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PROTON LONGITUDINAL RELAXATION RATES OF WATER IN AQUEOUS
ORTHOPHOSPHORIC ACID

KEY WORDS: Proton NMR, water of hydration, orthophosphoric acid,
longitudinal relaxation rate, concentration plots

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ABSTRACT

Longitudinal relaxation rates of water protons were determined for aqueous solutions of orthophosphoric acid at concentrations up to 85% by weight, and their concentration dependence was investigated. An appropriate choice of variables yielded an essentially linear plot for concentrations up to at least 15% by weight. Deviations from linearity are discussed and are interpreted in terms of mass-law effects. The use of parameters of this plot for deriving values for correlation ^{times} and for a hydration parameter is illustrated by application to observed data and data from the literature.

INTRODUCTION

Phosphoric acid is of key importance in biological systems and in the physical chemistry of biomolecules. Directly or indirectly, it gives rise to various derivatives (nucleotides, the phosphate-sugar backbones of the nucleic acids, and phosphorylated proteins) which are fundamental to all known living systems. Phosphate is the major intracellular buffer, with organic phosphates as additional buffers¹. It is a constituent of a range of buffers frequently employed in biochemical research¹⁻³ and, in consequence, in nuclear magnetic resonance (NMR) studies of biochemical systems^{4,5}. Our consideration of phosphoric acid arose in the course of an investigation of the proton relaxation rates of water in buffered solutions of globular proteins. It appeared appropriate, therefore, to complement our investigation with an examination of the proton relaxation rates of water in aqueous phosphoric acid itself.

The work reported here is concerned with these relaxation rates as a function of a fairly wide range of solute concentrations, as well as of other experimental variables (chiefly, instrument resonant frequency). The objectives were to ascertain whether the observed concentration dependence follows expressions suggested for other, more dilute systems^{6,7}, to refine these expressions and determine precautions necessary for data treatment, and to derive further information from the parameters obtained.

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EXPERIMENTAL

Materials and Sample Preparation

Materials used were Fisher⁸ ACS Certified 85% orthophosphoric acid, 99.8 atom % deuterium oxide and 99.5% benzene-d₆ from Thompson Packard, and all-glass distilled water, without further purification of reagents. However, the concentration of the acid designated as 85% H₃PO₄ was checked by standard titration and was found to be 83.04%. Sample solutions were prepared individually by weight with appropriate weighing precautions. To exclude the possibility of enhanced relaxation due to dissolved oxygen, preliminary measurements were made on both degassed and nondegassed samples. In no case was a significant difference found.

Measurements and Data Evaluation

The measurement of proton longitudinal relaxation rates R_1 by inversion recovery and the method of data evaluation used in the present study were essentially as described previously⁹.

RESULTS

Fig. 1 shows a typical family of plots of $\ln (A_\infty - A_t)$ vs. τ for a series of concentrations ranging from 0 to 83%. The negative of the slope of the resulting straight line is R_1 ¹⁰. For the case, e.g., of 15.5% (g anhydrous H₃PO₄/100 g solution), the slope of the line fitted to the experimental points by linear least squares was -0.539, with a standard error of the slope of 0.010.

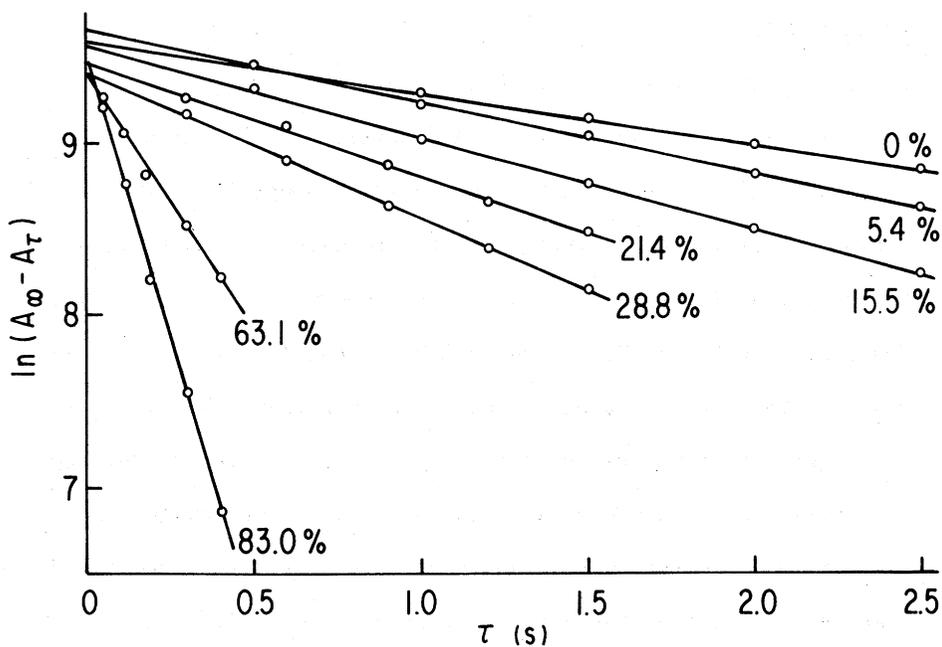


FIG. 1. $\ln (A_{\infty} - A_{\tau})$ vs. delay time τ for a series of concentrations of H_3PO_4 at 60 MHz, $30 \pm 1^\circ\text{C}$. For clarity, only some of the lines are shown. Points of intersection have no particular significance.

At this concentration, then, $\underline{R}_1 = 0.54 \pm 0.01 \text{ s}^{-1}$ (i.e., $\underline{T}_1 \equiv \underline{R}_1^{-1} = 1.85 \pm 0.03 \text{ s}$). Errors at other concentrations were of approximately the same order of magnitude. Table 1 gives a summary of \underline{R}_1 values, obtained in this fashion, as a function of weight percent in two series of measurements (I and II), each performed, in part, on the same series of solutions, but on different instruments as indicated. In addition, the table lists

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TABLE 1

Proton R_1 of Water as a Function of Orthophosphoric Acid Concentration

| Conc., wt. % ^a | I ^{b,e} | | II ^{c,e} | | III ^d | |
|------------------------------|----------------------------|---------------|----------------------------|--|------------------------------|----------------------------|
| | R_1 , s ⁻¹ | | R_1 , s ⁻¹ | | Conc., wt. % ^a | R_1 , s ⁻¹ |
| 83.0 | 6.71 ± 0.05 | | | | 82.5 | 4.7 ₆ |
| 63.1 | 3.00 ± 0.01 | | | | | |
| 44.6 | 1.54 ± 0.03 | | | | 50.5 | 1.49 ₃ |
| 28.8 | 0.842 ± 0.006 | | | | 29.2 | 0.80 ₆ |
| 21.4 | 0.673 ± 0.018 | | | | | |
| 15.5 | 0.539 ± 0.010 | | | | 15.7 | 0.47 ₆ |
| 9.13 | 0.443 ± 0.008 | 0.473 ± 0.019 | | | | |
| 5.43 | 0.405 ± 0.007 | 0.443 ± 0.016 | | | | |
| 3.19 | 0.361 ± 0.010 | 0.465 ± 0.028 | | | 2.7 | 0.25 ₆ |
| 2.09 | 0.347 ± 0.006 | 0.344 ± 0.009 | | | | |
| 1.03 | | 0.349 ± 0.009 | | | | |
| 0 | 0.310 ± 0.001 | 0.383 ± 0.019 | | | 0 | 0.25 ₀ |

^a Gram dry acid/100 gram solution

^b JEOL FX60Q; 60 MHz, 30±1°C.

^c Bruker WH-90; 90 MHz, 30±2°C.

^d Varian XL-100-15; 100 MHz, 31±2°C. Data taken from reference 11 (no error terms stated).

^e Error terms in all tables represent standard errors of the respective parameter. Each reported value of R_1 is the mean of four replicates.

a third series (III) of pertinent data from the literature¹¹

Resonant frequencies and temperatures were as indicated.

On the assumption of the so-called two-fraction fast-exchange model of Zimmerman and Brittin¹² for water in the presence of solute, relaxation rates should be linear functions of solute concentration in g solute/g solution, as shown both theoretically and empirically by Daskiewicz et al.⁶ and, later, by Cooke and Wien⁷, on the assumption that the solutions are very dilute. However, by using molalities, or concentrations in terms of g dry solute/g solvent, it may be shown, as follows, that the restriction to very low concentrations can be removed provided only that the model remains applicable.

In a system containing two water fractions (variously also termed states or phases, designated "f" and "b" to refer to "free", or bulk, and "bound", or solute-influenced water), with corresponding relaxation rates \underline{R}_f and \underline{R}_b , the assumption of fast exchange of water protons between these fractions implies that the correlation times τ_{Mf} and τ_{Mb} (the mean times of persistence of a proton in the particular fraction) are much smaller than \underline{R}_f^{-1} and \underline{R}_b^{-1} , respectively. The observed relaxation rate, \underline{R}_{obs} , then is the weighted average of the individual relaxation rates; the weights are the fractions of time for all water protons spent in the respective state and equal the fractional concentration of water protons, i.e., the fractional concentration of the water itself, in each state. Let \underline{h} be the degree of hydration, in the

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customary units of grams of b-fraction water per gram of anhydrous solute, and \underline{c} the solute concentration, in grams of anhydrous solute per gram of total water. Then⁹

$$\underline{R}_{\text{obs}} = \underline{R}_f + \underline{k} \underline{c}, \quad (1)$$

where
$$\underline{k} = (\underline{R}_b - \underline{R}_f) \underline{h} \equiv \underline{h} \underline{\Delta R}. \quad (1a)$$

The foregoing is based only on the two-fraction fast-exchange model independently of any particular mode of relaxation; according to the relaxation mode under consideration, the \underline{R} 's and \underline{k} 's may be subscripted with 1, 2, or lp . The derivation of eq. (1) is not dependent on any assumption regarding the value of \underline{c} , as contrasted with the condition $\underline{c} \ll 1$ in Refs. 6 and 7. The result is, furthermore, a simpler equation than was obtained elsewhere (equation preceding eq. (4) in Ref. 6).

Accordingly, eq. (1), while appearing to be formally identical to the eqs. (1) of both Refs. 6 and 7, differs in that the quantities \underline{k} and \underline{c} here have different significances: (i) \underline{c} , because of its units and for the reason that it is not subject to the condition $\underline{c} \ll 1$, and (ii) \underline{k} , for the reason that an error in the derivation of the cited authors prevented recognition of a simpler and more readily visualized meaning for this quantity. As shown by eq. (1a), the quantity \underline{k} is the product of two factors, one formally independent of degree of hydration, the other independent of relaxation effects. The first is the total excess

relaxation rate ΔR , being the difference between proton relaxation rates of bound and free water. The second is simply the degree of hydration.

Although these two factors are formally separated, without further information it is not possible to separate their effects on the experimentally determined k , or to obtain R_{1b} , the longitudinal relaxation rate of water seen as bound under the conditions of the experiment. Such additional information might consist of relaxation data at a second resonant frequency, or under a second mode of relaxation (i.e., transverse). In its absence, it is frequently expedient and, within limits, quite feasible, to discuss the experimental data by examining changes in the parameter k , which has been termed the hydration product⁹. It follows from eq. (1) that the ordinate intercept of the expected straight line resulting from a plot of $R_{1,obs}$ vs. c equals R_{1f} , the relaxation rate of free solvent protons, while the slope equals the hydration product k .

Fig. 2A represents a typical set of such data (a portion of set I of Table 1) plotted, following Daskiewicz et al.⁶ or Cooke and Wien⁷, against a concentration scale linear in percent. This concentration scale is equivalent to g solute/g solution when divided by 100; it is related to molarity by the factor $10 \rho/M$, where M is the solute molecular weight and ρ is the solution density, itself concentration dependent. Fig. 2B shows the same data plotted according to eq. (1), i.e., against a concentration

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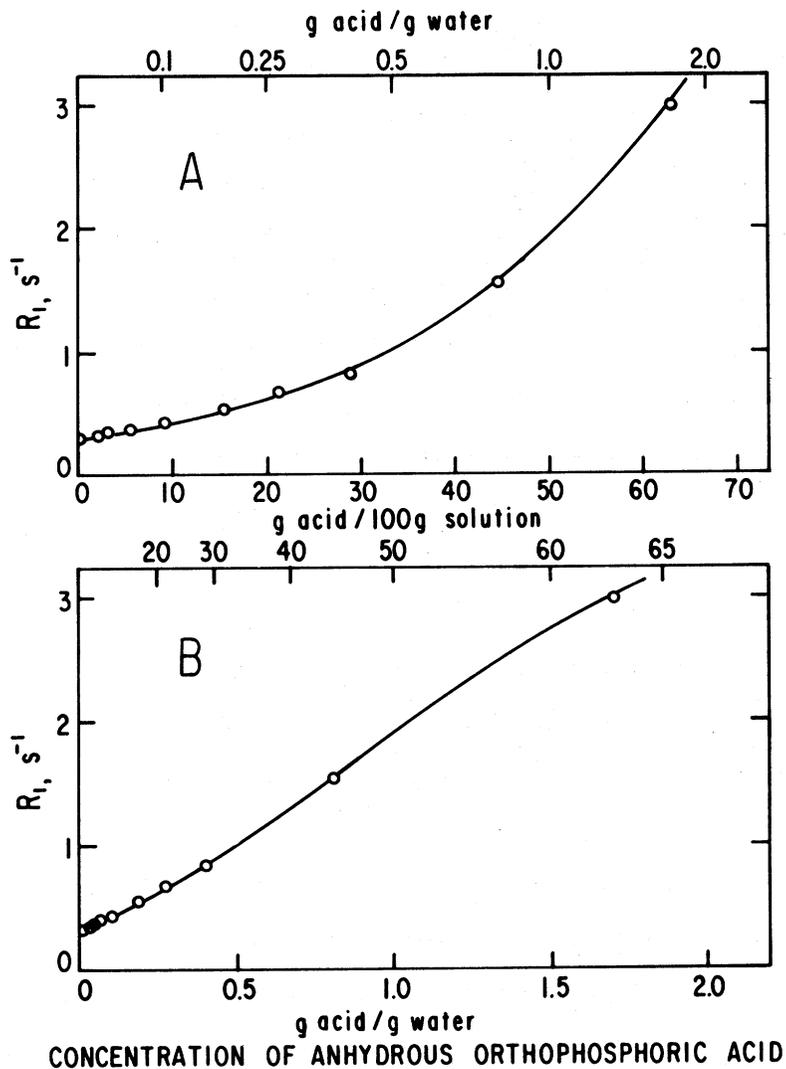


FIG. 2. Proton relaxation rates of water in orthophosphoric acid solutions (portion of data set I). Effects of change in concentration scales: A, concentration linear in g acid/g solution; B, concentration linear in g acid/g water. Corresponding nonlinear scale shown above each curve.

scale linear in g solute/g solvent; this scale is equivalent to molality when multiplied by the constant factor $1000/M(\text{H}_3\text{PO}_4) \cong 10.2$. It is appropriate in B to use the units chosen rather than the more customary molality, because of the way concentration was defined in the derivation of eq. (1) to be consistent with the customary units of \underline{h} . Table 2 lists, for each of the sets of data of Table 1 (I, II, and III), the least-squares values of \underline{R}_{1f} and \underline{k}_1 derived from those initial portions of the plots judged to be reasonably linear when plotted according to either references 6 and 7 (section A of table) or eq. (1) (section B).

DISCUSSION

Methods of Plotting

On the basis of the model employed, Daskiewicz et al.⁶ and Cooke and Wien⁷ predicted a plot of relaxation rates vs. concentration, in units of weight fraction, to be a straight line at low concentrations. Even then, however, the data of set I plotted in this manner (Fig. 2A) are not entirely linear, as is seen by examination of the values and errors of \underline{k}_1 in Table 2. Allowing for the difference in units, the higher values for the slope \underline{k}_1 in A compared with B, as well as the higher standard deviations, indicate that the fitted lines are chords of a more strongly curved plot. The same data show a considerably different picture in B, where the concentrations are in units consistent with eq. (1). Curvature still exists, but to a much smaller extent, and is evident only at higher concentrations. This kind

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TABLE 2

Relaxation Parameters Derived from Fitted Straight Lines^a

| Data treatment ^b | Data set ^c | R_{1f} , s ⁻¹ | k_1 | |
|-----------------------------|-----------------------|-------------------------------|---|---|
| | | | $\frac{\text{g soln.}}{\text{g H}_3\text{PO}_4}$.s ⁻¹ | $\frac{\text{g H}_2\text{O}}{\text{g H}_3\text{PO}_4}$.s ⁻¹ |
| A | I | 0.315 ± 0.006 | 1.47 ± 0.11 | |
| | II | 0.363 ± 0.026 | 1.33 ± 0.57 | |
| | III | 0.217 ± 0.031 | 1.93 ± 0.19 | |
| B | I | 0.317 ± 0.005 | | 1.29 ± 0.03 |
| | II | 0.365 ± 0.026 | | 1.25 ± 0.52 |
| | III | 0.249 ± 0.020 | | 1.24 ± 0.04 |

^a Error terms represent standard errors of the parameter.

^b A, according to Refs. 6 and 7: concentration in g solute/g solution. B, according to eq. (1): concentration in g solute/g solvent.

^c For sources of data, see footnotes, Table 1.

of plot, as typified by Fig. 2B for the points of set I, is essentially linear even above 2 m (16% by weight), subject to the qualifications to be discussed. Clearly, therefore, the use of lines fitted to data expressed in units of weight fraction, as in Fig. 2A, can result in misleading values of the derived parameters, the slopes in particular being significantly too high.

From the derivation based on the simple theory above, it follows that curve B is the one consistent with the customary definition of \underline{h} , and that only for this manner of plotting can a straight line with a well-defined constant slope be expected. The effect of changing from a type B to a type A plot for a given set of data can be predicted when it is assumed that the former can be represented, at least as a reasonable approximation, by the straight line of eq. (1), $\underline{R}_{\text{obs}} = \underline{R}_f + \underline{k}_B \underline{c}_B$, where subscripts "B" or "A" will refer to the plot type. The corresponding curve A is obtained by the easily verified change of variable, $\underline{c}_A = \underline{c}_B / (1 + \underline{c}_B)$, or $\underline{c}_B = \underline{c}_A / (1 - \underline{c}_A)$, where \underline{c}_A is expressed as a fraction rather than a percentage. Then the slope $\underline{k}_A = d\underline{R}_{\text{obs}} / d\underline{c}_A = (d\underline{R}_{\text{obs}} / d\underline{c}_B) (d\underline{c}_B / d\underline{c}_A) = \underline{k}_B / (1 - \underline{c}_A)^2$. Thus, for $\underline{c}_a = 5, 15, \text{ or } 25\%$, values for \underline{k}_B are 1.11, 1.38, and 1.78, respectively.

It follows that plot A must exhibit considerable upward curvature. (For $\underline{c}_A = 100\%$, \underline{k}_B should approach infinity, except that curve B by then would long since have deviated from linearity by flattening out, as shown below, and in accord also with the finite R_1 values known for solid samples.) It is seen that details of slight deviations from linearity, such as the sigmoid feature of curve B referred to below, would be masked in curve A. Such deviations, however, may well be significant, and their closer examination might yield information of interest pertaining to the system studied, which would thus be lost by the choice of an inappropriate concentration scale for the plot.

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If k_B has been evaluated from a linear plot B, R_{obs} can be expressed in terms of k_B and c_A to predict the shape of the corresponding curve A: $R_{\text{obs}} = R_f + k_B c_A / (1 - c_A)$; values of R_{obs} so calculated will reflect the curvature in A caused by the transformation from B. Any difference between these calculated values and experimental ones must, of course, be due to the same causes as any nonlinearities in B, as examined below. Such differences are not readily revealed on inspection of the always strongly curved plot A, whereas they are very apparent in the nearly linear plot B.

Limitations on Linearity

Much beyond 2 m , starting in this case near 4 m (29% by weight), B shows a slight upward curvature, as would appear more distinctly in a larger-scale plot of the first nine points only. At still higher concentrations, B becomes concave downward, as could be seen readily by plotting one more point, viz. the first point of Table 1. (These two extremes are not readily displayed on one graph if its scale is chosen, as here, to include as many points as possible without losing resolution entirely for the lower-concentration points). Preliminary observations (not shown here) had repeatedly shown this same inversion of curvature. The point of inflection, though evidently real, is not pronounced enough to be accurately identified.

The downwardly concave shape at high concentrations can be explained in part on the basis of decreases in h . It is

conceivable that the factor ΔR may not be entirely independent of concentration (e.g., in the case of aggregation or polydispersity, or because the assumptions of the two-fraction model for some reason might fail). However, the major share in any concentration dependence of k_1 must be due to the factor h , since it is subject to the law of mass action.

Consider the definition $h \equiv \underline{w}_b / \underline{c}$ and the general expression for a binding equilibrium, $K_b = \underline{w}_b / \underline{c}_f \underline{w}_f^n$, where \underline{w}_b , \underline{w}_f , \underline{c} , and \underline{c}_f are the concentrations, respectively, of bound water, free water, total solute, and free solute, n is the average number of occupied binding sites per solute molecule, K_b is the equilibrium constant in consistent units, and, as an approximation, concentration units are used to represent the corresponding activities. (Here we have used a single-step expression in place of the strictly correct but less tractable stepwise association with multiple equilibrium. This is justified for $n \leq 1$; for larger n , K_b becomes an overall constant, and conclusions derived from this simplification will still serve to provide information on the general shape of the curves.) The total water concentration, \underline{W} , in scale B equals unity by definition, and $\underline{w}_f = \underline{W} - \underline{w}_b = 1 - \underline{w}_b$; \underline{c}_b , the concentration of bound solute equals \underline{w}_b / n . Two extreme cases can be examined by inspection. At low \underline{c} , $\underline{w}_f \cong \underline{W} \cong 1$, and $K_b \cong \underline{w}_b / (\underline{c} - \underline{c}_b) = \underline{w}_b / (\underline{c} - \underline{w}_b / n)$. Then $\underline{w}_b \cong K_b \underline{c} / (1 + K_b / n)$ and $h \equiv \underline{w}_b / \underline{c} \cong n K_b / (n + K_b)$, which is a constant; i.e., at low \underline{c} , h can be predicted to be independent of concentration, and the relaxation

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rate vs. concentration plot will be a straight line. At high \underline{c} , on the other hand, $\underline{w}_b \cong \underline{W} \equiv 1$, and $\underline{h} \equiv \underline{w}_b/\underline{c} \cong 1/\underline{c}$; i.e., \underline{h} can be predicted to decrease as \underline{c} increases, and the plot will flatten out.

The analytical verification for the faintly sigmoid shape at intermediate concentrations can be found without difficulty from the above equilibrium expression by the usual test for a point of inflection. Since it is so faint, it is not useful for evaluating \underline{K}_b or \underline{h} , but neither does it materially detract from our approximation of the curve in this range by a straight line.

The preceding considerations cannot quantitatively account for the shape of the curve over its entire extent. This is not surprising, considering the changes in water structure which may take place over such extreme concentration ranges, as well as the existence of a variety of ionic and possibly oligomeric species of the acid^{13,14,15}, changing viscosities, changing activities of the various species¹⁶, preferential binding of water to one or more of them, and the possible occurrence of spin diffusion. (The latter, manifested as cross relaxation in the case of solutions¹⁷, has been observed in protein systems but would be negligible for a molecule as small as orthophosphoric acid. To the extent that it did exist in a given system, it would entail correction terms for \underline{k}_1 and \underline{h} without materially affecting qualitative conclusions⁹.) At any rate, the simple model employed here cannot be expected to be applicable over an extreme range, except, perhaps, as a first

approximation. For purposes of studying hydration behavior, however, the extended linear portion of this kind of plot is sufficient to allow the fitting of straight lines whose parameters contain information of interest for concentrations at least up to 2 m (16% by weight). Although at the lower concentrations most often encountered in work with dilute solutions, e.g., of proteins, the choice of concentration scale may make a negligible difference, it is clear that at medium and higher concentrations it can be critically important to employ molal (or equivalent) units instead of weight percentages or molarities.

Some further remarks may be made regarding Table 2. The parameters obtained from the three sets of data would be expected to differ somewhat since the data were obtained under unavoidably different conditions. Furthermore, the temperature was not precisely the same for all three. However, the temperature difference between the present measurements (I and II, at 30°C) and those of Morgan and Van Wazer¹¹ (III, at 31°C) is slight. In view of the difficulty of temperature control of the probe and the resulting uncertainty of $\pm 2^\circ\text{C}$ in the data of sets II and III, this nominal temperature difference was not judged significant enough to justify a temperature correction.

Application to Correlation Times and Hydrations

It is possible to inquire into the effect of the resonant frequency and to use this information to estimate correlation times and hydration values consistent with the data. Longitu-

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dinal relaxation rates R_{-1} , resulting from the magnetic dipolar interaction between the two protons on the water molecule, may be related to the correlation time for the interaction τ_c by¹³

$$R_{-1} = \underline{K} \tau_c [(1 + \omega_o^2 \tau_c^2)^{-1} + 4 (1 + 4 \omega_o^2 \tau_c^2)^{-1}], \quad (2)$$

where $\underline{K} = 0.3 \frac{\hbar^2 \gamma^4 r^6}{\omega_o^2} = 1.364 \times 10^{10} \text{ s}^{-1}$, $r = 1.524 \text{ \AA}$ is the proton internuclear distance for the water molecule, and ω_o is the Larmor frequency in radians/s. This expression is suited for relating R_{-1f} values to their corresponding correlation times τ_{cf} , but since it cannot be solved explicitly for τ_c , an iterative method must be employed. Next, by using R_{-1f} and k_{-1} values from Table 2 at two different resonant frequencies, ω_{o1} and ω_{o2} , and writing two eqs. (1a) and two eqs. (2) for the two sets of values R_{-1b} , one may obtain a set of four simultaneous equations in four unknowns: $(R_{-1b})_1$, $(R_{-1b})_2$, \underline{h} , and τ_{cb} . The computations here are slightly more complex, but again solutions for τ_{cb} as well as the other unknowns are found by iteration. The various values obtained in this way are listed in Table 3.

The three τ_c values for the free-water protons (4.6, 5.4, and 3.7×10^{-12} s, respectively) are of the same order of magnitude. The three τ_c values for the bound-water protons, obtained for the three possible combinations of two sets of data as described above, are 2.4, 2.6, and 2.5×10^{-10} s. These are in close agreement with each other, as are the corresponding \underline{h} and R_{-1b} .

TABLE 3

Parameters Derived from Table 2 by the Use of Eqs. (1a) and (2)^a

| Data set ^b | τ_{cf} , ps | Joint data sets ^c | τ_{cb} , ns | \underline{h} , g solvt./g dry solute | \underline{R}_{1b} , s ⁻¹ | At resonant frequency, MHz |
|-----------------------|---------------------|------------------------------|---------------------|---|---|----------------------------------|
| I | 4.64 ±0.07 | | | | | |
| | | I & II | 0.241 ±0.001 | 0.083 ±0.002 | { 16.0 15.4 | 60 90 |
| II | 5.35 ±0.37 | | | | | |
| | | II & III | 0.261 ±0.006 | 0.077 ±0.031 | { 16.6 16.3 | 90 100 |
| III | 3.65 ±0.28 | | | | | |
| | | III & I | 0.248 ±0.001 | 0.080 ±0.003 | { 15.6 16.4 | 100 60 |

^a Error terms represent standard errors of the parameter.

^b For sources of data, see footnote, Table 1.

^c For details, see section on Correlation Times and Hydrations.

The \underline{R}_{1b} values show a small but consistent sensitivity to frequency, as would be expected from eq. (2).

In the absence of comparable data from other methods, there is no ready means of assessing the significance of the values of \underline{h} . It may be observed, however, that there are fairly wide discrepancies among hydrations obtained by different methods (see, e.g., Ref. 9) and, in particular, that NMR hydration values obtained from experiments on frozen solutions generally are consid-

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erably higher than those obtained from concentration plots in conjunction with the correlation time dependence of the relaxation rates. Thus, Kuntz¹⁸ obtained for native ovalbumin a hydration of 0.33, compared with hydrations in the neighborhood of 0.02 obtained by Daskiewicz et al.⁶. Such values as those obtained in the present study, averaging 0.080, therefore are not unreasonable.

It should be pointed out that the nature of the system of equations by which \underline{h} is obtained renders this parameter exceedingly sensitive to errors in the two sets of \underline{k}_1 and \underline{R}_{1f} involved. Relative errors of more than a few percent in these (as is the case with sets II and III) are capable, under circumstances of worst-case combinations of errors, of causing order-of-magnitude changes in the resulting \underline{h} . For greater certainty in \underline{h} , all data sets should have equally small variances, and it would be desirable also to have greater difference in frequencies than those available here, in order to obtain more substantially different values for \underline{k}_1 between data sets. (The frequencies for sets II and III, 90 and 100 MHz, are particularly close). Less sensitivity to small data errors would be shown if the second set were derived, not from measurements at a second frequency, but from a second relaxation mode, for the reason that \underline{k} values for transverse relaxation rates generally exceed those for longitudinal relaxation by a factor of at least 2, and at times much more⁶. Better temperature control than was available for sets II and III would

likely have yielded somewhat better data also. Nevertheless, the precision of the data is sufficient to support the conclusions presented here.

Regarding the data of Morgan and Van Wazer¹¹, it is noteworthy that these authors were concerned only incidentally with the spin-lattice relaxation rates of water protons, and not at all with concentration plots and their possible linearity, of which they make no mention. Despite this, the foregoing data treatment is suitable for extracting information from the few data points in that literature source pertinent in the present context, and this information is found to be consistent with the other results.

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