Proton Spin Relaxation in Paramagnetic Ion Solutions: Deuterium Isotope Effect

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(Z. Naturforsch. 22 a, 2110—2111 [1967]; received 12 August 1967)

In aqueous paramagnetic ion solutions the observed rate of proton spin relaxation (1/T2) is controlled by the rate of relaxation in the primary hydration shell of the paramagnetic ion (1/T2), and by the rate of proton exchange between the hydration shell and the solvent. The relaxation rate is given by

\[ 1/T_2 = P(T_{2a} + \tau_{we})^{-1}, \]

where \( P \) is the fraction of protons in hydration shells, and \( \tau_{we} \) is the mean lifetime of a proton in the hydration shell. The effects of isotopic substitution have been studied by measurement of deuteron spin relaxation in D2O solutions, and of proton and deuteron relaxation in solutions of mixed isotopic composition. The present discussion will apply to cases like Cr3+ and VO2+, where the dominant exchange mechanism is proton transfer across hydrogen bonds, rather than exchange of whole water molecules. We seek to account for changes in the T2 of protons (and deuterons) with variation in the isotopic composition of the solution, as have been observed by MAZITOV and RIVKIND. If the solution contains a mixture of the isotopes H and D, the factor P in Eq. (1) is given by

\[ P = (n_x/n_w) (\beta_2/\beta_w), \]

where \( n_x \) is the hydration number, \( x \) is the paramagnetic ion concentration, \( u \) is the concentration of water molecules, and \( \beta \) is the fractional concentration of protons. The difference in zero-point vibrational energy, the chemical rate constants for H and D exchange differenced.

1 G. LANDQVIST and F. NOACK, Z. Physik 159, 311 [1960].
fer 7. Since the H and D systems are separately in equilibrium we have the usual relationship between rate constants and concentrations — i.e., \(k_{we}^H/k_{we}^D = H_x/H_z = K_H\), and similarly for D. Using these relations to eliminate \(k_{we}\) and \(D_x\) from the defining expressions for the \(\beta's\), we get homogeneous algebraic equations for \(H_x\) and \(D_x\). The condition for a non-trivial solution requires that \(\beta_H/\beta_D = (1 - K) \beta_D + K\), where \(K = K_H/K_D\).

For a dilute solution \(\beta_H\) is very nearly the same as the overall proton fraction \(\beta\). Thus, Eq. (1) becomes

\[
T^2x = (w/n_x)(T_{2x} + \tau_{xe})/\beta + K.
\]

The analogous expression for \(T^2D\) is obtained by replacing \(K\) by \(K^{-1}\), and \(\beta\) by \(1 - \beta\). The ratio of deuteron to proton relaxation times in the same solution comes out to be \(T^2D/T^2x = (T_{2x} + \tau_{xe})/K(T_{2x} + \tau_{xe})\) \(H_x\), which is not explicitly dependent on \(\beta\). The ratio \(K = K_H/K_D\) is temperature dependent — i.e.,

\[
K = \exp(\Delta G_D - \Delta G_H)/R T,
\]

hence the isotope effect will be most pronounced at low temperature.

The experimental results of Mazitov and Rivkina 5, 6 are in partial agreement with the above conclusions. The observed relaxation times are either constant, or decrease linearly with \(\beta\). For a 0.1 M solution of \(\text{CrNO}_3\), at 0 °C, both \(T^2x\) and \(T^2D\) data indicate \(K = 2\). For a 0.16 M solution of \(\text{VO}_3\), at 25 °C, the \(T^2x\) data are entirely compatible with the above picture, and give \(K = 1.6\). On the other hand, \(T^2D\) in the case of \(\text{Cr}^{3+}\), and \(T^2H, D\) in the case of \(\text{VO}^{2+}\) show at most slight variations with \(\beta\), contrary to what would be expected from Eq. (3).

The above analysis is based on the assumption of a simple "primary" isotope effect. In contrast, the explanation offered by Mazitov 5 invokes a dependence of the lifetimes, \(\tau_{xe}\) upon isotopic composition of the solution. Such a dependence would be classed as a secondary isotope effect 7, and may well be required for a complete explanation of the experimental results. However, the data presently available do not really permit one to draw definitive conclusions along these lines. This is because recent work has shown that unless the concentrations of proton donors like \(\text{H}_2\text{O}^+\) and \(\text{HSO}_4^-\) are suitably adjusted, the relaxation behavior of the system lies outside the realm of validity of the simple Eq. (1) 8, 9. Nevertheless, it seems clear that experimental studies of this kind will allow one to distinguish between primary and secondary isotope effects, as well as to make inferences regarding mechanisms of proton transfer reactions involving paramagnetic complex ions.

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Army Research Office (Durham), for partial support of this research.

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**Hydrogen Isotope Effect among the Different Dehydration Stages of CuSO\(_4\).5 H\(_2\)O**

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Several investigations are reported in the literature dealing with the fractionation of hydrogen isotopes between salt hydrates and their saturated solutions. The measurements by Dav et al. 1, Teis 2, and Uusitalo 3 showed either no isotope effect or an enrichment of deuterium in the solid phase. Barrer and Denny 4, however, found an inverse effect in several chloride and sulphate systems. Their result was a few per cent enrichment of the light isotope in the hydration water of the crystal. Based on the assumption that hydration effects in the crystal are similar to those of the ions in solution, their results are in agreement with calculations by Swain, Bader and Thornton 5, concluding that in solutions the hydration water of ions has a smaller D/H ratio than the bulk water. This conclusion has been supported in the case of the hydronium ion by NMR 6, 7 as well as by vapor pressure measurements 8.

Only one investigation is known searching for a difference in the D/H ratio of water liberated on step-wise dehydration of hydrated crystals. Anderson et al. 9 used water containing 0.5% D\(_2\)O for the hydration of anhydrous CuSO\(_4\) and found that on dehydration the first four molecules of water liberated were heavier than the fifth. The variations in their data, however, did not enable them to attach a quantitative significance to the results.

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3 Uusitalo, Suomen Kem. 31 B, 362 [1958].