(intensity roughly that of the 191-M line) of 185.8 kev is observed. It cannot be assigned to any expected transition.

The spins assigned to the 77.4- and 269-kev levels are consistent with the available data. Tentatively, we designate the two levels as $\frac{1}{2}+$ or $\frac{3}{2}+$ and $\frac{3}{2}+$ or $\frac{1}{2}+$, respectively. The $\frac{1}{2}+$ assignment for the spin of the 77.4-kev level is preferred since the 201.9-kev transition from the 279-kev ($d_{5/2}$) level to the 77.4-kev level is not observed.

Some comments may be made regarding the systematics of L shell conversion. This is the first $E3$ isomeric transition for which adequate resolution of the L lines has been obtained. The establishing of the systematics of L conversion for a transition of this multipole order, energy, and Z is invaluable for deciding multipole orders of other transitions. For the $E3$ isomeric transition of 130 kev in Au, the (L_{I}:L_{II}:L_{III}) ratio is ($<0.1:\sim 2.5:1$). Taking the K-shell internal conversion coefficient as 2.0 and the K/L ratio as 0.133, the empirical values of the absolute L-shell internal conversion coefficients are (L_{I}: <0.4; L_{II}: 10.4; L_{III}: 4.2). Rutledge, Cork, and Burson[11] have reported that for certain transitions, designated by them as $E3$, the L conversion is predominantly L_{I}. These transitions occur in Se($Z=34$). In order to establish that the conversion is in the L_{I} shell, one has to measure the $K-L$ energy difference well enough to distinguish between $K-L_{\mathrm{I}}=9.99$ kev and $K-L_{\mathrm{II}}=10.18$ kev. However, it would not be impossible that for this low Z, $E3$ L conversion occurred in the L_{I} shell. It has been pointed out[6] that for the $E2$ transition of 247 kev in Cd^{111m}, the L conversion is probably mostly in the L_{I} shell, as borne out by the calculations of Gellman *et al.*

For the 166-kev $M4$ in Hg, the L ratio is $1:<0.1:1.5$. The theoretical estimate of Tralli and Lowen[12] would predict the ratio to be $1:<0.5:\sim 2.2$.

The 134-kev $E2$ has an L ratio of 0.04:1.1:1 as compared to the theoretical value (obtained by interpolation of the data of Gellman *et al.*) of 0.1:1.4:1. Owing to the absence of theoretical data and the paucity of experimental data on $E3$ transitions, one cannot yet distinguish between $E2$ and $E3$ transitions on the basis of L ratios alone.

We are indebted to Dr. M. Goldhaber for his continued interest in this problem.

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[11] Rutledge, Cork, and Burson, Phys. Rev. **86**, 775 (1952).

[12] N. Tralli and I. S. Lowen, Phys. Rev. **76**, 1541 (1949).

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Nuclear Magnetic Resonance in Thallium Compounds*

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A precision, resonance absorption measurement has been made of the ratio of the magnetic moments of Tl^{205} and Tl^{203}. The experimental ratio is $\mu^{205}/\mu^{203}=1.009838\pm 0.000001$. This result, when compared with the value observed by Berman for the ratio of hyperfine structure separations in the $^2P_{\frac{1}{2}}$ state, $\Delta\nu^{205}/\Delta\nu^{203}=1.00974\pm 0.00003$, establishes the reality of effects attributable to the finite nuclear size.

Shifts of about 0.2 percent have been found in the thallium resonance position in Tl^{+3} compared to Tl^{+1} compounds. The resonance shifts in aqueous solutions varied linearly with the anion concentration. Complex formation and interionic electronic exchange interactions, respectively, account qualitatively for the observed effects.

INTRODUCTION

These experiments were initiated to obtain data for comparison with theoretical values for the nuclear magnetic shielding. Thallium is one of the very few elements with two different, simple oxidation states, Tl^{+1} and Tl^{+3}, for which nuclear magnetic resonances might be observed and any differences in position compared with theory.[1,2] However, we have found the nuclear magnetic shielding to depend not only upon the oxidation state of the thallium but also upon the anions present in solution. Moreover, the magnetic shielding changes remarkably in solutions of different concentration. Here, results are given for several compounds and concentrations.

In addition, we have made a precision determination of the ratio of the Tl^{205} and Tl^{203} magnetic moments, because this ratio is important in analyzing hyperfine structure anomalies. Berman[3] reported recently a precise value for the ratio of the hyperfine structure separations of the $^2P_{\frac{1}{2}}$ ground states of Tl^{205} and Tl^{203} by the atomic beam magnetic resonance method. This ratio differs by 9 to 12 parts in 10^5 from values determined for the ratio of the magnetic moments by nuclear magnetic resonance methods.[4-7] But the combined

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† U. S. Atomic Energy Commission Predoctoral Fellow.

[1] W. E. Lamb, Jr., Phys. Rev. **60**, 817 (1941).

[2] W. C. Dickinson, Phys. Rev. **81**, 717 (1951).

[3] A. Berman, Phys. Rev. **86**, 1005 (1952).

[4] W. G. Proctor, Phys. Rev. **75**, 522 (1949).

[5] H. L. Poss, Phys. Rev. **75**, 600 (1949).

[6] R. E. Sheriff and D. Williams, Phys. Rev. **82**, 651 (1951).

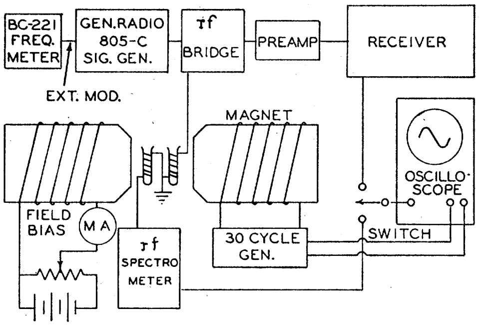

FIG. 1. Block diagram of experimental arrangement used in measuring the magnetic moment ratio.

errors in the ratios was about 8 parts in 10^5, with 5 parts from the nuclear magnetic resonance value, so the reality of the difference was not established with certainty. However, as pointed out by Berman,[3] a difference of about the magnitude observed should arise from the finite size of the nucleus. We undertook a more precise measurement of the magnetic moment ratio in order to obtain a better value for the difference, if any.

EXPERIMENTAL DETAILS

Most of the apparatus and procedures used here have been described.[8,9] A block diagram of the setup for measuring the magnetic moment ratio is given in Fig. 1. It is a double resonance apparatus, one part being a bridge system, the other a spectrometer, with separate coils and samples, and a manual switch for displaying the resonance from either system on a common oscilloscope. The magnetic field of 6365±2 gauss was supplied by a permanent magnet.[8] The rf bridge used is a null-T type.[10] The rf spectrometer is a regenerative oscillator.[9] The two sample coils were mounted side by side, separated by about 5 mm. The coils had a common ground in the support probe on which they were mounted. The samples were contained in thin-walled 10-mm o.d. Pyrex test tubes; care was taken to insure that both samples were identical for a given set of measurements.

The magnetic moment ratio was obtained by measuring directly the frequency difference between the resonance frequencies of the two isotopes in the same field and also measuring the actual resonance frequencies of the two isotopes. The magnetic moment ratio, since both spins are $\frac{1}{2}$, is then given by the equation

$$\mu_{\mathrm{Tl}^{205}}/\mu_{\mathrm{Tl}^{203}}=\nu_{\mathrm{Tl}^{205}}/\nu_{\mathrm{Tl}^{203}}=1+\Delta\nu'/\nu_{\mathrm{Tl}^{203}},$$

where $\Delta\nu'$ is the *directly measured* difference in the two resonance frequencies. A similar equation is used to compute the ratio from the resonance frequency of Tl^{205}. The increased precision of our measurement of this ratio results largely from the direct measurement of $\Delta\nu'$, which is fairly small, instead of computing the ratio from the two resonance frequencies themselves. The stability and high homogeneity[8] of the field of the permanent magnet were also essential.

$\Delta\nu'$ was measured in the following manner. The General Radio 805C signal generator and rf bridge system were tuned approximately to the resonance of one isotope, and the spectrometer to the other. The rf bridge resonance was centered on the oscilloscope by adjusting the dc field biasing current. The bias field was kept as constant as possible and varied no more than about 0.03 gauss during a series of measurements. The spectrometer resonance was then displayed on the same scope by means of the switching system shown in Fig. 1, and tuned to center. The frequency difference was then the difference between the frequency of the signal generator and the frequency of the spectrometer. The output of a Signal Corps BC-221 frequency meter was connected to the external modulation terminal of the signal generator, producing side bands separated by the frequency of the meter. The frequency meter was adjusted so the first side band of the signal generator zero beated against the frequency of the spectrometer, as indicated by a stationary spectrometer resonance pattern on the scope. Loose coupling of the two systems was provided by the common ground of the two sample coils. The frequency separation, $\Delta\nu'$, was then just the frequency of the frequency meter itself. In a given run ten measurements of $\Delta\nu'$ were made in the manner outlined above; half of the measurements were made with the coil connections interchanged to correct for the very small field difference between the two sample coils. The actual frequency of the signal generator or the spectrometer was measured by loosely coupling the frequency meter with either the rf bridge preamp or the spectrometer and zero beating.

The chemical and concentration shifts in the thallium resonance were measured with a simple rf bridge system similar to that included in Fig. 1. In most cases, including the samples used for the magnetic moment ratio experiment, the resonance line widths were governed by the inhomogeneities in the magnetic field, and the lines could be positioned accurately on the oscilloscope. The shifts were measured by interchanging samples in the rf coil and noting the difference in the field biasing current needed to center the resonance first from one sample and then from the other. This method eliminates the field corrections required in a double probe system, but it has the disadvantage that the signal generator may drift a small amount while samples are interchanged and the bridge rebalanced. The error introduced by frequency drift was minimized by doing the measurements rapidly and by inverting the order of measuring the samples halfway through a

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[7] H. E. Walchli, "A Table of Nuclear Moment Data", Preliminary Issue, Oct. 1, 1952, p. 89; we learned of this result after completing our measurements.

[8] H. S. Gutowsky and C. J. Hoffman, J. Chem. Phys. **19**, 1259 (1951).

[9] Gutowsky, Meyer, and McClure, Rev. Sci. Instr. (to be published).

[10] W. N. Tuttle, Proc. Inst. Radio Engrs. **28**, 23 (1940).

series of measurements so a constant drift would tend to cancel out. It is believed that most of the error was in centering the resonance line, especially for the weaker lines, with probable errors of ±0.02 gauss for most of the measured shifts, and maximum systematic errors in the calibration of the field biasing current of ±1 percent of the measured shift.[8]

The samples used were either of commercial origin, of cp grade, or were prepared as described in the text.

RESULTS AND DISCUSSION

The Ratio of the Magnetic Moments

This ratio was measured in two different samples. One was a 1.4 molar aqueous solution of thallous acetate and the other a thallic solution prepared by dissolving Tl_2O_3 in *aqua regia*. The magnetic moment ratio was the same in the two oxidation states. The results of the several series of measurements are given in Table I. These measurements give an average of

$$\mu_{Tl^{205}}/\mu_{Tl^{203}}=1.009838\pm0.000001.$$

This value agrees quite well with the earlier less precise values[4–7] which are given also in Table I.

The ratio of the hyperfine structure separations of the ${}^2P_{\frac{1}{2}}$ ground states of Tl^{205} and Tl^{203} has been reported by Berman[3] as

$$\Delta\nu_{Tl^{205}}/\Delta\nu_{Tl^{203}}=1.00974\pm0.00003.$$

This ratio is smaller than our magnetic moment ratio by an amount

$$\Delta=9.8\pm3\times10^{-5}.$$

The uncertainty in this value of Δ is due almost entirely to the uncertainty in the ratio of the hyperfine structure separations, but the errors are small enough certainly to prove the reality of the difference.

In the first-order theory of hyperfine structure, Δ is zero. However, the theory assumes the nucleus to be both a point charge and a point magnetic dipole. These assumptions are valid enough for electrons whose wave functions are negligible in the region of the nucleus; but otherwise, as is true for electrons in the $S_{\frac{1}{2}}$ and $P_{\frac{1}{2}}$ states, some error is introduced. The finite size of a nucleus changes the electrostatic potential within the nucleus from that of a point charge and thus changes the electronic wave function in the immediate vicinity of the nucleus from that in a pure Coulombic field. The resulting change in the hyperfine structure differs for isotopic nuclei because the nuclei differ in size, thereby changing the ratio of the hyperfine splittings. In much the same way the finite distribution of the magnetic moment in a nucleus modifies the electronic wave function in the region of the nucleus from that applying to a point dipole. If the distribution of magnetic moment is different in two isotopic nuclei, their hyperfine splittings are perturbed by different amounts, and the ratio is also changed.

Crawford and Schawlow[11] have considered the effect on the hyperfine structure, of the non-Coulombic potential in the region of the nucleus, while Bohr and Weisskopf[12] have investigated the effect of the finite distribution of the magnetic moment. From these two theories Berman[3] calculated values for Δ of

$$\Delta_1=9.3\times10^{-5},$$

for a uniform distribution of charge and neglectable nonelectrical forces in the nucleus;

$$\Delta_1=10.4\times10^{-5},$$

for a surface distribution of charge; and

$$\Delta_2=1.4\times10^{-5},$$

a *maximum* value for the effect of the finite magnetic moment distribution. These combine to give theoretical values for Δ of 11.8 and 10.7×10^{-5} which are to be compared with the experimental value of $9.8\pm3\times10^{-5}$. The excellent accord suggests the validity of the theories used in the calculation. But the uncertainties, experimental and in Δ_2, are too great to differentiate between the nuclear models proposed in calculating Δ_1. However, some preference is given to the model in which the nuclear charge is distributed uniformly.

Chemical and Concentration Effects

Our observations of chemical shifts in the thallium resonance were concerned primarily with the concentration dependence in aqueous solutions. Most thallium compounds are sparingly soluble in water, if at all, so the investigation was limited mainly to $TlC_2H_3O_2$, $TlNO_3$, and $Tl(NO_3)_3$. The sample to which the shifts were referred was taken somewhat arbitrarily as a 2.39 molar thallous acetate solution; a saturated solution was not chosen because the solubility was found to be highly temperature dependent. The resonance shifts are reported as $\Delta\sigma$ which is defined by

$$\Delta\sigma=10^4\times(H_s-H_r)/H_r,$$

TABLE I. The ratio of the thallium magnetic moments.

Source	Run	Sample	$\mu_{Tl^{205}}/\mu_{Tl^{203}}$	
This research	1	$TlC_2H_3O_2$	1.009 8389	
	2	$TlC_2H_3O_2$	1.009 8380	
	3	Tl_2O_3+*aqua regia*	1.009 8379	
	4	Tl_2O_3+*aqua regia*	1.009 8382	
	5	Tl_2O_3+*aqua regia*	1.009 8363	
	6	Tl_2O_3+*aqua regia*	1.009 8367	
		Average	1.009 838	(1)
Proctor[a]			1.009 7	(2)
Poss[b]			1.009 86	(5)
Sheriff and Williams[c]			1.009 83	(5)
Walchli[d]			1.009 822	(19)

[a] See reference 4.
[b] See reference 5.
[c] See reference 6.
[d] See reference 7.

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[11] M. F. Crawford and A. L. Schawlow, Phys. Rev. **76**, 1310 (1949).

[12] A. Bohr and V. F. Weisskopf, Phys. Rev. **77**, 94 (1950).

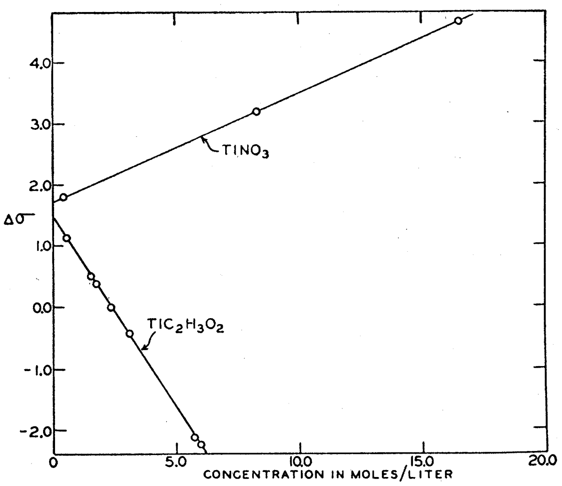

FIG. 2. Chemical shifts in the thallium resonance in aqueous solutions of various composition. The $TlNO_3$ solutions were about 0.5 molar in $TlNO_3$; with nitric acid making up the balance of the nitrate ion concentration, which is plotted. The $TlC_2H_3O_2$ solutions contained no other solute.

where H_s and H_r are the resonance magnetic fields, at a fixed rf frequency, for the unknown sample and the reference, respectively. The reported observations are of Tl^{205} because its absorption is much stronger than that of Tl^{203}. All measurements were made at room temperature which varied between 22° and 28°C.

A set of measurements was made on both isotopes to confirm the isotopic independence of the shifts. The shift was observed between a thallous acetate and a thallic nitrate solution. The shift obtained in a series of five measurements was 8.745 gauss for both Tl^{203} and Tl^{205}. The exact agreement is fortuitous since the probable errors in the measurements for each isotope were ± 0.045 gauss.

$TlC_2H_3O_2$

The chemical shifts found in thallous acetate solutions of various concentrations are given in Fig. 2. The concentrations were determined by a method given in Kolthoff and Sandell.[13] It can be seen that the concentration dependence of the resonance shift is linear over the observed range, from 0.5 to 6.0 molar. The slope of the straight line is -0.62 liter mole^{-1}.

Other observations were made on solutions containing both thallous acetate and sodium acetate. The thallous acetate concentration was kept between 1.8 and 2.0 molar while the concentration of sodium acetate was varied. In Fig. 3 the thallium resonance shifts are plotted against the total concentration of the acetate ion, giving again a linear relation. Moreover, the slope of the line is -0.60 liter mole^{-1} which is the same, within experimental error, as that for the solutions containing only thallous acetate. The sodium resonance was investigated in the mixed solutions, but no measurable shifts in its position were detected.

The shifts, $\Delta\sigma$, were measured for two thallous acetate solutions at a lower field of 4180 gauss, using another permanent magnet.[9] The resonance shifts in gauss, $(H_s - H_r)$, were directly proportional to H_r, that is, $\Delta\sigma$ was independent of the applied magnetic field. This is consistent with the field dependence of the chemical shifts in nuclear magnetic shielding.[14]

$TlNO_3$

Included in Fig. 2 are the resonance shifts observed for thallous nitrate. The lowest concentration, 0.48 molar,[15] was a saturated solution at 27°C. The other two solutions were thallous nitrate dissolved in nitric acid. The resonance shifts are plotted against the total nitrate concentration. The thallous concentration was estimated to be 0.5 molar in the more concentrated nitric acid solution and 0.3 molar in the other.

The shifts appear to depend upon the nitrate concentration and not upon the thallium concentration. Measurements were made at higher temperatures on more concentrated, saturated, aqueous thallous nitrate solutions, and shifts in the same direction and of the same magnitude were found as those of the nitric acid solutions in Fig. 2. These measurements have not been included, however, since the concentrations are uncertain, and the data are only qualitative.

The three points in Fig. 2 lie almost exactly on a straight line, with a slope of 0.18 liter mole^{-1}. It is noteworthy that the thallous acetate and thallous nitrate data extrapolate to almost the same point at zero concentration, but that there is a slight difference which is outside experimental error provided the straight line extrapolation is valid.

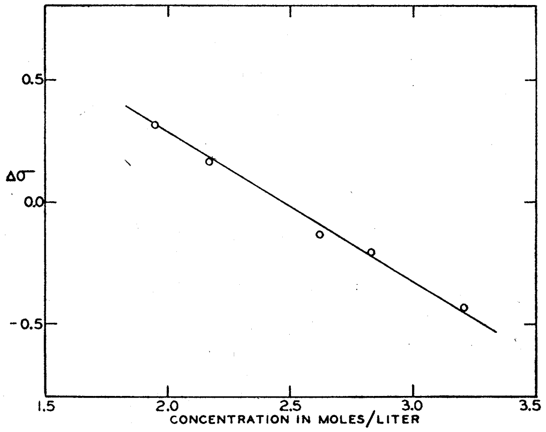

FIG. 3. Chemical shifts in the thallium resonance in mixed $TlC_2H_3O_2$ and $NaC_2H_3O_2$ solutions. The $TlC_2H_3O_2$ concentration was kept constant at about 1.8 molar. The shifts are plotted against the total acetate concentration.

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[13] I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis* (The Macmillan Company, New York, 1949), revised edition, p. 637.

[14] N. F. Ramsey, Phys. Rev. **78**, 699 (1950); **86**, 243 (1952).

[15] This value was interpolated from solubility data given by Lord Berkeley, Trans. Roy. Soc. (London) **A203**, 189 (1904).

$Tl(NO_3)_3$

In water, thallic nitrate hydrolyzes immediately to thallic oxide, but is stable in nitric acid solutions. Consequently, the samples were prepared by dissolving solid thallic nitrate in nitric acid of different concentrations. The quantities were chosen such that the thallic nitrate concentration was about 1.5 molar in the various solutions. The $Tl(NO_3)_3$ was obtained by dissolving Tl_2O_3 in $8N$ nitric acid and evaporating the excess water and nitric acid in a vacuum desiccator. Analysis of the actual samples was difficult so the nitric acid concentration was estimated from the original concentration of the acid and the change in volume when the solid $Tl(NO_3)_3$ was added. Further uncertainty in the nitrate concentrate arises from variations in the amount of solid $Tl(NO_3)_3$ dissolved and in the occlusion of HNO_3 with the solid.

The resonance shift is given in Fig. 4 as a function of the nitric acid concentration. The data appear to give a straight line within the very limited accuracy with which the concentrations are known. The slope of this line is 0.18 liter $mole^{-1}$, which is the same as the slope of the similar graph for $TlNO_3$.

Other Thallium Compounds

The thallium resonance in solid $TlC_2H_3O_2$ was observed with a narrow band amplifier. The line was broad, with a separation of 1.5 gauss between the points of inflection. The shift was found to be -2.67.

A dilute solution of $TlCl_3$ was prepared by passing Cl_2 through a suspension of TlCl[16] in water. The resonance shift, $\Delta\sigma$, was measured to be -21.8 in this solution. Measurements on solutions of Tl_2O_3 in various mixtures of HCl and HNO_3 indicated the thallic $\Delta\sigma$ decreases with chloride concentration.

Discussion of the Resonance Shifts

It is a relatively simple matter to compute the nuclear magnetic shielding of the spherically symmetric, free atoms and ions. But the theoretical values[1,2] have not been subjected to experimental verification. It was our original thought that if Tl^{+1} and Tl^{+3} in aqueous solution might be considered as equivalent to the free ions from a nuclear magnetic resonance standpoint, a measurement of their resonance shift could be compared with theory. The experimental shift in the Tl^{+3} with respect to the Tl^{+1} resonance, extrapolated linearly to infinite dilution, is about -19. On the other hand, the resonance shift predicted by Lamb's equation[1] is -0.15. This was computed[17] from the radial charge density of the $6s$ electrons of the thallous ion, determined by Williams[18] using the Hartree self-consistent field method. Since the observed shift is more than a hundred times the theoretical value, it seems clear the ions cannot be considered as monatomic, but that there is a very large chemical effect from hydration of the ions or from complex formation. In fact thallic ion is known to form a large number of complexes, for instance[19,20] $TlCl_2^+$ and $TlCl_4^-$; and a few complexes have been suggested for thallous ion.

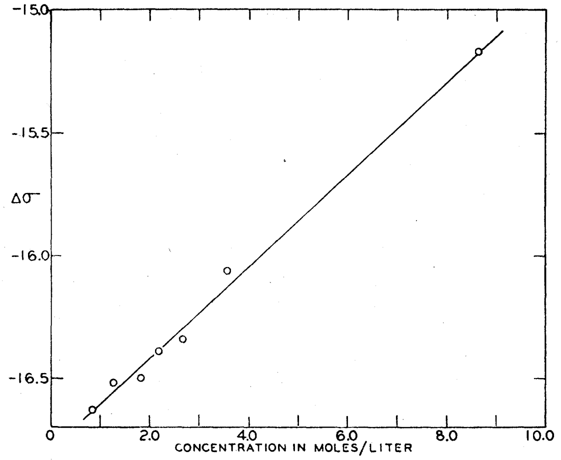

FIG. 4. Chemical shifts in the thallium resonance in mixed $Tl(NO_3)_3$ and HNO_3 solutions. The $Tl(NO_3)_3$ concentration varies about 1.5 molar; the concentrations plotted are approximate values for HNO_3 alone.

The existence of chemical effects is not surprising, therefore, but several of the observed aspects warrant closer scrutiny. The experimental evidence shows the shifts in the thallium resonance to depend only upon the nature and the concentration of the anions in the solutions. Thus, in the mixed solutions containing $TlC_2H_3O_2$ and $NaC_2H_3O_2$ the shifts were the same as in pure $TlC_2H_3O_2$ solutions containing the same amount of acetate, the Na^+ ion in the mixed solutions being without apparent effect. Moreover, the resonance shifts are linear in the anion concentration; and with a given anion, the concentration dependence is the same for *both* Tl^+ and Tl^{+3} in spite of the large shift between the Tl^+ and Tl^{+3} states. At least this is the case for the nitrate solutions within the rather large experimental error.

The position of the proton resonance has been found to be concentration dependent[21] in aqueous solutions of electrolytes which ionize to give hydrogen containing ions, and where rapid chemical exchange averages the chemical shifts over the different hydrogen containing chemical species to give a single narrow resonance. The thallium concentration effects could arise in a similar manner from fast exchange among the thallium ions and one or more complex forms. For $TlC_2H_3O_2$, where the different chemical states of the thallium might be

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[16] This method of preparing $TlCl_3$ is similar to that given by A. S. Cushman, Am. Chem. J. **26**, 505 (1901).

[17] We wish to thank Dr. W. C. Dickinson for an earlier estimate of the shift, made from the wave functions for Hg and Hg^{++}, giving the value -0.13.

[18] F. Williams, J. Chem. Phys. **19**, 457 (1951).

[19] G. Harbottle and R. W. Dodson, J. Am. Chem. Soc. **73**, 2442 (1951).

[20] R. Benoit, Soc. Chim. France **5–6**, 518 (1949).

[21] H. S. Gutowsky and A. Saika, J. Chem. Phys. **21** (to be published).

taken as the ion and the undissociated molecule, shifts of the proper order of magnitude can be calculated by taking the shift of the undissociated molecule to be that of the solid $TlC_2H_3O_2$, and using the dissociation constant calculated by Robinson and Davies[22] from conductance data. However, this mechanism cannot give the linear dependence of the shift over the large concentration ranges investigated.

Nonetheless, the existence of the chemical effects demonstrates that the electronic distribution about the thallium nucleus and, consequently, its magnetic shielding, are altered in some manner from the free ion by the anions and water molecules surrounding it. Besides the chemical equilibrium mechanism which appears inadequate, we have considered polarization and electronic exchange effects. The electric fields generated by nearby ions and molecular dipoles strongly polarize the thallium ions. The effect of the polarization on the magnetic shielding of the thallium nucleus was calculated as a second-order perturbation, assuming point charges and dipoles. Although the computed effect on the shielding is large for a given orientation, the net effect is zero when all orientations are equally probable as is the case in the solutions. The only satisfactory model of those we have considered is based on electronic exchange effects, intermediate in nature between the covalent bonding implied in the analysis in terms of chemical equilibria and the purely Coulombic interactions considered in the polarization model.

Ordinarily, in not too concentrated solution, the cation of a strong electrolyte is surrounded by a layer of water molecules of hydration, with the anions remaining outside this layer. However, Fajans[23] has shown by means of refractivity measurements on solutions of strong electrolytes that this shell of water molecules is sometimes penetrated by the anions, and that the amount of penetration increases with concentration. This penetration is essentially a replacement by an anion of one of the water molecules surrounding the cation, forming an "ion pair." This "ion pair" is not quite the same as a "truly undissociated molecule," since the time of association may be less than the time needed by the molecule to execute a single vibration along its bond. Thus, the association can be regarded as little more than a sticky collision. If electronic exchange interactions occur during the association, the diamagnetic shielding of the nuclei would be reduced from the free ion values. This can be seen from Ramsey's[14] theory of nuclear magnetic shielding in molecules; the electronic exchange introduces the second-order paramagnetic term, which is absent for the free ions.

The ideas expressed above lead directly to a qualitative explanation of the experimental results. The shift in the thallium resonance will be proportional to the average number of anions and of water molecules surrounding the thallium ions. The average numbers should be proportional linearly to the total concentration of anions, so the shift should depend linearly on the anion concentration. The direction of the shift depends upon the relative values of the thallium ion-water and of the thallium ion-anion interactions. The direction of the shifts observed for $TlC_2H_3O_2$ correspond to the Tl^+ anion interaction being larger than the Tl^+ H_2O, while the shifts for $TlNO_3$ correspond to the reverse situation. The decreasing order of interaction, acetate, water, and nitrate, is reasonable in terms of the general chemical properties of the species.

The large resonance shift between the thallous and thallic solutions results probably from the formation of a stable coordination complex by Tl^{+3}, such as $Tl(NO_3)^{+2}$ in the nitrate solutions, filling the low-lying 6*s* orbital. Therefore, the concentration dependent shifts in both thallous and thallic solutions involve electronic exchange with the thallium 6*p* orbitals. This could account for about the same concentration dependence being observed in the thallous nitrate and thallic nitrate solutions, providing the reasonable assumption is made that the different manner in which the 6*s* orbital is filled in the two ions does not affect very much the solvent and anion interactions with the 6*p* orbitals.

The question arises as to why effects of the sort reported here have not been observed in other ions. It may be simply that the effects occur, but are too small to be observed in the lighter elements previously investigated. In this connection we should mention that preliminary measurements on cesium chloride solutions have shown some concentration dependence of the Cs^{133} resonance, but the shifts are much smaller than those in thallium. The largeness of the thallium shifts may be attributable partly to the fact that in this case we are not dealing with the rare gas electron configurations possessed by most ions.

Besides their bearing upon the structure of solutions of electrolytes, these results demonstrate it is not always possible to regard ions in solution as equivalent to free ions as far as magnetic resonance is concerned. Therefore, the use of shielding fields calculated for free ions to compute corrected magnetic moments from measurements on ions in solution may not be valid in many cases. In any event, the possibility of concentration dependence should be considered when nuclear magnetic moments are measured using ionic salts in solutions.

The equipment for this work was provided mainly by a grant-in-aid from the Research Corporation. Also, we wish to thank Mr. R. E. McClure for his assistance with some of the preliminary chemical shift measurements and with the comparison of the shifts for Tl^{203} and Tl^{205}.

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[22] R. A. Robinson and C. W. Davies, J. Chem. Soc. **1937**, 574 (1937).

[23] K. Fajans, Trans. Faraday Soc. **23**, 357 (1927).