

Ultrasonic Relaxation Spectra in Aqueous Solutions of Dextran and Polyethylene Glycol

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fit the theoretical (solid) curves for a single relaxation extremely well, although this does not preclude the existence of other relaxation processes at far lower frequencies or with much smaller amplitudes. A similar treatment of the data presented by Hawley and Dunn for polyethylene glycol (M.W. 20 000) yields a maximum above 10 MHz with deviations from a single relaxation process at low frequencies. The simplest interpretation is that multiple relaxations occur, but that at frequencies >10 MHz the fastest process predominates. All of the data can be fit quite precisely with the assumption of the two relaxation processes.

Viscoelastic theories of free⁶ and nonfree⁷ draining random coils predict a series of relaxations occurring at the relaxation frequencies, $f_p = K_p RT / M \eta [\eta]_0$, where K_p is a constant, η is the solvent viscosity, and $[\eta]_0$ is the low-frequency intrinsic solution viscosity for a polymer of molecular weight M . The excess sound absorption attributable to shear viscosity is given by²

$$\frac{\Delta\alpha}{c^2} = \frac{4\pi RT}{3\rho V^3 M} \sum_{p=1}^N \frac{1/f_p}{1 + (f/f_p)^2},$$

where c is the concentration, ρ is the density, V is the sound velocity, and $\Delta\alpha$ is the excess sound absorption coefficient.

Three points should be noted: (1) The theory of viscoelastic processes predicts a distribution of relaxation times for polymers of all molecular weights. This distribution of relaxation times will fit the data if the additional assumption of a molecular weight dependent amplitude coefficient is made.⁸ However, all of the data can be fit more simply and precisely by a maximum of two relaxation times; one is sufficient for low molecular weight polymers even for an extended frequency range both above and below the relaxation frequency (cf. Fig. 1). (2) The relaxation frequency is expected to decrease in urea solutions of polyethylene glycol since η and $[\eta]$ increase. However, for molecular weights below 3400 the relaxation frequency has been found to remain constant and for higher molecular weights to actually increase. This increase occurs sharply over a small range in urea concentration which is difficult to reconcile with any viscoelastic properties, but is in agreement with a mechanism involving co-operative polymer-solvent interactions. The average deviation of the corresponding amplitudes from their average value is $\leq 10\%$. (3) Finally, as recognized by Hawley and Dunn, the magnitude of the absorption predicted on the basis of viscoelastic effects is considerably less than observed, so that viscoelastic relaxation itself cannot adequately account for the experimental results.

Thus the *simplest* explanation of all of the data is that previously proposed: In the frequency range 10–200 MHz a single relaxation process occurs, which involves co-operative polymer-solvent interactions.^{2–5} Insufficient data is available to establish the nature of the

additional relaxation process(es) occurring at lower frequencies.

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⁸ S. A. Hawley (private communication).

Ultrasonic Relaxation Spectra in Aqueous Solutions of Dextran and Polyethylene Glycol*

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In an investigation of the ultrasonic absorption in aqueous solutions of dextran (polyanhydroglucose), we have observed¹ that the spectral characteristics can be described by the distribution of relaxation times specified by Rouse² for the dynamic behavior of free-draining random coils. We have pointed out that while this model provides a suitable distribution which correctly predicts a number of structural details of the relaxation spectra, the absorption is somewhat greater than can be simply attributed to the solution viscoelasticity—the property for which the model is intended to describe. Further, the possibility is cited¹ that the observed absorption results from a coupling of the normal modes with an unspecified process involving the aqueous environment. While this interpretation is admittedly vague, it is at least semantically identical to the position Hammes and Roberts have defended in the preceding comments for polyethylene glycol solutions. We have merely suggested that the dynamic behavior of the polymer provides such a cooperative process.

The magnitude of the relaxation in solutions of polyethylene glycol is somewhat less than for dextran, and the evidence concerning the relaxation behavior is not as conclusive. Insofar as we are able to discern from the available information, however, there is nothing which precludes the involvement of normal modes in determining the absorption. This includes the fact that Hammes and Roberts have observed that in the frequency range 10–175 MHz the absorption in solutions of polyethylene glycol over the molecular weight range

400–20 000 can be represented quite well by a single relaxation fit. The technique³ employed to provide these fittings, however, is based on the *a priori* assumption that a single relaxation is implicated. One can not readily establish this is, in fact, the case for all molecular weights solely from the data of Hammes and co-workers. The studies of O'Brien⁴ and of Kessler⁵ extend the relaxation spectra a decade lower in frequency and establish that for molecular weights above 4500 more than one relaxation is involved.

It is interesting that evidence suggesting relevance of the normal mode distribution can be derived from the data of Hammes and co-workers. The normal mode distribution is such that by far the largest contribution arises from the first term or primary mode. Relaxation measurements in the vicinity of or lower than the characteristic frequency (f_1) of this mode will be dominated by its presence. If f_1 is computed from intrinsic viscosity measurements, one finds⁶ that at a molecular weight of about 3500, $f_1 = 10$ MHz, the lower limit of the observations of Hammes and Roberts. For lower molecular weights, f_1 is in their experimental range and the observed behavior will approach that of a single relaxation. At higher molecular weights, f_1 will be receding from their range toward lower frequencies. They observe elsewhere⁷ that the apparent single relaxation frequency decreases with increasing molecular weight and reaches a limiting value at a molecular weight of 3400. This behavior is in fact very close, perhaps fortuitously, to that expected from the normal mode distribution. It is not surprising that we have been able to provide reasonable fittings to all the data presented in the above comments utilizing the normal mode distribution with the presumption factor as the only adjustable parameter. These fittings are similar in appearance at lower molecular weights to those illustrated in Fig. 1 (preceding comment) but gradually broaden with increasing molecular weight and account for the additional evidence provided by O'Brien and Kessler.

Hammes and Roberts also mention the observation that under some circumstances the single relaxation frequency increases in urea solution. Both the viscosity of the solvent and the intrinsic viscosity increase with increasing urea concentration and the calculated f_1 should decrease. This argument would have validity if all other apparent single relaxation parameters remained constant though this is not the case. Their

data⁷ reveal, for example, that at molecular weight 4500 while the apparent relaxation frequency increases by about 50%, the relaxation strength also shows a tendency to increase rather unsystematically by as much as 50%. Again this behavior is at least reconcilable with a normal mode distribution.

While the compatibility of the normal mode distribution with the experimental data only suggests its relevance for polyethylene glycol, the single relaxation formulation can hardly be considered an alternative. Criteria which establish the limits of applicability of the single relaxation representation for a given frequency range, relaxation strength, and associated errors are well known.⁸ To this point these considerations have not been demonstrated by Hammes and co-workers, and it is our opinion that further commentary on the relevance of single relaxation representation should be in this context.

* This investigation was supported in part by the National Institute of Health and in part by the Office of Naval Research.

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⁶ Discussion of the calculation of f_1 is found in Ref. 1.

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⁸ K. F. Herzfeld and T. A. Litovitz, *Absorption and Dispersion of Ultrasonic Waves* (Academic, New York, 1959), p. 73.

Errata

Erratum: Vibrational Relaxation in CO₂ and CO₂-Ar Mixtures Studied Using a Shock Tube and a Laser-Schlieren Technique

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The term k used on page 2217 has been defined as the mole fraction of argon. This is incorrect, it should be defined as the fraction by weight.