

Field dependence of nuclear magnetic relaxation of ^{207}Pb in aqueous $\text{Pb}(\text{ClO}_4)_2$

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(Received 5 November 1973)

Nuclear magnetic relaxation times of the ^{207}Pb resonance have been measured as a function of temperature and concentration at field strengths of 16.9, 11.7, and 6.56 kG in aqueous $\text{Pb}(\text{ClO}_4)_2$. Longitudinal relaxation is composed of spin-rotation, chemical shift anisotropy, and dipolar contributions in a 3.5M solution, while spin-rotation strongly dominates the relaxation at all temperatures between the melting and boiling points in a 1.15M solution. T_2 accurately equals T_1 at 1.15M, as is expected for a dominant spin-rotation interaction, but is 20–30% shorter in the 3.5M solution, possibly due to a minor relaxation component arising from scalar coupling to naturally abundant H_2^{17}O . Chemical shifts of ^{207}Pb have also been measured in aqueous $\text{Pb}(\text{ClO}_4)_2$ and $\text{Pb}(\text{NO}_3)_2$. The chemical shift and relaxation data show that ClO_4^- penetrates the Pb^{+2} hydration sphere at concentrations above about 2M, but no effects of such penetration are seen at lower concentration.

INTRODUCTION

Previous measurements of chemical shifts and nuclear relaxation times of various magnetic isotopes in electrolyte solutions have provided a great deal of information about the structure and dynamics of solvated ions. Chemical shift measurements, particularly of ^{17}O , provide a singularly unambiguous method for determining primary hydration numbers of ions with relatively labile hydration spheres.¹ Chemical shifts of the nuclei of dissolved ions are very sensitive probes of the solution environment and have frequently been used in studies of ion-pairing and complex formation.² Relaxation times, on the other hand, primarily reflect changes of translational and reorientational correlation times with variations in concentration or temperature. They have been used to study ionic self diffusion³ as well as motions of molecules in the first solvation sphere. Naturally abundant isotopes of the large majority of common monatomic ions (i. e., the alkali metals, the alkaline earths, the halogens except ^{19}F , aluminum, etc.) have nuclear spins greater than $\frac{1}{2}$ and therefore possess nuclear quadrupole moments. Relaxation of these nuclei is, in virtually every case, dominated by interactions between the electric quadrupole moment and fluctuating electric field gradients at the nucleus due to thermal motion of the surrounding charge distribution. Rates of quadrupolar relaxation are given by the product of a reorientational correlation time and a mean squared quadrupole coupling constant. Unfortunately these factors cannot be measured separately in solution, and it is therefore difficult to obtain detailed motional or structural information from the ion relaxation times.

The ^{207}Pb isotope possesses a nuclear spin of $\frac{1}{2}$ and is of interest because its relaxation results from a competition of several interactions which, if separated experimentally, may contain direct information about the hydration sphere. For example, the formation of labile complexes can produce a field-dependent T_2 mechanism which arises from random fluctuations in the ^{207}Pb Larmor frequency as the metal ion exchanges between chemically shifted sites.⁴ This contribution varies as the square of the field strength and has been used in a

variety of model systems to obtain rate constants for chemical exchange. The longitudinal relaxation rate can be written as a sum of terms

$$(T_1)_{\text{obs}}^{-1} = (T_1)_{\text{D-D}}^{-1} + (T_1)_{\text{SR}}^{-1} + (T_1)_{\text{SC}}^{-1} + (T_1)_{\text{CSA}}^{-1}$$

corresponding to nuclear dipole-dipole coupling, spin-rotation coupling, scalar coupling and chemical shift anisotropy. All of these relaxation mechanisms have been discussed in detail elsewhere,^{5,6} and we point out here only a few specific aspects that pertain to aqueous solutions and are useful for distinguishing different components of the relaxation rate through temperature and field dependent studies. The spin-rotation term is proportional to a correlation time τ_J for the net angular momentum vector, with respect to the ^{207}Pb nucleus, of molecules in the cation hydration sphere. This correlation time cannot be interpreted as simply as that for rigid molecules undergoing Brownian reorientation. In the simplest case of rigid spherical top molecules, τ_J , as well as $(T_1)_{\text{SR}}^{-1}$, increases with increasing temperature and is related to the angular reorientation time, τ_θ , by Hubbard's relation,⁷ $\tau_\theta \tau_J = I/6kT$. This relation is accurate strictly in the small step diffusion limit. The intramolecular dipolar contribution is proportional to τ_θ , and consequently $(T_1)_{\text{SR}}^{-1}$ and $(T_1)_{\text{D-D}}^{-1}$ vary in opposite directions with changing temperature, their product remaining constant [since $\tau_J \propto T^{-1}(T_1)_{\text{SR}}^{-1}$]. Molecules in a hydration sphere are not necessarily bound electrostatically into a rigid, coherently reorienting entity, however, even on a time scale comparable to τ_J ($< 10^{-12}$ sec). If the hydration sphere is nonrigid, a relaxation mechanism can still arise from local time-dependent magnetic fields associated with the relative motion of the ion and its molecular surroundings. Liquid xenon provides a model of spin-rotation interactions in liquids composed of freely diffusing particles. Local fields resulting from interatomic collisions provide the dominant relaxation pathway of the spin- $\frac{1}{2}$ ^{129}Xe isotope.⁸ T_1 of ^{129}Xe is found to be independent of temperature, but there appears at present to be no theoretical justification for assuming that free diffusion also leads to a temperature independent relaxation contribution for ion nuclei in electrolyte solutions. Nevertheless, an experimental verification

of the specific temperature dependence implied by Hubbard's relation would certainly support a hypothesis that the hydration sphere reorients as a rigid entity over intervals the order of 10^{-11} sec.

$(T_1)_{\text{CSA}}^{-1}$ and $(T_1)_{\text{SC}}^{-1}$ are field dependent contributions which vary respectively as H_0^2 and H_0^{-2} (H_0 is the external field strength). When the resonant nucleus is in a rigid molecule, $(T_1)_{\text{CSA}}^{-1}$ is proportional to the angular correlation time, τ_{Θ} . The correlation time must again be interpreted differently for the aquated Pb^{+2} ion. The appropriate interpretation depends on whether the chemical shift anisotropy arises from asymmetry in the primary hydration sphere, or from the formation of asymmetric complexes or ion pairs; this question is best decided by the concentration dependence of $(T_1)_{\text{CSA}}^{-1}$. Only for the scalar component does the correlation time retain the same interpretation that it has in less labile liquid systems. Scalar relaxation in general results from modulation of the spin-spin coupling between a pair of magnetic isotopes. If the coupling is modulated by nuclear relaxation of one of the spins, τ_{SC} is the relaxation time of that spin. If chemical exchange modulates the coupling, then τ_{SC} is approximately equal to the inverse rate constant for chemical exchange.⁵

The results of a systematic study of ^{207}Pb relaxation in aqueous $\text{Pb}(\text{ClO}_4)_2$ solutions is reported below. Perchlorate solutions were chosen because of the very small tendency toward ion-pairing exhibited by this anion. Competing relaxation mechanisms have been separated by varying the concentration and temperature, as well as through measurements at several field strengths. Chemical shifts of the ^{207}Pb resonance are also reported in $\text{Pb}(\text{ClO}_4)_2$ and $\text{Pb}(\text{NO}_3)_2$ solutions. The chemical shift and relaxation measurements provide some information about the extent of ion-pairing in aqueous $\text{Pb}(\text{ClO}_4)_2$ and about molecular motions in the hydration region. It is hoped that they will also provide a basis for interpreting relaxation in structurally more complex solutions, such as those of the lead halides.

EXPERIMENTAL

Relaxation times of ^{207}Pb were measured using a variable frequency Bruker B-KR-322s pulsed NMR spectrometer and a Fabri-Tek Model 1064 signal averaging computer.¹⁰ The magnet was locked externally using a broad-band NMR field lock that has been described previously.¹¹ A $180_0-\tau-90_0$ sequence was used to measure T_1 , and the phase-shifted Carr-Purcell sequence with a pulse spacing of 6 msec was used for T_2 . The number of scans required for satisfactory definition of the decay varied from 32 to 128 accumulations, and the resulting accuracy for both T_1 and T_2 is estimated to be $\pm 10\%$. The temperature was stabilized within $\pm 1^\circ\text{C}$ by a Bruker temperature controller calibrated at each temperature by a thermometer in a dummy sample tube.

All $\text{Pb}(\text{ClO}_4)_2$ solutions were prepared by diluting a 4.2M stock solution with doubly distilled water. The stock solution was prepared by weight by dissolving reagent grade PbO in 70% perchloric acid. Samples used for relaxation measurements were transferred to 10 mm sample tubes degassed by 10 freeze-pump-thaw cycles

and sealed under vacuum. Samples used only for chemical shift measurements were not degassed. Reagent grade $\text{Pb}(\text{NO}_3)_2$ was dried to constant weight, and a 1.91M stock solution was prepared using doubly-distilled water. Samples were prepared by dilution and were sealed, without degassing, in 10 mm NMR tubes.

RESULTS

Relaxation times for ^{207}Pb in aqueous $\text{Pb}(\text{ClO}_4)_2$ have been measured as a function of concentration between 0.5 and 4.20 M at 27.5°C , and as a function of temperature and field strength at 1.15 and 3.50M. These results are summarized in Figs. 1-4. All solutions contained approximately 1M excess perchloric acid to suppress hydrolysis. The more highly concentrated solutions are mobile liquids over most of their liquid range but become increasingly viscous within about 15° of the melting point. Solidification of the 3.5M solution occurred gradually between about -24 and -30°C to form a solid which appeared to be glassy and was sometimes opaque and sometimes quite clear.

Longitudinal relaxation rates for ^{207}Pb in the 3.5M $\text{Pb}(\text{ClO}_4)_2$ sample are plotted as a function of inverse temperature at field strengths of 16.9, 11.7, and 6.56 kG in Fig. 1. The presence of a minimum near room temperature at all three field strengths indicates that at least two distinct mechanisms contribute to the observed relaxation rate. $(T_1)_{\text{obs}}^{-1}$ increases with increasing temperature in the high temperature region and is field independent. This behavior is characteristic of a dominant spin-rotation interaction. Scalar coupling of ^{207}Pb to ^1H or ^{17}O of water could in principle produce a relaxation component with the observed temperature dependence, but it has been shown previously⁹ that the magnitude of this contribution is too small, even employing the most favorable assumptions with respect to correlation times and scalar coupling constants, to account for the observed relaxation rate. The data in Fig. 1 quantitatively reinforce this conclusion since $(T_1)_{\text{obs}}^{-1}$ is asymptotically field independent in the high temperature region, while a scalar component varies theoretically as the inverse square of magnetic field strength. Thus spin-rotation appears to be the only important relaxation mechanism in the high temperature limit. It is not immediately clear, however, which rotating molecular entity gives rise to this interaction. This question is considered further below.

Relaxation in the low temperature region is clearly field dependent and increases with increasing field. The only T_1 mechanism with this field and temperature dependence arises from chemical shift anisotropy, and is described by the expression

$$(T_1)_{\text{CSA}}^{-1} = \frac{8}{7} (T_2)_{\text{CSA}}^{-1} = \frac{2}{15} \gamma^2 H_0^2 (\sigma_{\parallel} - \sigma_{\perp}) \tau_c \quad (1)$$

This equation assumes that the shielding tensor, σ , is isotropic in one plane, and σ_{\parallel} and σ_{\perp} are the in- and out-of-plane shielding components respectively. γ is the gyromagnetic ratio of ^{207}Pb , H_0 is the field strength, and τ_c is a correlation time for reorientation of the unique axis of the shielding tensor. The other T_1 mechanism that can possibly be field dependent (excluding scalar

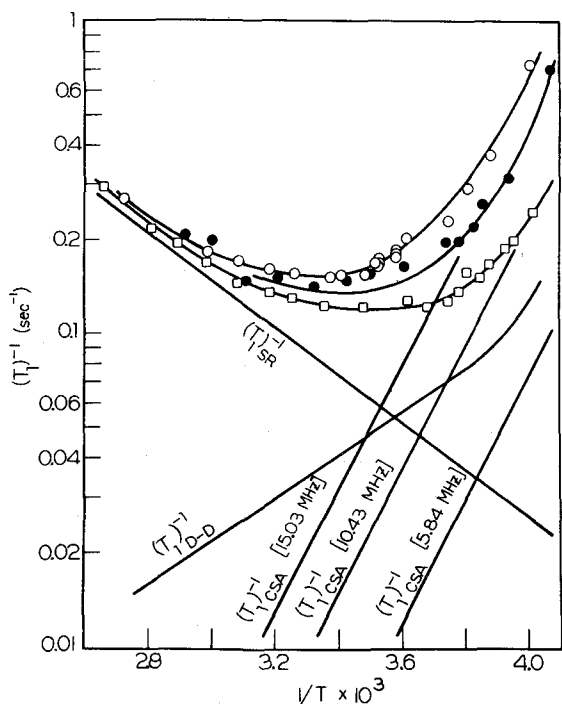


FIG. 1. Longitudinal relaxation rates of ^{207}Pb in 3.5M aqueous $\text{Pb}(\text{ClO}_4)_2$ at field strengths of 16.9 kG (O), 11.7 kG (●) and 6.56 kG (□). Separation of relaxation mechanisms is described in the text.

coupling to ^{17}O for reasons given above) is dipolar relaxation in a solution that is sufficiently viscous that the extreme narrowing approximation, $(\omega_I + \omega_S)^2 \tau_c \ll 1$, no longer applies.^{5,6} Failure of the extreme narrowing approximation leads to a dependence of $(T_1)_{\text{obs}}^{-1}$ on $(\omega_I - \omega_S)^{-2}$, however, which is in the opposite direction to the observed field dependence. Furthermore the field dependence of T_1 persists to quite high temperatures at which the solution is a normal mobile liquid, and it must therefore be attributed entirely to chemical shift anisotropy, except possibly in the glassy solid.

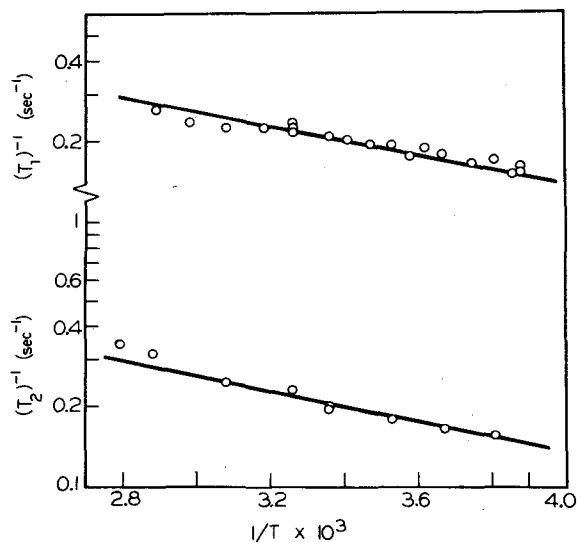


FIG. 2. Longitudinal and transverse relaxation rates of ^{207}Pb in 1.15M aqueous $\text{Pb}(\text{ClO}_4)_2$ at a field strength of 16.9 kG.

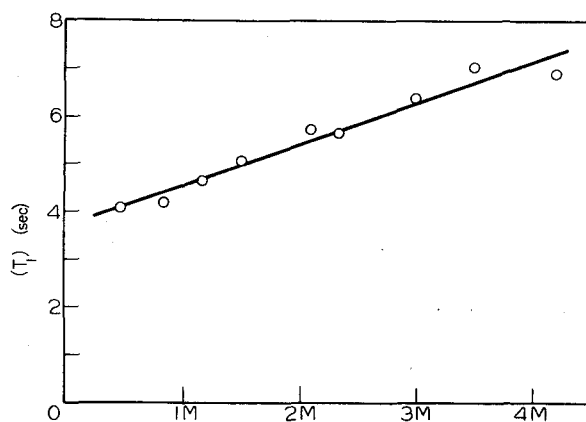


FIG. 3. T_1 versus concentration in aqueous $\text{Pb}(\text{ClO}_4)_2$ at 27°C.

The absolute magnitude of the chemical shift anisotropy contribution to the total relaxation rate can be computed at any temperature using Eq. (1) and measured values of $(T_1)_{\text{obs}}^{-1}$ at two field strengths. Since the field dependence of $(T_1)_{\text{obs}}^{-1}$ results entirely from $(T_1)_{\text{CSA}}^{-1}$, we can write

$$(T_1)_{\text{obs}}^{-1}(\omega_1) - (T_1)_{\text{obs}}^{-1}(\omega_2) = (T_1)_{\text{CSA}}^{-1}(\omega_1) - (T_1)_{\text{CSA}}^{-1}(\omega_2),$$

which, using Eq. (1) gives

$$(T_1)_{\text{CSA}}^{-1}(\omega_1) = [(T_1)_{\text{obs}}^{-1}(\omega_1) - (T_1)_{\text{obs}}^{-1}(\omega_2)] [1 - (\omega_2/\omega_1)^2]^{-1}.$$

The curves shown in Fig. 1 were plotted by drawing curves through the experimental data at 5.84 MHz and 15.03 MHz, and then computing, at successive temperatures, values of $(T_1)_{\text{CSA}}^{-1}$. A substantial portion of $(T_1)_{\text{obs}}^{-1}$ cannot be accounted for by spin-rotation and chemical shift anisotropy contributions alone, and the difference is attributed to dipolar relaxation. A check on the quantitative separation of mechanisms is provided by the data at 10.43 MHz, which should agree with the computed curve for $(T_1)_{\text{obs}}^{-1}$ at this frequency. The fit at all three frequencies is excellent, and observed deviations are definitely within experimental error. The computed curve assigned to dipolar relaxation shows Arrhenius behavior above -10°C , with an activation energy of 3.16 kcal/mole. A slight nonlinearity in $(T_1)_{\text{D}}^{-1}$ is evident below -10°C , but little significance is attributed to this feature, which is scarcely outside experimental uncertainty.

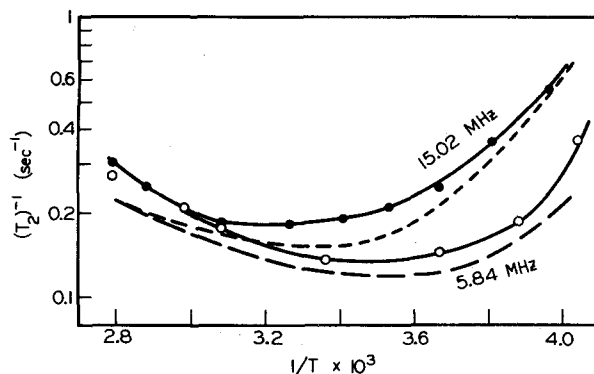


FIG. 4. Transverse relaxation rates of ^{207}Pb in 3.5M aqueous $\text{Pb}(\text{ClO}_4)_2$ at 16.9 kG (●) and 6.56 kG (O). T_1 data at the same field strengths are shown as dashed lines.

Figure 2 contains Arrhenius plots of $(T_1)^{-1}$ and $(T_2)^{-1}$ in a 1.15M $\text{Pb}(\text{ClO}_4)_2$ solution at 16.9 kG. Identical straight lines are drawn through both sets of data, and the good fits obtained show that T_1 equals T_2 within experimental error. All evidence of the chemical shift anisotropy contribution has vanished at 1.15 M, and spin-rotation appears to dominate relaxation over the entire temperature range. The suppression of $(T_1)_{\text{CSA}}^{-1}$ at the lower concentration is easily understood, since the most probable source of anisotropy in the shielding tensor is the formation of PbClO_4^+ ion pairs, which although not stable according to Bjerrum's criterion,¹² probably have a transient existence in concentrated lead solutions. Since the influence of chemical shift anisotropy is entirely negligible at 1.15M, $(T_1)_{\text{Obs}}^{-1}$ results principally from spin-rotation with the possibility of a minor dipolar contribution at low temperature. A comparison of the T_1 data at 1.15M with the quantitative $(T_1)_{\text{SR}}^{-1}$ and $(T_1)_{\text{D-D}}^{-1}$ assignments at 3.5M shows that $(T_1)_{\text{SR}}^{-1}$ increase with increasing concentration. Also, the activation energy for $(T_1)_{\text{SR}}^{-1}$ increases very markedly (from 1.26 kcal/mole to 3.49 kcal/mole between 1.15 and 3.5M. It is interesting that the T_1 data at 1.15M are quite linear on an Arrhenius plot and do not curve upward at low temperature as would be predicted if the dipolar contribution were appreciable. In rigid molecular systems $(T_1)_{\text{SR}}^{-1}$ and $(T_1)_{\text{D-D}}^{-1}$ vary with temperature in an approximately inverse manner. The behavior in aqueous solution is apparently similar, with the result that $(T_1)_{\text{D-D}}^{-1}$ decreases both in magnitude and activation energy with decreasing concentration. If the activation energy of $(T_1)_{\text{D-D}}^{-1}$ is much smaller at 1.15M than at 3.5M the dipolar contribution would be difficult to detect from the data in Fig. 2. For this reason a small low temperature dipolar contribution cannot be ruled out.

The variation of T_1 with concentration at 25 °C is shown in Fig. 3. Relaxation at this temperature is dominated by spin-rotation, and thus the increase in T_1 with concentration reflects primarily similar changes in $(T_1)_{\text{SR}}$ that have been discussed above.

Transverse relaxation rates of ^{207}Pb in the 3.5M solution are shown at two frequencies in Fig. 4. The T_1 data at these frequencies are given in Fig. 1 and are shown as dashed curves in Fig. 4 for comparison. T_1 and T_2 exhibit qualitatively very similar temperature and field dependence except that T_2 is systematically shorter than T_1 by 20–30%. This difference is not much greater than experimental uncertainty, but we believe that it is real since measured values of T_2 accurately equal measured T_1 values in the more dilute 1.15M solution. Rather surprisingly the observed difference shows no detectable dependence upon temperature or field strength. A relatively small difference (~17%) between T_1 and T_2 is expected when $(T_1)_{\text{Obs}}^{-1}$ is dominated by chemical shift anisotropy, but this interaction is appreciable only when $(T_1)_{\text{CSA}}^{-1}$ is large and cannot explain the systematic difference observed in the high temperature region and at 5.84 MHz. Two other common relaxation mechanisms, those due to scalar coupling and to chemical exchange between chemically shifted sites, also shortens T_2 relative to T_1 . The latter interaction increases as the square of the field strength and cannot provide an ex-

planation for the field independence of $(T_2)_{\text{Obs}}^{-1} - (T_1)_{\text{Obs}}^{-1}$ that is apparent in Fig. 4. On the other hand, scalar coupling of ^{207}Pb to either ^{17}O or ^1H (or conceivably even $^{35,37}\text{Cl}$) provides a field-independent T_2 contribution given by the expression

$$(T_2)_{\text{SC}}^{-1} - \frac{1}{2} (T_1)_{\text{SC}}^{-1} = \frac{1}{3} A^2 S(S+1) \tau_{\text{SC}} ,$$

where A is the scalar coupling constant and τ_{SC} is the correlation time for the scalar interaction. In aqueous $\text{Pb}(\text{ClO}_4)_2$ solutions chemical exchange between all solution species is rapid compared to relaxation rates of ^{17}O , ^1H , or $^{35,37}\text{Cl}$. τ_{SC} can therefore be identified physically with: (1) The mean lifetime of water molecules in the first hydration sphere, (2) the proton exchange time, or (3) the rate constant for dissociation of PbClO_4^+ , depending on the nucleus to which ^{207}Pb is coupled. Scalar coupling to protons can almost certainly be neglected as a T_2 contribution because the proton exchange time in 1 molar acid is exceedingly short, probably the order of 10^{-10} – 10^{-11} sec. Scalar coupling to ^{17}O may well produce a T_2 contribution of the observed magnitude ($\sim 0.05 \text{ sec}^{-1}$). Assuming that the first hydration sphere contains eight water molecules, that $(A/2\pi) = 500 \text{ Hz}$ for ^{207}Pb – ^{17}O coupling, and taking account of the fact that ^{17}O is 0.037% abundant, we calculate a T_2 contribution of 0.05 sec^{-1} when the exchange time is $4(10^{-7}) \text{ sec}$. This exchange time is somewhat longer than a value inferred previously from ultrasonic measurements (see the following section), but its order of magnitude is not unreasonable. An appreciable scalar contribution to T_2 could be identified unambiguously from studies on solutions enriched in H_2^{17}O . This contribution provides, at least in principle, a method for measuring the exchange rate of water molecules in the first hydration sphere of diamagnetic ions.¹³

Chemical shifts of ^{207}Pb in aqueous $\text{Pb}(\text{ClO}_4)_2$ and $\text{Pb}(\text{NO}_3)_2$ are shown as a function of concentration in Fig. 5. The general behavior of these shifts is similar to that observed for several other ion resonances in aqueous electrolyte solutions. At concentrations below 1 molar the perchlorate solution is shifted to low field and the nitrate solution is shifted to high field. The convergence of these curves helps to define the resonance position at infinite dilution, which is placed at $11.08820 \pm 0.00010 \text{ MHz}$ in Fig. 5. The chemical shift is essentially independent of temperature, as is expected from a previous detailed study of chemical shifts of ions.¹⁴

DISCUSSION

Investigations using ultrasonic and Raman spectroscopy have provided a certain amount of direct spectroscopic information about the lability of the first hydration sphere of Pb^{+2} and about the ability of oxyanions to coordinate directly to the cation, forming complexes such as PbClO_4^+ . Ultrasonic studies of dilute Pb^{+2} solutions have not, to our knowledge, been reported, but studies of similar divalent cations, Ca^{+2} , Sr^{+2} and Ba^{+2} , show ultrasonic dispersions corresponding to the exchange of H_2O from the first hydration sphere with rate constants $k_{\text{ex}} = 3.0(10^8)$, $3.5(10^8)$, and $7.2(10^8) \text{ sec}^{-1}$, respectively.¹⁵ Pb^{+2} is probably quite similar to Sr^{+2} in its hydration properties, since its ionic radius and heat of hydra-

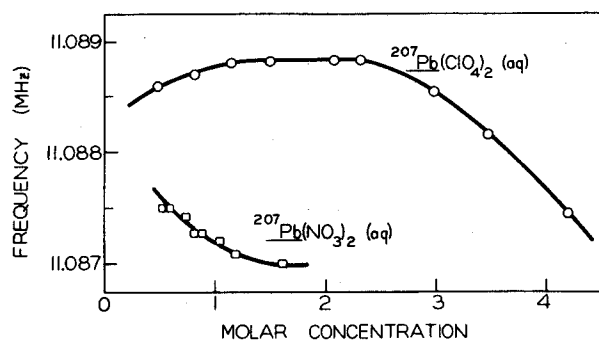


FIG. 5. Chemical shifts of ^{207}Pb versus concentration in aqueous $\text{Pb}(\text{ClO}_4)_2$ and $\text{Pb}(\text{NO}_3)_2$ at 27°C .

tion are close to that of Sr^{+2} and intermediate between Ca^{+2} and Ba^{+2} .^{16,17} Thus it is probable that the half life of the Pb^{+2} hydration sphere with respect to water exchange is approximately $4(10^{-9})$ sec, and that the lifetime of specific water molecules in the hydration sphere is the order of $3(10^{-8})$ sec.

The question of penetrability of the hydration sphere by the oxyanions, NO_3^- , SO_4^{2-} , and ClO_4^- , has been studied by Hester and Plane^{18,19} using Raman spectroscopy. The vibrational symmetry of these ions is lowered in certain concentrated electrolyte solutions, and the splitting of vibrational modes that are degenerate in the isolated anion is used as a criterion for the formation of contact ion pairs. Vibrational splittings were observed in the large majority of saturated nitrate solutions, but among saturated perchlorate solutions only $\text{In}(\text{ClO}_4)_3$, out of 15 perchlorate salts investigated, showed evidence of ion pairing. $\text{Pb}(\text{ClO}_4)_2$ showed only the T_d fundamentals, which lead Hester and Plane¹⁸ to conclude that inner sphere coordination does not occur in solutions of this and most other perchlorate salts. Irish and Walrafen²⁰ have also pointed out, however, that the NO_3^- splittings are not proportional to concentration in aqueous $\text{Ca}(\text{NO}_3)_2$ and that a substantial splitting remains in the limit of infinite dilution. Thus, the splitting does not prove the occurrence of direct interionic contact, but the lack of splitting in the case of ClO_4^- ion does suggest that there is little or no contact ion pairing even in saturated $\text{Pb}(\text{ClO}_4)_2$. This conclusion is also supported by some less direct evidence,²¹ most of it based on negative results, such as the absence of broadening of the ^{35}Cl resonance in perchlorate solutions of many transition metal ions.²²

Our relaxation and chemical shift data present a rather different picture of interionic interactions in aqueous $\text{Pb}(\text{ClO}_4)_2$. Chemical shift anisotropy dominates the low temperature relaxation of 3.5M solutions and can only be due to the presence of substantial concentrations of PbClO_4^+ . Estimates, based on Eq. (1), of $\Delta\sigma$ show that the absolute value of the anisotropy must be extremely large to account for the observed relaxation rates. Assuming that every Pb^{+2} ion is coordinated to ClO_4^- and that the correlation time for reorientation of ion pairs is 10^{-10} to 10^{-11} sec, the computed anisotropy falls in the range 1000–3000 ppm. This value is substantial even relative to the known range of ^{207}Pb chemical shifts in diamagnetic compounds.²³ The actual value of $\Delta\sigma$ will be

somewhat larger than this estimate since ion pairing is almost certainly incomplete in a 3.5 solution. $(T_1)_{\text{CSA}}^{-1}$ is strongly concentration dependent as expected and is negligible at 1.15M. Thus, the relaxation data provide very strong evidence for direct $\text{Pb}^{+2}-\text{ClO}_4^-$ ionic contact, at least at high (~ 3 M) concentration. The chemical shift data in Fig. 5 are also concentration dependent in a manner that suggests significant ion pairing in concentrated solutions. The ^{207}Pb chemical shift in aqueous $\text{Pb}(\text{ClO}_4)_2$ varies in a low field direction in dilute solutions, passes through a maximum in the neighborhood of 2M, and at higher concentrations falls sharply in a high field direction. The presence of an extremum in the chemical shift data probably results from the increasing influence of direct ion contact, which produces a high-field shift at concentrations above 2M. The initial low-field shift would then be due to longer range interactions between the anion and the Pb^{+2} hydration sphere. This interpretation fits well with the relaxation results, which show a chemical shift anisotropy contribution at 3.5M but not at 1.15M. Deverell²⁴ has observed a similar extremum in the ^{35}Cl chemical shift in concentrated LiCl solutions and likewise attributed this feature to the onset of direct interionic contact. The extremum in aqueous LiCl occurs at quite high concentrations (~ 8 M), where most of the water present is bound in the Li^+ hydration sphere. The mole ratio of Li^+ to H_2O is 1 : 7 at this concentration. The Pb^{+2} hydration sphere is thermodynamically less stable than that of Li^+ , and penetration of the anion is noticeable when the mole ratio of Pb^{+2} to H_2O is 1 : 18.

ACKNOWLEDGMENT

Financial support from the National Science Foundation and from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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