for all the points, there is a clear tendency that the values of α/ν^2 at the lowest frequencies decrease with increasing solute concentrations. It is therefore

consistent with the present work to consider the previously published relaxation strength as sort of an intermediate A-value. The value of k_{-n} obtained by the fitting procedure is 2.9×10^8 sec^{-1}, which means it is approximately a factor of 7 larger than the one given in the previous work.

CONCLUSION

It is shown that the relaxation strength of the ultrasonic relaxation spectrum caused by the H-bond association of NMA, can be considered as a product of two factors, Q and Z. Q depends on the thermodynamic properties of the solute/solvent mixture while Z depends on the properties of self association of solute. Q is shown to be independent of the NMA concentration at least up to 0.5 M while Z is shown to increase in this concentration range. Consequently the relaxation strength must increase with increasing solute concentration.

The experimentally observed decrease in the relaxation strength previously reported [8] thus at a first glance seems to contradict that the H-bond association of NMA can be responsible for the observed relaxation. The computed relaxation spectra predict, however, an increase in α/ν^2 at lower frequencies at which the ultrasonic absorption technique as yet does not permit measurements to be made. Consequently the relaxation time obtained by fitting the data to the one relaxation time equation does not correspond to the largest eigenvalue of the coefficient matrix only. Although this relaxation time is proportional to the reciprocal of the largest eigenvalue in the limit $C \rightarrow 0$, already at a solute concentration of 0.05 M the remaining eigenvalues play a role in the relaxation spectrum. This explains the observed decrease with concentration of the measured relaxation strength which is to be considered as an intermediate relaxation strength connected with high frequency part of the relaxation spectrum.

It is to be noticed, that although the experimental results fit the one relaxation time equation within experimental error in a wide frequency and concentration range, a decrease in the calculated A-parameter with increasing solute concentration indicates that the relaxation spectrum covers more than the frequency range investigated and that an increase of α/ν^2 at lower frequencies is to be expected.

The proportionality factor between the largest eigenvalue of the coefficient matrix and the reciprocal of the relaxation time measured for dilute solutions is a rough estimate of the common depolymerization rate constant.

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