Nuclear Magnetic Relaxation of $^{207}$Pb in an Aqueous Medium

This communication reports some preliminary results concerning mechanisms of magnetic relaxation of the $^{207}$Pb nucleus in aqueous electrolyte solution. In order that the present results should reflect, as far as possible, interactions between the lead nucleus and its unperturbed hydration sphere, we have chosen to study relaxation in acidic perchlorate solutions, in which ion association is generally regarded to be negligible (I).

A standard solution 3.5 $M$ in Pb(ClO$_4$)$_2$ was prepared by dissolving reagent grade PbO in doubly distilled lead-free 70% HClO$_4$. The sample was degassed by a series of freeze–pump–thaw cycles and sealed under its own vapor pressure in a 10 mm o.d. tube. Relaxation times were measured using a Bruker B-KR 322S variable frequency (4–60 MHz) pulsed spectrometer at a fixed frequency of 10.431350 MHz operating in the triplet mode. The magnetic field was held constant by means of an external proton lock. The sample temperature was controlled within ±0.5°C with a Bruker B-ST 100/700 variable temperature accessory. Sampling techniques and other experimental details are described elsewhere (2).

The temperature dependence of $T_1$ is shown in Fig. 1. At least two distinct mechanisms dominate relaxation above and below the maximum at 35°C. The behavior of $T_1$ above 35°C is characteristic of either the spin–rotation interaction or of scalar coupling modulated by chemical exchange (2). A scalar interaction arises from coupling between lead nuclei and $^{17}$O of water molecules surrounding the hydration sphere. An upper limit to this contribution to $T_1$ can be estimated from the theoretical relation:

$$ (T_1)_\text{sc}^{-1} = \frac{2}{3} A^2 S(S+1) \frac{\tau_5}{1 + (\omega_1 - \omega_2)^2 \tau_5} NC, $$

where $A$ is the coupling constant, $\tau_5$ is the exchange time, $N$ is the coordination number of lead and $C$ the natural abundance (0.037%) of $^{17}$O. No coupling constants between lead and oxygen have previously been measured, but Jameson and Gutowsky’s (3) collection of coupling constants of directly bonded elements indicates that $A/2\pi$ does not exceed 1 KHz. Similarly the exchange time is unknown, but the value that gives the largest possible relaxation contribution is obtained when $(\omega_1 - \omega_2)\tau = 1$. Assuming these values for $A$, $\tau_5$ and a primary hydration number of six, we find that $(T_1)_\text{sc}(^{207}\text{Pb}) \approx 200$ sec. This value is larger by an order of magnitude than the experimental relaxation times, and, therefore, an appreciable scalar contribution can be ruled out.

We are left with spin–rotation as the dominant relaxation mechanism above 35°C. The hydrated lead ion probably does not represent a well defined molecular species, and, thus, details of the motion that gives rise to this interaction are of special interest. Although the $T_1$ measurements appear not to provide an unambiguous description of the motion, calculation of the angular momentum correlation time suggests that relevant motions are not those for a rigid hydration sphere but rather pertain to
individual water molecules on the ionic surface. To examine this question we will use
the measured spin–rotation component and Hubbard's (4) rate expression,

\[(T_1)_{\text{sr}}^{-1} = 2kT C_0 \tau_{J/h^2} \]

(1)
to compute \(\tau_J\) assuming (1) that the hydration sphere of Pb\(^{+2}\) is rigid for times comparable
to the angular momentum correlation time and (2) that the coordination sphere of
Pb\(^{+2}\) is octahedral. The spin–rotation constant, \(C_0\), for lead in a site of cubic symmetry

![Graph of T\(_1\) vs. Temperature](image)

**Fig. 1.** \(T_1\) of \(^{207}\)Pb in 3.5 M Pb(ClO\(_4\))\(_2\) solution versus temperature.

can be determined directly from recent optical pumping data in conjunction with
Flygare's (5) expression relating the scalar \(C_0\) to the paramagnetic part of the shielding
constant, \(\sigma_p\),

\[C_0 = \left( \frac{e^2}{6mc^2} \right) \left( \frac{\pi}{M_p \mu_N \gamma_{Pb}} \right)^{-1} \left( \frac{\sigma_p}{3I} \right) \]

(2)

[the symbolism is that given in Ref. (6)] \(\nu \sigma_p\) equals the chemical shift in hertz between
resonances of the vapor phase diamagnetic lead atom and the hydrated lead ion.
Optical pumping experiments (7) have determined that the effective \(^{207}\)Pb magnetic
moment in the vapor is 0.2049440 \(\mu_N\)(\(^1\)H). From this value we compute a resonance
frequency of 10.2484 MHz in the field maintained by our proton lock, for which \(\nu\)
(\(^1\)H) = 50.00560 MHz. The hydrated lead ion was resonant at a frequency of 10.43135
MHz in the same field, giving \(\sigma_p = -183 \text{ kHz}\).

Before either the spin–rotation constant or \(\tau_J\) can be calculated from Eqs. (1, 2), it is
necessary to estimate the moment of inertia, \(I\).

In accord with the assumptions stated above, we take the basic molecular unit to be
the primary hydration sphere. The crystallographic radius for Pb\(^{+2}\), \(r_{Pb} = 1.2 \text{ Å} \) (8),
and the crystallographic radius of oxygen, \(r_o = 0.66 \text{ Å} \) (8), are consistent with a distance
of 1.95 Å between the lead nucleus and the center of mass of a water molecule. On this
basis, \(I\) is computed to be \(45.5 \times 10^{-39} \text{ gm-cm}^2\) and a value of 41.1 kHz is obtained for
\(C_0/2\pi\).

The two unknown quantities in Eq. (1) are \(\tau_J\) and the value of \((T_1)_{\text{sr}}^{-1}\) due to the spin–
rotation interaction. If it is assumed that the spin–rotation contribution at 35°C is equal
to the contribution from the relaxation mechanism dominant below 35°C then \((T_1)_o = 14.2 \text{ sec}\), which gives the value \((T_1)^{-1} = 0.0705 \text{ sec}^{-1}\) at 35°C.

The resulting angular momentum correlation time predicted from this model is extraordinarily short: \(\tau_J = 3.0 \times 10^{-16} \text{ sec}\). This time scale is short even relative to that of molecular vibrations. Although structured liquids can be expected to have very short angular momentum correlation times [values of shorter than \(3.7 \times 10^{-14} \text{ sec}\) have, in fact, been measured for some simple liquids (9)], it is difficult to conceive of any rotational motion of a massive molecular unit that could correspond to this time scale. The fastest motion for a rigid hydration sphere is probably that in which the sphere breaks out of one hydrogen-bonded configuration and reorients into another. This motion probably has a duration longer than \(10^{-14} \text{ sec}\). In view of the extreme shortness of our computed \(\tau_J\), it seems likely that the solvation sphere is nonrigid during intervals comparable to \(\tau_J\), in which case a spin–rotation constant based on the chemical shift is not applicable.

We have not commented on the mechanism of relaxation below 35°C. Detailed studies, involving isotopic substitution and variable frequency measurements are now in progress and should permit an unambiguous determination of the mechanism. If the low temperature measurements allow determination of the angular correlation time, an interesting comparison of \(\tau_\theta\) and \(\tau_J\) [related by Hubbard's relation (4) for diffusive motions] may be possible.

ACKNOWLEDGMENT

Acknowledgment is made to the National Science Foundation and to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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R. M. Hawk*
R. R. Sharp

Department of Chemistry
University of Michigan
Ann Arbor, Michigan 48104

Received October 24, 1972

* Ethyl Corporation Research Fellow.