

TRANSPORT PROPERTIES OF POLYMER SOLUTIONS

A Comparative Approach

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ABSTRACT A variety of transport properties have been measured for solutions of the water soluble polymer poly(ethylene oxide)(PEO) with molecular weights ranging from 200 to 14,000, and volume fractions ranging from 0–80%. The transport properties are thermal conductivity, electrical conductivity at audio frequencies (in solutions containing dilute electrolyte), and water self-diffusion. These data, together with dielectric relaxation data previously reported, are amenable to analysis by the same mixture theory. The ionic conductivity and water self-diffusion coefficient, but not the thermal conductivity, are substantially smaller than predicted by the Maxwell and Hanai mixture relations, calculated using the known transport properties of pure liquid water. A 25% (by volume) solution of PEO exhibits an average dielectric relaxation frequency of the suspending water of one half that of pure water, with clear evidence of a distribution of relaxation times present. The limits of the cumulative distribution of dielectric relaxation times that are consistent with the data are obtained using a linear programming technique. The application of simple mixture theory, under appropriate limiting conditions, yields hydration values for the more dilute polymer solutions that are somewhat larger than values obtained from thermodynamic measurements.

INTRODUCTION

It is well established that hydration effects play an important role in the transport properties of biological systems. However, a precise understanding of these effects has not been achieved, and the properties of “biological” water remain controversial. A variety of transport properties have been studied in tissues and suspensions of biological macromolecules, including water self-diffusion (for a review see Hazelwood, 1979), electrical conductivity (e.g., Bull and Breese, 1969), dielectric permittivity and relaxation (for a review see Schwan, 1957), and thermal conductivity (e.g., Kong et al., 1982). While these properties arise from different molecular processes, each is governed on a macroscopic level by Laplace’s equation. Therefore, on the macroscopic level there is a fundamental underlying connection among them (Batchelor, 1974). We believe that a comparison of these transport properties in polymer-water solutions can help elucidate the effects of hydration on the transport properties of the more complex biological systems.

The present study will compare the above mentioned transport properties in aqueous solutions of poly(ethylene oxide) (PEO), which is one of the simplest polymers that is completely miscible with water. This choice of systems was motivated by dielectric relaxation studies by Kaatz et al. (1978a,b) and by our own dielectric studies on microemulsions (Foster et al., 1982; Epstein et al., 1983) in

which the ethylene oxide group was the principal water soluble moiety of the surfactant. These dielectric studies disclosed large changes in the relaxation properties at microwave frequencies, compared with those of pure liquid water, which clearly arise from hydration effects. We found that corresponding changes can be observed in some, but not all, of the transport properties mentioned above.

The hydration properties of PEO solutions have been extensively studied. A variety of thermodynamic studies (summarized in Molyneux, 1975) suggests that the stoichiometric amount of hydration water (i.e., that directly associated with the polymer at any instant) corresponds to two water molecules per ethylene oxide (EO) group. Because the EO group can accept two protons in forming hydrogen bonds (Franks, 1973), a hydration number of 2 is expected on simple chemical grounds as well. Thus, there is a firm basis for comparing the apparent hydration of the PEO obtained from the transport measurements, with values obtained by other methods. Curiously, Kaatz (1978a,b) obtained a value of 5.4 water molecules of hydration per EO group, which is twice that expected from the above arguments. Because “hydration” is not a precisely defined quantity, it can be expected to vary with experimental method. Thus, Kaatz’s results, while not necessarily incorrect, are puzzling. A second purpose of the present study is to understand the reasons for this discrepancy.

A final goal of this work is to examine the transport

properties of this simple model system using methods of analysis (mixture theory) that are similar to those used in the studies on the biological macromolecules that are cited above. We find that our results confirm and extend this earlier work.

MATERIALS AND METHODS

For the present measurements, PEO was used as obtained from Aldrich Chemical Co., Inc. (Milwaukee, WI), with weight average molecular weights ranging from 200 to 14,000 daltons. For the electrical conductivity measurements, the polymer was dissolved in 0.1 N KCl; the remaining measurements were performed using distilled water. In calculating volume fractions of the polymer, a partial specific volume of 0.885 cm³/g was assumed. All measurements were performed at 25°C.

Electrical conductivity measurements were performed using a Hewlett-Packard model HP4192 impedance analyzer (Hewlett-Packard Co., Palo Alto, CA) under computer control, with a conductivity cell similar to that described by Pauly and Schwan (1966). The conductivity was constant between 1 and 100 kHz, ruling out electrode polarization or other artifacts.

The self-diffusion coefficients of the water were measured using a JEOL FX90Q Fourier transform NMR spectrometer (JEOL USA, Analytical Instruments Div., Cranford, NJ), operating at 90 MHz for protons. The pulsed-field-gradient technique was employed using the homospoil coils in the spectrometer to establish the field gradient, similar to that described by Stilbs (1982). In PEO, the only exchangeable protons are on the terminal OH groups, and the required corrections to the water self-diffusion coefficients due to proton exchange are consequently negligible.

Thermal conductivity measurements were performed using a thermistor probe technique similar to that described previously (Balasubramanian and Bowman, 1977). A small thermistor was immersed in the sample and subjected to a step temperature increase of 2°C within a few milliseconds; the voltage across the thermistor was subsequently sampled at 25 Hz with 12-bit resolution by microcomputer. A linear regression of the power developed in the thermistor against the inverse square root of time yields the steady state power dissipation whose inverse is a linear function of the inverse of the thermal conductivity of the sample. This technique avoids the problems due to convective currents that are established by thermal gradients in liquids, and yields values for the thermal conductivity that are accurate to 1–2%, as judged from measurements on fluids of known thermal conductivity.

The basis for interpreting the results is mixture theory, which relates the transport properties of the bulk material to those of the suspended and continuous phases. As in the studies on the biological molecules cited above, we have made the logical extension of the mixture theory to solutions, so that the transport properties of the solution can be predicted from those of its components. A variety of mixture theories have been proposed, of which the most widely used is the Maxwell-Fricke relation (Fricke, 1924):

$$\Lambda_s/\Lambda_w = \frac{\chi\Lambda_w + \Lambda_p - p\chi(\Lambda_w - \Lambda_p)}{\chi\Lambda_w + \Lambda_p + p(\Lambda_w - \Lambda_p)} \quad (1)$$

where Λ is a generalized conductivity, the subscripts s, p, and w refer, respectively, to the solution, the polymer, and water, and p is the volume fraction of the dry polymer (solute). The shape factor χ takes on the value 2 for spherical particles, and 1.5 for thin, rodlike particles of random orientation. We would expect that the appropriate value for the polymer species would be somewhere between these rather narrow limits. To first order in Λ_p/Λ_w , Eq. 1 reduces to

$$\Lambda_s \approx \Lambda_w \left[\frac{\chi(1-p)}{\chi+p} \right] + \Lambda_p p \left[\frac{1+\chi}{\chi+p} \right] \quad (2)$$

The generalized conductivity Λ could be interpreted as the electrical conductivity σ (for the measurements at low frequencies) or thermal conductivity K . For the dielectric relaxation measurements at microwave frequencies, it would be interpreted as the complex conductivity σ^* defined as

$$\sigma^* \equiv \sigma + j\omega\epsilon'\epsilon_r \quad (3)$$

where ϵ' is the relative permittivity, ω the circular frequency, and ϵ_r is a constant (the permittivity of free space). For the self-diffusion measurements, the generalized conductivity would be the quantity $(1-p)D$, where D is the self-diffusion coefficient measured by pulsed NMR. The additional factor $(1-p)$ is needed because the NMR technique measures mean-square displacements of water in the aqueous region only, while the true diffusion coefficient is defined in terms of transport through the entire volume (Clark et al., 1982; Lauffer, 1961).

The Maxwell-Fricke relation has obvious limitations that should be noted. First, the appropriate value of the shape factor is not known for the polymers that are used in this study; however, it is most likely to be between 2 (for spherical species) and 1.5 (for randomly oriented rodlike species). We have chosen the value 2 for subsequent analysis. The transport properties in solution will depend on the frictional properties of the polymer, which, for a random coil polymer like PEO, can be approximated by considering the polymer to consist of a chain of spherical monomeric units, each having a shape factor equal to 2. Because the same shape factor would apply to all of these transport properties, a comparative study is still valid in spite of some uncertainty in choosing the value of this parameter.

The second major limitation is that the Maxwell-Fricke equation does not properly take into account the presence of neighboring species and is correct only to first order in p (Chiew and Glandt, 1983). However, the errors that result are generally small when the generalized conductivity of the solute is much less than that of the continuous medium, which is the case at present. For comparison, the Hanai mixture expression (Hanai, 1968), based on a calculation which is more consistent in its treatment of neighboring particles, predicts

$$\left(\frac{\Lambda_s - \Lambda_p}{\Lambda_w - \Lambda_p} \right) \left(\frac{\Lambda_w}{\Lambda_s} \right)^{1/3} = 1 - p. \quad (4)$$

As will be seen, the results from the Maxwell-Fricke and Hanai equations are quite close. The results from the Maxwell-Fricke relation for randomly oriented rods are intermediate between those for spheres and the Hanai results, and are not considered in the following discussion.

RESULTS

Three transport properties of the PEO solutions of varying molecular weights are shown in Figs. 1–3. The predictions of the Maxwell-Fricke and Hanai theories are shown for comparison. These were calculated assuming that the properties of the water are identical to those of the pure liquid. The transport properties of the pure polymer were found from Figs. 1–3 in the limit where p approaches 1. The thermal conductivity of the polymer was 0.31 times that of water, while the ionic conductivity and water self-diffusion was zero (as expected).

The dielectric relaxation properties of a great many solutions of water soluble polymers, covering a wide range of molecular weights, were reported by Kaatz et al. (1978a,b). These measurements were performed between 0.4 and 35 or 70 GHz, where the dipolar relaxation of the water would be the dominant source of the dielectric dispersion since the polymer itself is expected to have a low

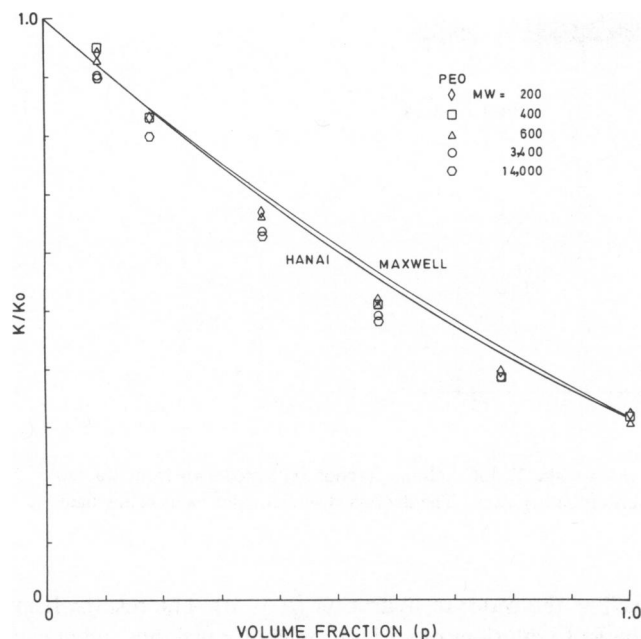


FIGURE 1 Thermal conductivity K of PEG solutions, divided by that of pure water (K_0) vs. volume fraction p of the solution. Also shown are the predictions of the Maxwell (Eq. 1) and Hanai (Eq. 4) mixture relations.

permittivity at these frequencies. A complex permittivity plot of the dielectric properties of a solution of PEO of molecular weight 37,400 at a volume fraction p of 0.25 is presented in Fig. 4. (This is the highest PEO concentration for which relaxation data were reported.) The plot shows a

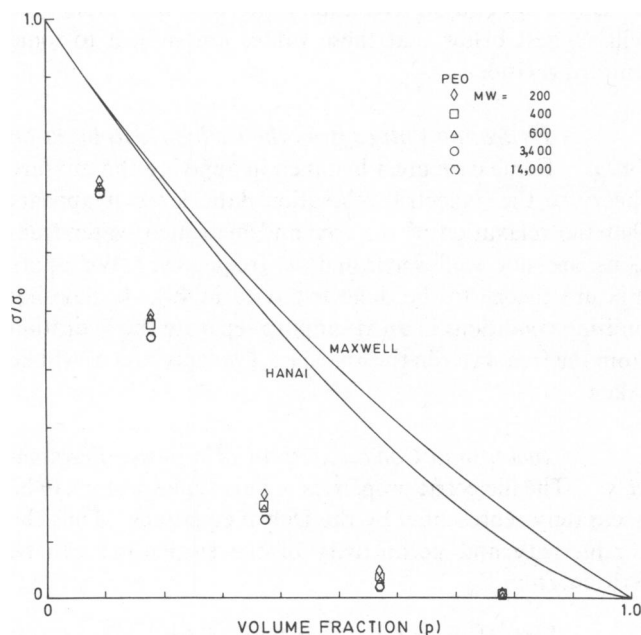


FIGURE 2 Electrical conductivity σ of PEG solutions in 0.1 N KCl, divided by the conductivity of the neat electrolyte, σ_0 , vs. the volume fraction p of the polymer. Also shown are the predictions of the Maxwell and Hanai mixture relations.

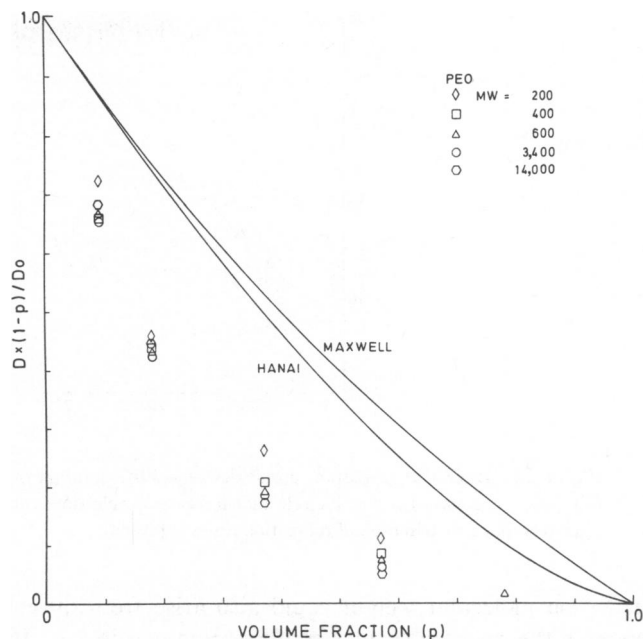


FIGURE 3 Normalized water self-diffusion coefficient (measured by a pulsed NMR technique) vs. the volume fraction p of the polymer. The quantity D is the apparent self-diffusion coefficient of the solution measured by pulsed NMR and D_0 is that of pure liquid water; the need for the factor $(1 - p)$ is explained in the text. The Maxwell and Hanai predictions are also shown.

depressed semicircular locus indicating a distribution of relaxation times in the sample. The center frequency of the relaxation of the PEO solution, corresponding to the apex of the semicircle, is ~ 10 GHz, one-half that of pure water at the same temperature.

The work of Kaatz (1978b) and Figs. 1–3 suggest a slight dependence of the transport properties on the molecular weight of the polymer. Kaatz interpreted this as resulting from changes in the flexibility of the polymer as a function of molecular weight. Perhaps a more fundamental interpretation of this effect could be based on the variation of free volume with molecular weight in these solutions. In the model summarized by Ferry (1980), the transport coefficients are related to the frictional coefficient of the solution, which in turn is related to the free volume of the solution. This treatment has led to successful interpretations of the transport properties of polymer solutions, in particular the self-diffusion coefficients of solvents (Ferry, 1980). This earlier work suggests that solutions of lower molecular weight should have more free volume and hence higher values for the transport properties. However, it should be noted that the magnitude of this effect in the PEO solutions is much less than one would expect on the basis of the previous studies on polystyrene-cyclohexane (Ferry, 1980). This could arise from a stronger mutual interaction between the PEO and water than between polystyrene and cyclohexane, which could significantly dampen the molecular weight effect. In part, some depen-

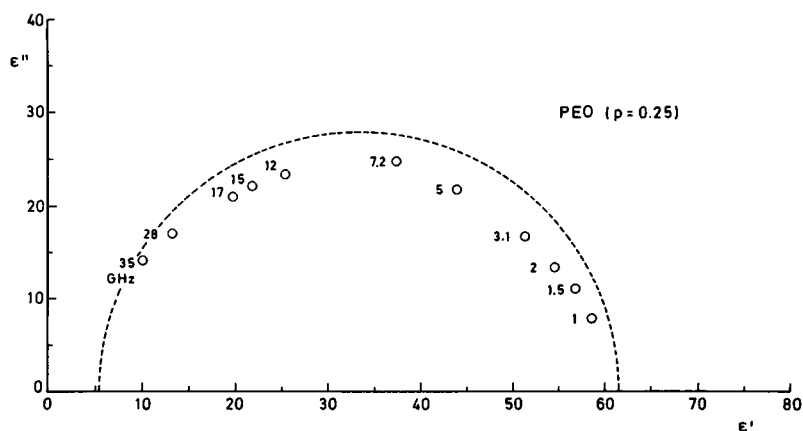


FIGURE 4 Dielectric relaxation properties of a PEG solution of molecular weight 37,400, volume fraction 0.25, redrawn from Kaatz (1978a). Also shown is a semicircle that indicates single time constant relaxation behavior. The depressed semicircular locus of the data indicates that a distribution of relaxation times is present.

dence on molecular weight could also arise from differences in the macromolecular conformation in solution. In all of the properties considered here, the molecular weight effect becomes very small for solutions of PEO with molecular weights above ~500 daltons.

DISCUSSION

The results shown in Figs. 1–4 show that three of the transport properties (water self-diffusion, ionic conductivity, and dielectric relaxation) deviate significantly from the predictions of the mixture theories, while one (thermal conductivity) is only slightly lower than predictions. The simplest interpretation is that the self-diffusion coefficient, electrical conductivity, and dielectric relaxation frequency of the hydration water are all significantly reduced compared with their respective values in pure solution, but the thermal conductivity was not. We will return to this point in a later section.

In the following discussion, we will estimate the apparent hydration of the PEO from the various transport properties, using an approach previously employed in our studies of hydration effects in microemulsions (Foster et al., 1982a; Epstein et al., 1983), and in DNA gels (Foster et al., 1984). We then consider the rather different hydration values obtained by Kaatz (1978a,b), and suggest possible explanations for the differences. Finally, we consider possible physical mechanisms leading to the different transport properties of the hydration water.

Apparent Hydration of the PEO from Self-Diffusion and Conductivity Data

The basic assumption in this calculation is that the transport through the combined polymer and its hydration water is negligible compared with that through the surrounding “bulklike” water. An excluded volume p' can be calculated from the Maxwell or Hanai equations, that includes the volume fraction of anhydrous polymer (p) as

well as the water of hydration ($p' - p$). The results, from the PEO solutions of various molecular weights and choice of two mixture theories, are shown in Table I. For the two most dilute solutions, the apparent volume fractions average 2.5 and 2.3 times those of the anhydrous polymer from the Maxwell and Hanai formulas, respectively, corresponding to 3.3 and 2.8 water molecules per EO group. Table I also shows the apparent volume fraction for a solution of $p = 0.25$, which was interpolated from the data, for comparison with the dielectric data to be discussed below.

It should be noted that the hydration values thus calculated are lower limits that would pertain if the transport through the hydration water were negligible. We will suggest below that these values are subject to some upward revision.

Hydration Values from the Dielectric Relaxation Data. Some care must be taken in applying the mixture theory to the dielectric relaxation data, since it appears that the relaxation of the free and hydration water fractions are not well separated in frequency. We apply mixture theory to the dielectric data in Fig. 4, choosing limiting conditions in an attempt to separate the hydration from the free water in the analysis. Two approaches will be taken.

Increase in Conductivity at Microwave Frequencies. The dielectric properties of pure liquid water can be accurately represented by the Debye equations. Thus the conductivity and permittivity of the suspension can be written, from Eq. 2,

$$\sigma = \frac{(2\pi f^2/f_c)(\epsilon_s - \epsilon_\infty)\epsilon_t}{1 + (f/f_c)} \left[\frac{1 - p'}{1 + p'/2} \right] + \sigma_p \left[\frac{1 + \chi}{\chi + p'} \right]^2$$

$$\epsilon = \left[\frac{\epsilon_s - \epsilon_\infty}{1 + (f/f_c)^2} + \epsilon_\infty \right] \left[\frac{1 - p'}{1 + p'/2} \right] + \epsilon_p \left[\frac{1 + \chi}{\chi + p'} \right]^2 p' \quad (5)$$

TABLE I
APPARENT HYDRATION OF PEO SOLUTIONS
FROM TRANSPORT MEASUREMENTS

Molecular weight	p	σ/σ_0	p'		$(1-p)D/D_0$	p'	
			Maxwell	Hanai		Maxwell	Hanai
200	0.09	0.723	0.20	0.19	0.724	0.20	0.19
	0.18	0.489	0.41	0.38	0.458	0.44	0.41
	0.37	0.182	0.75	0.68	0.260	0.65	0.59
	0.57	0.048	0.93	0.87	0.111	0.84	0.77
	0.78	0.009	0.99	0.96			
	0.25*	0.376	0.53	0.48	0.385	0.52	0.47
400	0.09	0.703	0.22	0.21	0.659	0.26	0.24
	0.18	0.478	0.42	0.39	0.436	0.46	0.43
	0.37	0.165	0.77	0.70	0.208	0.72	0.65
	0.57	0.037	0.95	0.89	0.085	0.88	0.81
	0.78	0.006	0.99	0.97			
	0.25*	0.363	0.54	0.49	0.352	0.55	0.50
600	0.09	0.714	0.21	0.20	0.666	0.25	0.24
	0.18	0.486	0.41	0.38	0.432	0.47	0.43
	0.37	0.158	0.78	0.71	0.191	0.74	0.67
	0.57	0.034	0.95	0.90	0.072	0.90	0.83
	0.78	0.005	0.99	0.97	0.015	0.98	0.94
	0.25*	0.365	0.54	0.49	0.343	0.56	0.51
3,400	0.09	0.707	0.22	0.21	0.656	0.26	0.25
	0.18	0.455	0.44	0.41	0.426	0.47	0.43
	0.37	0.137	0.81	0.73	0.186	0.74	0.67
	0.57	0.023	0.97	0.92	0.058	0.92	0.85
	0.25*	0.340	0.56	0.51	0.338	0.57	0.51
14,000	0.09	0.706	0.22	0.21	0.681	0.24	0.23
	0.18	0.453	0.45	0.41	0.442	0.46	0.42
	0.37	0.137	0.81	0.73	0.174	0.76	0.69
	0.57	0.027	0.96	0.91	0.051	0.93	0.86
	0.25*	0.337	0.57	0.52	0.351	0.55	0.50

*Interpolated from other data in the table. (For comparison with dielectric relaxation data.)

where ϵ_s and ϵ_∞ are the limiting values of the relative permittivity at low and high frequencies, and f_c is the relaxation frequency. The values of these parameters that pertain to pure liquid water at 25°C are, respectively, 78.5, 5.2, and 19.7 GHz (Kaatze, 1978a). In Eq. 5, the first terms represent the contribution of the free water to the permittivity and conductivity. At sufficiently high frequencies, the increase in conductivity with frequency should be dominated by the dielectric relaxation of the free water. Thus a plot of the conductivity vs. the function $x = [(2\pi f^2/f_c)\epsilon_\infty]/[1 + (f/f_c)^2]$ should tend, at high frequencies, to a linear function with slope $[(\epsilon_s - \epsilon_\infty)(1 - p')]/(1 + p'/2)$. The results of this analysis are shown in Fig. 5. A linear regression analysis of the conductivity against x , together with Eq. 5, leads to an apparent volume fraction p' of 0.60, corresponding to 3.0 water molecules per EO group. The dielectric relaxation frequency of this bound water (taken to be the frequency at which the conductivity of the slowly relaxing fraction is one-half of its limiting value of 90 mS/cm) is ~ 4 –5 GHz, or roughly one quarter that of the pure liquid. A similar analysis of the microwave dielectric properties of oil in water microemulsions sug-

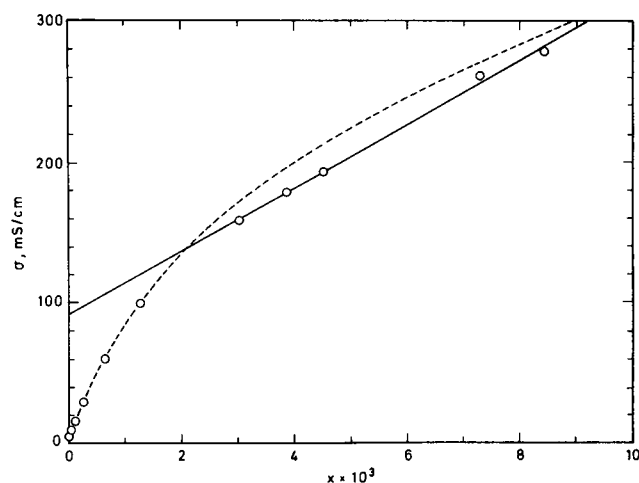


FIGURE 5 The same data from Fig. 4, in which the conductivity at microwave frequencies, σ , is plotted vs. the quantity x defined in the text. Also shown (---) is the fitted function, Eq. 5. A linear regression of the conductivity data above 12 GHz against x (—) yields a slope of 22.72×10^{-3} mS/cm, and an intercept of 91.36 mS/cm.

gested a relaxation frequency of the hydration water of roughly 5 GHz in suspensions of volume fraction water above ~ 0.6 , decreasing to ~ 2 GHz in systems of lower water content (Foster et al., 1982a; Epstein et al., 1983).

Permittivity at High Frequencies. For single time constant (Debye) relaxation as described in Eq. 5, the permittivity increase $(\epsilon - \epsilon_\infty)$ at high frequencies will fall

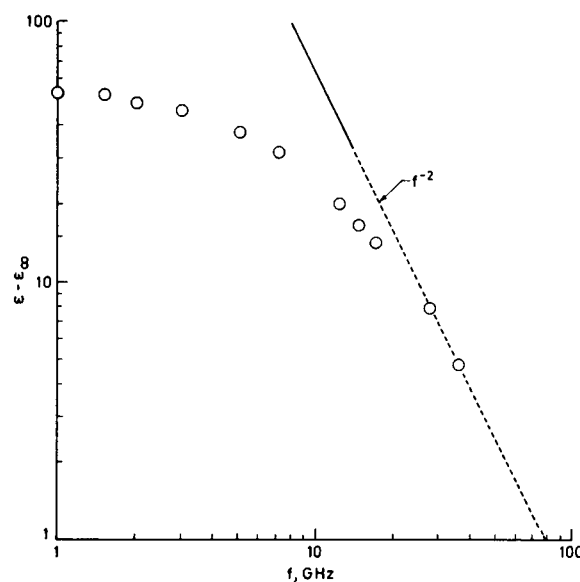


FIGURE 6 The permittivity data from Fig. 4, minus the high frequency limiting permittivity ϵ_∞ (assumed to be 4), vs. the frequency f . The data tend towards a limiting slope of -2 (---) characteristic of single time constant relaxation, suggesting that at these high frequencies the relaxation chiefly arises from the free water in the solution. Using mixture theory, the hydration is estimated from the permittivity at the two highest frequencies (see text).

off as the inverse square of the frequency. This behavior is clearly evident in Kaatz's data (Fig. 6). It can be assumed that the hydration water has relaxed at the highest frequencies of measurement (27 and 35 GHz) and has a relative permittivity of 4 to 5. From the measured complex permittivity of the solution and the known complex permittivity of pure water, and assuming a relative permittivity of $4 + 0j$ for the combination of the polymer and its water of hydration at high frequencies, a volume fraction p' of 0.45 or 0.48 is found from the Hanai or Maxwell expressions at 35 GHz. A similar analysis of the data at 27 GHz yields values of p' of 0.43 and 0.46, for the Hanai and Maxwell relations, corresponding to hydration values of 1.6 and 1.8 water molecules per EO group. However, this calculation is sensitive to the assumed permittivity of the combined polymer and its water of hydration; a choice of $4 + 6j$ for this quantity yields a volume fraction of 0.60 (or a hydration number of 3.0) using the Maxwell relation and the dielectric data at 35 GHz. For a PEO solution of the same concentration, the (interpolated) conductivity and self-diffusion data would yield hydration values of 2.2 and 2.8 water molecules per EO group using apparent volume fractions p' of 0.50 and 0.55 from the Hanai and Maxwell formulas (Table I).

Previous Calculation of PEO Hydration from the Dielectric Data. From the data shown in Fig. 4, Kaatz (1978a,b) obtained a hydration number of 5.4 water molecules per EO group, which is nearly twice the value we obtained. Moreover, the relaxation frequency of the hydration water was found to be 9.5 GHz, which is twice that presently obtained. We will suggest two possible reasons for this disagreement. Because important limitations in the interpretation of dielectric data are suggested, we will comment at some length.

□ RANGE OF TRADEOFFS IN INTERPRETING DIELECTRIC RELAXATION DATA Kaatz et al. (1978a,b) numerically fitted the data in Fig. 4 to a sum of relaxation terms representing the free and hydration water and the polymer:

$$\epsilon' - j\epsilon'' + \frac{\epsilon_m - \epsilon_\infty}{\epsilon_w} \left[\frac{Z_{hc}}{1 + (j\omega\tau_h)^{1-h}} + \frac{\epsilon_w - Z_{hc}}{1 + (j\omega\tau_w)^{1-h_w}} \right] + \frac{\epsilon_s - \epsilon_m}{1 + (j\omega\tau_o)} + \epsilon_\infty \quad (6)$$

The identification of the symbols in Eq. 6, and the values that were obtained for the solution whose dielectric properties are shown in Fig. 4, are in Table II. (The function used to represent the free water deviates only slightly from the single time constant approximation in Eq. 5 above.) The uncertainty limits that are indicated in Table II were quoted from Kaatz (1978a,b), and reflect the numerical uncertainties in fitting the data to Eq. 6.

TABLE II
IDENTIFICATION OF PARAMETERS IN EQ. 6

Parameter	Identification	Value
ϵ_m	total contribution of free and hydration water to the permittivity at frequencies below ~1 GHz	$56.5^{+0.8}_{-0.8}$ (fitted)
ϵ_∞	limiting value of the permittivity at high frequencies	5.2 ± 0.2 (fitted)
ϵ_s	limiting value of the permittivity at low frequencies	$61.5^{+0.3}_{-0.3}$ (fitted)
c_w	total concentration of water (mol/liter)	41.54 (known)
c	concentration of polymer (mol/liter) (calculated on a monomer basis)	6.82 (known)
Z_h	number of hydration water molecules per monomer	$5.4^{+0.2}_{-0.2}$ (fitted)
ω	measurement frequency (rad/s)	
h	distribution parameter for the hydration water (zero for single time constant relaxation)	$0.06^{+0.02}_{-0.02}$ (fitted)
h_w	distribution parameter for bulk water relaxation	0.007 (known)
τ_h	mean relaxation time of hydration water (ps)	$16.9^{+1.5}_{-0.5}$ (fitted)
τ_w	mean relaxation time of free water (ps)	8.25 (known)
τ_u	mean relaxation time of the polymer (ps)	90^{+0}_{-8} (fitted)

The values given pertain to a PEO solution of molecular weight 37,400, with volume fraction 0.25. From Kaatz et al. (1978a).

The tradeoffs that can be made in interpreting dielectric data were studied by Colonomos and Gordon (1979). These authors applied linear programming techniques to obtain absolute bounds on the cumulative distribution function, defined as

$$\Sigma(\tau) = \int_0^\tau \rho(\tau') d\tau' \quad (7)$$

where $\rho(\tau')$ is the strength of the contribution at relaxation time τ' . This approach determines the total ranges of cumulative distribution functions that can account for the data, within specified experimental limits. Clearly, it would be difficult to distinguish among models which correspond to cumulative distribution functions that fall within such limits. It should be noted that Colonomos and Gordon (1979) originally considered the cumulative distribution function of microscopic relaxation times, by including a local field correction that relates the microscopic dipolar correlation time to the bulk macroscopic dielectric relaxation time. (These two quantities might differ by as much as 50%, depending on the local field correction used.) In view of the microscopic heterogeneity in the present samples, it is difficult to apply these local field theories directly to the PEO solutions. Instead we apply their analysis to the macroscopic relaxation.

We repeated the calculations described by Colonomos

and Gordon (1979), for the data shown in Fig. 4, using a conventional revised Simplex algorithm and procedures essentially the same as described in their paper. The smallest assumed errors that would lead to a consistent solution were $\sim 5\%$ in both the permittivity and loss, which is an indication of the maximum scatter in Kaatz's data. This is consistent with the stated experimental errors of 2%, which were presumably calculated on a root-mean-square basis. The results are shown in Fig. 7. On the perhaps questionable assumption that no component of water in the solution can exhibit a relaxation time shorter than that of the pure liquid, the contribution of the fastest relaxing component can range from 0 to 22% of the total; the macroscopic relaxation times of most of the remainder are somewhere between 2 and 7 times longer than that of the pure liquid water. Clearly, a wide range of tradeoffs can be made in interpreting the data. The problem is analogous to that in spectroscopy of resolving spectral lines that are not well separated, except that at microwave frequencies the "lines" are extremely broad because the process is one of relaxation and not resonance.

□ USE OF MIXTURE THEORY Eq. 6 is formally similar to Eq. 5, except that the weight factor $(1 - p)/(1 + p/2)$ is missing. This factor results from the development of the mixture theory from the solution of Laplace's equation for the suspension. In the mixture theory, the contribution of a suspended phase to the measured bulk permittivity will depend on the permittivity of both the suspended and continuous phases. The Maxwell-Fricke and Hanai mixture theories were developed for suspensions of spherical or spheroidal particles and do not strictly apply to the more

complex polymer solutions. Given the lack of a more precise theory, Kaatz's (1978a,b) decision to avoid mixture theory was entirely reasonable and perhaps correct; it does, however, lead to quite different results.

Our conclusions from this analysis are (a) the different hydration values that were calculated from the same data result in part from a different choice of model, in particular the use of dielectric mixture theory; and (b) in any event, the data themselves are consistent with a wide range of cumulative distribution functions, which corresponds to a wide range in possible tradeoffs between the amount and dielectric relaxation frequency of the hydration water. The analysis we have chosen, application of mixture theory to the dielectric data in the high frequency limit, assumes only that the dielectric relaxation frequency of the hydration water is lower than that of the bulklike water and should yield more accurate estimates of the polymer hydration. Moreover, the results so obtained are more consistent with the corresponding results from the other transport properties. Significantly, both treatments yield hydration values that are considerably larger than expected thermodynamically.

Effect of Transport in Hydration Water on Hydration Estimates. In view of the high dielectric relaxation frequency of the hydration water, the ionic conductivity and water self-diffusion coefficient might not be negligible in the hydration water. This introduces another adjustable parameter into the calculations that further complicates the interpretation of the data. A simple calculation shows the sensitivity of the mixture theory to this effect.

We consider, for example, the conductivity of the PEO solution of molecular weight 3,400 with a volume fraction of 0.18, which from Table I is 0.455 times that of the electrolyte in which it is suspended. The effect of a finite conductivity of the hydration water can be included in the model by applying the mixture theory twice, once to estimate the "equivalent" conductance of the hydrated polymer, and the second time to calculate the overall conductivity of the solution. A similar procedure was used by Pennock and Schwan (1969) in dielectric relaxation studies of hemoglobin at ultra-high frequencies. Using the Maxwell-Fricke equation (Eq. 1) and assuming conductivities of the hydration water of 0, 1/10, 1/4, and 1/2 that of the electrolyte in the absence of the polymer, requires volume fractions p' of the hydrated polymer, respectively, of 0.44, 0.48, 0.56, and 0.80 to produce the observed conductivity of the solution. The corresponding hydration values were 3.1, 3.5, 4.5, and 7.3 water molecules per EO group. The same calculation, applied to the (interpolated) conductivity of a 25% by volume solution yielded respective hydration values of 2.7, 3.1, 3.9, and 6.4 water molecules per EO group. A similar calculation, using the Hanai theory, would yield slightly lower hydration values.

An independent estimate of the values of the ionic

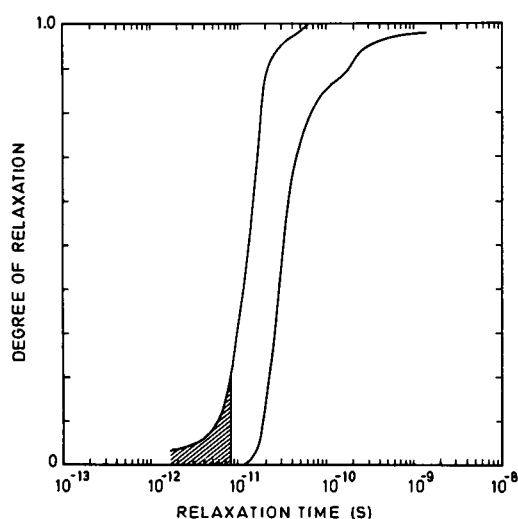


FIGURE 7 Range of cumulative distribution functions that are consistent with the data shown in Fig. 4, calculated using a modified Simplex routine using the procedure of Colonomos and Gordon, 1979 (see text). The hatched area represents the range corresponding to relaxation times less than the mean relaxation frequency of pure liquid water at 25°C, and is presumably unrealistic.

conductivity or water self-diffusion coefficient can be obtained from Figs. 1–3 directly. The ratio p'/p for the polymer solutions is roughly constant for polymer concentrations ≤ 0.37 (Table I). For the solutions with p of 0.57, this ratio has decreased; it becomes still lower for the more concentrated solutions. Because the number of water molecules is less than twice the number of EO groups, we expect that most of the water in this solution is in the hydration layers surrounding the polymer. The mixture theory can be applied to these data to estimate the average conductivity (or water self-diffusion coefficient) of the solvent, using the volume fraction of anhydrous polymer (p). It was found that the average conductivity and self-diffusion coefficient of the water are, respectively, 0.10 and 0.22 times those of the bulk water. Consequently, a more probable hydration value for the 18% (by volume) PEO solutions would be closer to four water molecules per EO group, with somewhat lower values for the 25% (by volume) solution. It appears that the transport through the hydration water, while small, still requires a significant correction to the hydration estimates.

Comparison with Results from Other Dispersed Systems

It is of interest to compare the present results from the PEO solutions with the respective transport properties of other dispersed systems. We note without discussion that the water self-diffusion and ionic conductivity of a variety of protein solutions exhibited decreases, relative to the bulk water, that closely resembled those measured in PEO solutions of similar volume fraction. In contrast, the thermal conductivity of protein solutions was close to the predictions of the Maxwell-Fricke relation (several pertinent studies are cited in the introduction).

The dielectric properties of a variety of microemulsions have recently been reported (Foster et al., 1982; Epstein et al., 1983). Some of these microemulsions were stabilized by surfactants containing the EO group; others were stabilized by ionic surfactants instead. For suspensions of the same total volume fraction, all of the microemulsions exhibit dielectric relaxation properties that are strikingly similar to those of PEO solutions of comparable volume fraction. The dielectric relaxation frequency of the hydration water, calculated from the Maxwell and Hanai mixture theories, ranged from 4–5 GHz (in suspensions of volume fraction below ~ 0.4) to ~ 2 GHz in more concentrated suspensions.

The dielectric properties of various protein solutions and tissues have been reported at ultra-high and microwave frequencies (e.g., Schwan, 1965; Pennock and Schwan, 1969; Grant et al., 1968; Foster et al., 1980; Foster et al., 1982*b*). These data are more difficult to interpret than those from nonionic polymer solutions or microemulsions because of a variety of relaxation processes associated with ionic effects and partial orientation of polar sidechains that

also occur. The conductivity at microwave frequencies of muscle and protein solutions, if plotted vs. the quantity x defined above, discloses a dielectric relaxation at low gigahertz frequencies, superimposed on a relaxation whose center frequency is the same as that of pure liquid water (Foster et al., 1980, 1982); use of Eq. 5 leads to hydration values of 0.4–0.5 grams of water per gram of dry protein, which is in the range that is conventionally accepted.

Several authors have observed that the average dielectric relaxation time of water in tissues calculated from the dielectric data at microwave frequencies appears to be ~ 20 – 25% longer than that of the bulk liquid at the same temperature (Masszi, 1976; Nightingale et al., 1983). In all such cases, it appears that a distribution of dielectric relaxation times is also present. This behavior is also seen in Fig. 4; the much larger shift in these data is principally due to the larger solid content, with a correspondingly greater fraction of hydration water. This longer average relaxation time together with a distribution of relaxation times, is expected if the hydration water in the tissue relaxes more slowly than in the bulk liquid.

It is curious to note that ionic conductivity measurements in protein solutions suggest protein hydration values that are somewhat higher than those conventionally accepted, when analyzed using mixture theories similar to those employed here. This was noted by Bull and Breese (1969) and much more forcefully by Pauly and Schwan (1966). Similar observations have been made about water self-diffusion data from tissues (Clark et al., 1982; Hazelwood, 1979). Pauly and Schwan (1966), in their study of the conductivity of the cytoplasm of erythrocytes, suggested the presence of a kinetic effect (the “frictional effect”) that also contributed to the unexpectedly low conductivity.

Molecular Mechanisms

The principal observations are that the ionic conductivity and water self-diffusion coefficient are reduced in the PEO solutions considerably below the predictions from the mixture theory, assuming that the transport properties of the solvent water are identical to those of the bulk water, and the dielectric relaxation frequency of the hydration water is considerably lower than that of the pure liquid. The thermal conductivity, in contrast, is closer to the predictions of the mixture theory. Thus it appears that the thermal conductivity of the hydration water is comparable, while the other transport properties of this water are much less, than the respective transport properties of the bulk liquid.

The simplest interpretation is that the average “viscosity” of the water in the solution is increased by the hydration interaction. In bulk solution, the ionic conductivity, self-diffusion coefficient, and dipolar relaxation rate vary inversely as the viscosity of the medium. The first result is a well-known empirical rule in chemistry (Wald-

en's rule); the second and third follow from simple diffusion theory (Abragam, 1961) and are well-supported empirically. No such relation holds for the thermal conductivity. The PEO solution of volume fraction 0.25 exhibits a mean dielectric relaxation frequency one half that of the pure liquid, and the ionic conductivity and self-diffusion coefficient are each depressed by a factor of 2 also. Similar results were found for oil in water microemulsions of widely varying volume fraction (Foster et al., 1982a). While this reasoning is only intuitive and a more precise interpretation is needed, the concept of "viscosity" of the interfacial water clearly has some value in interpreting the results. It is important to note, however, that there is a broad distribution of dielectric relaxation times present, so the concept of "average viscosity" is problematic. Perhaps a more defensible hypothesis would be that the rotational and translational correlation times are both increased by similar factors when the water molecule is in the hydration layer surrounding the polymer. At least in the more dilute solutions, the ionic conductivity and self-diffusion coefficients are depressed by similar factors, so that ionic interaction phenomena would not appear to be the dominant mechanism for the conductivity decrease; such effects might however be important in the more concentrated polymer solutions.

The principal deduction in this study is that the apparent hydration of the PEO, calculated using the mixture theory, is somewhat higher than that expected from thermodynamic arguments. This estimate must be treated with caution, since it is subject to a range of tradeoffs as well as to uncertainties in the mixture theory itself. However, the result is consistent, and the effect is presumably real.

The simplest explanation is that the transport properties are subject to various kinetic effects that are not related in any simple way to thermodynamic properties such as vapor pressure, that are also used to calculate "hydration." A variety of such effects can be suggested. For example, the Stokes-Einstein calculation of the diffusion coefficient pertains to a particle diffusing in a viscous fluid of infinite extent. The presence of a nearby surface will cause an increased drag on the particle by virtue of the stationary boundary condition that is imposed. This is the basis of the "frictional effect" proposed by Pauly and Schwan (1966), who estimated its magnitude using macroscopic hydrodynamic calculations. An analogous molecular interpretation would be that the ions or water molecules must displace other water molecules as they move about, and the nearby presence of heavier polymer molecules would impede this motion.

A second, related, effect would arise from the inability of water molecules near hydrophobic regions of the polymer to orient themselves so as to form hydrogen bonds to the molecule. Because the diffusion of a water molecule or ion requires the reorientation of nearby water molecules, this would affect the kinetic properties of water molecules

in secondary hydration layers as well. The importance of such effects would be suggested by Kaatze's observation (Kaatze, 1978a,b), which is repeated in our dielectric studies on microemulsions, that the dielectric relaxation properties of a great many solutions of hydrophilic polymers vary only slightly with the chemical nature of the polymer and appear to depend mostly on the number of nearest neighbor water molecules that surround the polymer. Such nonspecific effects would suggest a physical, rather than chemical, mechanism.

CONCLUSIONS

Several transport properties of a hydrophilic polymer appear to reflect in a similar manner hydration interactions between the solvent water and the polymer. A comparison of these properties helps in the separation of the "obstruction" effect (due to the geometry of the suspension, which is dealt with by the mixture theory) from the "hydration" effect (the modification of the properties of the water by the polymer). To our knowledge, this is the first systematic attempt to correlate such a broad range of transport properties in the same systems. It appears that the rotational and translational correlation times that determine the transport are increased by factors of 4 or more, with considerable uncertainty because of the tradeoffs that can be made in interpreting such data. The simple Maxwell or Hanai theories are remarkably able to provide a consistent interpretation of the total set of data. However, this yields hydration values that somewhat exceed the two water molecules per EO group that is expected from chemical considerations. The reason, apparently, is a contribution from kinetic effects in addition to chemical interactions such as hydrogen bonding. Similar effects apparently are present in biological solutions as well. We suggest that a comparison of these transport properties is a potentially fruitful approach to the study of the water in more complex biological systems.

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