

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, WASHINGTON STATE UNIVERSITY, PULLMAN, WASHINGTON, AND CORNELL UNIVERSITY, ITHACA, NEW YORK]

Approximate Thermodynamic Formation Constants of Some Complexes of Lead(II) and Thallium(I) from Polarographic Data

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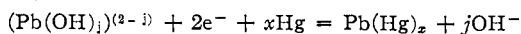
The polarographic method of DeFord and Hume³ is capable of yielding approximate values of thermodynamic equilibrium constants for the formation of complex ions. Solutions of varying low ionic strength may be employed to advantage provided that activity coefficients, observed or estimated, are available. Polarographic data obtained under these conditions yielded these values of $\log K^0$: $[\text{PbNO}_3]^+$ (aq.), 1.08; $[\text{Pb}(\text{OH})_3]^-$ (aq.), 13.90; $[\text{TlNO}_3]$ (aq.), 0.38; $[\text{TlCl}]$ (aq.), 0.46. From experiments at constant ionic strength of 1.0 M , $\log K^0_{\text{TlCl}}$ was calculated to be 0.64.

A now well-known relationship between the half-wave potential of an ion in a given concentration of complexing agent and the association constant of the complex formed was presented some years ago by DeFord and Hume.^{3a} While this relationship is theoretically able to yield thermodynamic association constants, generally only concentration constants have been obtained. This has resulted because of a necessary condition for polarographic studies which requires a substantial excess of supporting electrolyte over the reducible species. Investigations are commonly carried out at constant ionic strengths of 1.0 or greater with a mixture of electrolytes, one of which is complexing in character. At high ionic strengths and in the mixed electrolyte solutions, estimation of activity coefficients is difficult and, hence, concentration constants only usually are obtained. Furthermore, DeFord and Anderson^{3b} have shown that half wave potentials vary considerably with ionic strength, and hence concentration equilibrium constants would also be a function of ionic strength.

In his treatment of the $[\text{Pb}(\text{OH})_3]^-$, Vlcek⁴ has presented a method for determining thermodynamic constants from the relationship

$$(E^{0_{1/2}})_s - (E^{0_{1/2}})_c = \frac{RT}{nF} \ln K_i^0$$

where $(E^{0_{1/2}})_s$ is the "standard" half-wave potential for the aquated ion at $\mu = 0$; and $(E^{0_{1/2}})_c$ is the "standard" half-wave potential for a reaction involving reduction of the complex ion. In this instance, the reaction is



From a plot of $E_{1/2}$ obtained in "non-complexing" media (sodium nitrate solutions) *vs.* $\mu^{1/2}$, $(E^{0_{1/2}})_s$ is obtained as the intercept at $\mu^{1/2} = 0$. In a similar plot for $E_{1/2}$ obtained in the presence of sodium hydroxide, the value of $(E^{0_{1/2}})_c$ is obtained as the intercept. From the same data, a plot of $E_{1/2}$ *vs.* $\log (\text{OH}^-)$ has as a slope jRT/nF , which allows the identification of the species present, and in this instance $j = 3$. This method is limited to the case where a particular complex species exists over a wide enough range of concentration to allow extrapolation to $\mu^{1/2} = 0$.

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(2) Taken in part from a M.S. Thesis of D. K. Roe, Washington State University, 1956.

(3) (a) D. D. DeFord and D. N. Hume, *THIS JOURNAL*, **73**, 5321 (1951); (b) D. D. DeFord and D. L. Anderson, *ibid.*, **72**, 3918 (1950).

(4) A. A. Vlcek, *Collection Czech. Chem. Commun.*, **20**, 400 (1955).

While it is only rarely so employed, the DeFord and Hume method may be used at varying ionic strength. This procedure allows low ionic strengths to be employed where the activity coefficients may be estimated from the Guggenheim⁵ extension of the Debye-Hückel equation if measured values are not available. The half-wave potential of the metal ion is simply determined as a function of concentration of the complexing agent with no attempt made to keep the ionic strength constant. Care must be exercised to plot the proper functions so that the intercept is truly a constant. The only restriction, which applies also to Vlcek's procedure, is that the concentration of the complexing electrolyte be sufficiently higher than the reducible species so that the reduction process is diffusion controlled.

Formation of $[\text{PbNO}_3]^+(\text{aq})$.—The lead nitrate system provides a good case in point. It has previously been investigated polarographically and by other methods⁶ at $\mu = 2.0$, and concentration constants were reported. The set of data reported by Vlcek on the variation of $E_{1/2}$ for lead ion in solutions of 0.02 to 1.0 M sodium nitrate are exactly the data needed for the varying ionic strength method. Vlcek was interested only in obtaining the association constant for $[\text{Pb}(\text{OH})_3]^-$, and he made no attempt to interpret the nitrate data in terms of complex formation.

DeFord and Hume's equation is stated as

$$(E^{0_{1/2}})_s - (E_{1/2})_c + \frac{RT}{nF} \ln I_s/I_c = \frac{RT}{nF} \ln F_0(X)$$

where $F_0(X) = 1/f_s + K_1^0 C_x f_x / f_{\text{mx}} + K_2^0 C_x^2 f_x^2 / f_{\text{mx}^2} + \dots$

The notation is that used by those authors.

In Table I are presented values of $F_0(X)$ calculated from Vlcek's data, assuming $I_s/I_c = 1$ since this ratio was not reported. Previous experience has shown this to be a reasonable assumption. The activity coefficients for lead ion at various values of μ were obtained from the Guggenheim equation. The necessary value of β was taken as 0.7, a value estimated from the observed mean ion activity coefficients of lead perchlorate at $\mu = 0.1$. It is necessary to take the value of β as that of a strong electrolyte where association is unimportant, and for this reason the value of β from the observed stoichiometric activity coefficients of lead nitrate

(5) E. A. Guggenheim, "Thermodynamics," 3rd ed., North-Holland Publishing Co., Amsterdam, 1957, p. 356.

(6) H. M. Hershenson, M. E. Smith and D. N. Hume, *THIS JOURNAL*, **75**, 507 (1953).

would not suffice. It was assumed that $f_{\text{NO}_3^-}$ equals $f_{\text{PbNO}_3^+}$ and, in this instance, the two cancel and numerical values are unnecessary. The value of $(E_{1/2})_s$ was taken from Vlcek's plot of $E_{1/2}$ vs. $\mu^{1/2}$ as the intercept at $\mu^{1/2} = 0$. In spite of the fact that nitrate complexes lead ion, this procedure is permissible because complex formation occurs only to a limited extent, and the extent of association decreases as nitrate concentration decreases.

Values of $F_1(X) = [F_0(X) - 1/f_s] f_{\text{m}x}/f_x C_x$ were then calculated and plotted vs. C_x , whereon the intercept at $C_x = 0$ was 12, corresponding to the average value of k_1^0 in Table I. The slope was zero indicating no other complex species was present in appreciable amounts. The value of $\log K_1^0$ was 1.08, which is in good agreement with the thermodynamic value 1.18 reported from spectrophotometric measurements⁷ and from conductivity measurements.⁸

Formation of $[\text{Pb}(\text{OH})_3]^-$ (aq).—In a similar fashion, Vlcek's data for the lead-hydroxide system may be treated. Calculation of successive values of $F_j(X)$ shows that in the hydroxide solutions, the species Pb^{++} , $\text{Pb}(\text{OH})^+$, $\text{Pb}(\text{OH})_2$ and $\text{Pb}(\text{OH})_4^-$ are present in insignificant amounts. The equation for $F_3(X)$ then reduces to

$$F_3(X) = F_0(X)/(C_x^3 f_x^2)$$

It was assumed that $f_{\text{Pb}(\text{OH})_3^-} = f_{\text{OH}^-} = f_{\pm(\text{NaOH})}$ in these solutions. In Table II are presented values of $F_3(X)$ up to 0.5 M NaOH. It is observed that $F_3(X)$ is reasonably constant up to about 0.5 M. The average value of $F_3(X)$ under these conditions is 7.9×10^{13} or $\log K_3^0 = 13.90$. This is in excellent agreement with the value 13.95 obtained from the same data by Vlcek's method and from solubility methods.⁹

TABLE I

VALUES OF $F_1(X)$ FOR LEAD-NITRATE ASSOCIATION AS A FUNCTION OF SODIUM NITRATE CONCENTRATION (DATA FROM REFERENCE 4)

[NaNO ₃] (mole/l.)	$-E_{1/2}$ (v. vs. n.c.e.)	$-\log f_{\text{pb}^{++}}$	$F_0(X)$	$F_1(X)$ (X)
0.00	0.4060 ^a
.02	.4135	0.236	1.95	11.5
.035	.4160	.300	2.36	10.3
.050	.4185	.342	2.86	13.2
.070	.4205	.383	3.35	13.3
.100	.4225	.428	3.90	12.2
.180	.4260	.497	5.12	11.0
.500	.4340	.540	9.55	12.2
1.00	.4385	.412	13.57	11.0

^a Obtained from a plot of $E_{1/2}$ vs. $\mu^{1/2}$.

Formation of $[\text{TlCl}](\text{aq.})$ at Varying Ionic Strength.—Vlcek⁴ also has reported data for the variation of $E_{1/2}$ for thallium(I) ion in potassium chloride and sodium nitrate solutions, and these data are summarized in Tables III and IV. Values of $F_0(X)$ were calculated using values of $(E_{1/2})_s$ obtained in the same manner as in the case of lead ion. Again no values of I_s/I_c were reported and they were assumed to be unity.

(7) W. D. Bale, E. W. Davies and C. B. Monk, *Trans. Faraday Soc.*, **52**, 816 (1956).

(8) G. H. Nancollas, *J. Chem. Soc.*, 1458 (1955).

(9) A. B. Garrett, S. Vellenga and C. M. Fontana, *THIS JOURNAL*, **61**, 367 (1939).

TABLE II

VALUES OF $F_3(X)$ FOR LEAD-HYDROXIDE ASSOCIATION AS A FUNCTION OF SODIUM HYDROXIDE CONCENTRATION (DATA FROM REFERENCE 4)

NaOH (mole/l.)	$-E_{1/2}$ (v. vs. n.c.e.)	$F_0(X)$ ^a	$F_3(X)$ ($\times 10^{-13}$)
0.02	0.6640	5.13×10^8	8.5
.049	.6965	6.76×10^8	8.8
.098	.7215	4.79×10^{10}	8.7
.150	.7370	1.55×10^{11}	8.2
.295	.7600	9.33×10^{11}	7.2
.490	.7770	3.39×10^{12}	6.0

^a Calculated using $(E_{1/2})_s = -0.4060$ v. vs. n.c.e.

TABLE III

VARIATION OF $E_{1/2}$ FOR THALLOUS ION WITH POTASSIUM CHLORIDE CONCENTRATION AT 25° AND VALUES OF $F_j(X)$ (DATA FROM REFERENCE 4)

C_x (mole/l.)	$-E_{1/2}$ (v. vs. n.c.e.)	$F_0(X)$	$F_1(X)$ ($\beta = 0.1$)	$F_1(X)$ ($\beta = 0.2$)
0.00	0.4833 ^a
.02	.4880	1.202	2.88	3.16
.05	.4905	1.323	2.36	2.56
.10	.4940	1.517	2.83	3.12
.20	.4985	1.808	2.96	3.20
.30	.5015	2.03	2.85	3.05
.41	.5050	2.24	2.77	2.95
.50	.5075	2.56	3.21	3.26
.70	.5135	3.24	3.73	3.59
1.00	.5205	4.25	4.10	3.67
2.00	.5375	8.26	4.61	3.29

^a Estimated from a plot of $E_{1/2}$ vs. $\mu^{1/2}$.

TABLE IV

VARIATION OF $E_{1/2}$ FOR THALLOUS ION WITH SODIUM NITRATE CONCENTRATION AT 25° AND VALUES OF $F_j(X)$ (DATA FROM REFERENCE 4)

C_x (mole/l.)	$-E_{1/2}$ (v. vs. n.c.e.)	$F_0(X)$	$F_1(X)$ ($\beta = 0.1$)	$F_1(X)$ ($\beta = 0.2$)
0.00	0.4830 ^a
.05	.4900	1.313	2.11	2.33
.10	.4930	1.477	2.31	2.61
.20	.4970	1.728	2.41	2.67
.30	.5000	1.942	2.45	2.68
.50	.5045	2.31	2.47	2.60
1.00	.5160	3.60	3.14	2.89

^a Estimated from a plot of $E_{1/2}$ vs. $\mu^{1/2}$.

Two series of activity coefficients for thallos ion and chloride ion were calculated using the Guggenheim equation. The adjustable parameter β , which is characteristic of a given salt is usually of the order of 0.1 or greater for 1:1 electrolytes where association is unimportant. The activity coefficients desired are ionic activity coefficients as contrasted with the stoichiometric activity coefficients. Because of this, the values of β for thallos chloride and thallos nitrate must be those of strong electrolytes. Since potassium chloride is generally assumed to be unassociated, and since thallos ion and potassium ion have similar ion size parameters, one set of activity coefficients was calculated using $\beta_{\text{TlCl}} = \beta_{\text{KCl}} = 0.10$ as listed by Guggenheim.⁸ The second set of activity coefficients was calculated using $\beta = 0.20$, a value exhibited by a number of strong electrolytes. While the Guggenheim equa-

TABLE V

HALF-WAVE POTENTIALS OF THALLIUM(I) IN x M SODIUM CHLORIDE AND $(1 - x)$ M SODIUM PERCHLORATE MIXTURES IN VOLTS vs. S.C.E.,^a AND VALUES OF $F_1(X)$

(Cl ⁻) (moles/l.)	$-E_{1/2}$ (no max. suppressor)	$-E_{1/2}$ (gelatin suppressor, 0.003%)	$-E_{1/2}$ (Triton X-100 suppressor, 0.0001%)	$\log I_a/I_c$ (smoothed values)	$-\log f_{Tl^+}$ (from eq. 5)	$F_1(X)$ b, c	$F_1(X)$ b, d (ClO ₄ ⁻ complex)
0.000	0.4650	0.4666	0.4670	0.000	0.403
.100	.4671	.4671	.4679	.007	.379	4.35	7.00
.200	.4690	.4691	.4698	.012	.356	4.73	5.66
.300	.4711	.4709	.4701	.015	.332	4.07	4.38
.4004718	.4718	.017	.299	4.48	4.32
.5004728	.4727	.019	.285	4.12	4.03
.6004759	.4749	.020	.262	4.47	4.29
.7004768	.4770	.022	.238	4.76	4.52
.8004781	.4779	.023	.215	4.57	4.32
.9004803	.4783	.024	.192	4.34	4.09
1.0004810	.4802	.026	.168	4.58	4.30

^a Data taken from ref. 2; see this document for complete experimental details and procedure. ^b Calculated with $(E_{1/2})_s = -0.4433$ volt vs. s.c.e. using data from Triton solutions. ^c f_{Tl^+} from column 6; $\beta_{TlClO_4} = -0.17$, ^d f_{Tl^+} equals 0.604.

tion is most satisfactory at low ionic strengths, it was employed here over the entire range because it provides as good an estimate as any other equation over the region of ionic strength involved.

Two series of $F_1(X)$ values were then calculated for $Tl^+ - Cl^-$ association and the values were plotted vs. C_x . It was observed that the intercepts and slopes were affected slightly by the change in β , giving an extrapolated value of $K_1^0 = 2.7$ for $\beta = 0.1$ and 3.1 for $\beta = 0.2$. The slope for $\beta = 0.1$ was positive (1.4) while that with $\beta = 0.2$ was 0.1. Since it is unlikely that β would be less than 0.1 or more than 0.2, the mean was chosen as the best value to represent the data, and thus $K^0_{TlCl} = 2.9$ with an estimated error of ± 0.5 . Furthermore, it is unlikely that the positive slope of the plot is indicative of more than a failing of the activity coefficient treatment at the higher ionic strengths.

Formation of $[TlNO_3](aq.)$.—The data for the variation of the half-wave potential for thallous ion with increasing concentrations of sodium nitrate are listed in Table IV, and the data were treated similarly to the chloride data. Again, two sets of values of $F_1(X)$ were calculated using $\beta = 0.1$ and 0.2 and were plotted vs. C_x . Again the intercept, K_1^0 varied slightly with β , being 2.2 for $\beta = 0.1$ and 2.5 for $\beta = 0.2$. The mean value for K_1^0 was 2.4 ± 0.5 , or $\log K_1^0 = 0.38$. This value is in excellent agreement with a value of 0.33 reported from solubility measurements and values of 0.33–0.44 from conductivity measurements.¹⁰

Formation of $[TlCl](aq.)$ at Constant Ionic Strength.—The values of the half-wave potential of thallous ion as a function of chloride concentration in sodium chloride–perchlorate mixtures at $\mu = 1.0$ are presented in Table V and include sets of data obtained in $3 \times 10^{-3}\%$ gelatin, $1 \times 10^{-4}\%$ Triton X-100 and in the absence of a maximum suppressor.

Polarograms of all solutions first were determined automatically using the Sargent Model XXI recording polarograph to observe the general characteristics of the wave, and then, to obtain more precise potential-current data, an essentially manual pro-

cedure was employed. The potential was set, the current allowed to come to a steady value and then the potential was determined with an external potentiometer. All potentials were corrected for the internal resistance (i.r. drop) across the cell and were considered to be precise within ± 0.5 mv. The current measured was in every case that corresponding with the maximum pen excursion without damping. Plots of $E_{d.e.}$ as $\log i/(i_d - i)$ were taken from these plots. All measurements were taken at 25° using a cell described elsewhere.¹¹

It is observed that the presence of a maximum suppressor had slight effect on the observed half-wave potential as far as 0.3 M sodium chloride solution, beyond which such comparison cannot be made because of the appearance of a maximum in solutions without suppressor. In the case of gelatin, this behavior was expected because Randles and Somerton^{12,12a} had previously found that gelatin had no measurable effect on the reversibility of the electrode reactions. At concentrations above 0.30 M sodium chloride, where a maximum suppressor is required, gelatin and Triton behave similarly. They either have the same effect or none at all.

These data were processed using calculated activity coefficients of the thallous ion in the mixed electrolyte, using the equation

$$\log f_s = -0.509 Z_+^2 \mu^{1/2} / (1 + \mu^{1/2}) + \frac{2}{\ln 10} (\beta_{TlClO_4} m_{ClO_4^-} + \beta_{TlCl} m_{Cl^-})$$

where $\beta_{TlClO_4} = -0.17$ and $\beta_{TlCl} = +0.10$.^{5,13} By use of this observed value for β_{TlClO_4} , all effects due to interaction of thallous and perchlorate ions, including any association, are included in the activity coefficient, and by choosing β_{TlCl} equal to β for a strong electrolyte, association of thallous and chloride ions is excluded from the activity coefficient. The necessary activity coefficients of chloride (and perchlorate) ion in the mixtures can be estimated from Harned's rule,¹⁴ making use of

(11) D. K. Roe and C. J. Nyman, *Chemist Analyst*, **49**, 27 (1960).

(12) J. E. B. Randles, *Discussions Faraday Soc.*, **1**, 11 (1947).

(12a) J. E. B. Randles and K. W. Somerton, *Trans. Faraday Soc.*, **48**, 951 (1952).

(13) E. A. Guggenheim and J. C. Turgeon, *ibid.*, **51**, 747 (1955).

(14) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths' Scientific Publications, London, 1955, pp. 427, 440.

(10) J. Bjerrum, G. Schwarzenbach and L. G. Sillen, "Stability Constants of Metal-Ion Complexes. Part II. Inorganic Ligands," Special Publication No. 7, The Chemical Society London, 1958, p. 56.

the fact that $f_{(\text{NaCl})} = 0.657$ and $f_{(\text{NaClO}_4)} = 0.629$ at $\mu = 1.0$. Actually, very little difference would be observed if it was assumed that the activity coefficients of chloride and perchlorate were constant over the range of solutions investigated.

Values of $F_1(X)$ listed in column 7 of Table V were obtained using the activity coefficients just outlined and the value of $(E^{0,1/2})_s$ obtained earlier (after correction for the 40 mv. difference between the s.c.e. and the n.c.e.). No observed values of $I_{\mu=1.0}/I_{\mu=0}$ are available, and this ratio was assumed to be unity. The $F_1(X)$ values were plotted vs. C_x and the value of K_1^0 given by the intercept is 4.5. The slope of the plot was zero, showing no indication of any additional species present.

An alternative procedure based on the formation of a thallos perchlorate complex is possible. Thallos perchlorate solutions have an unusually small stoichiometric activity coefficient and have a β coefficient of -0.17 . Guggenheim and Turgeon¹⁸ have indicated that when β is less than -0.1 , ion association is important in 1:1 electrolytes. Furthermore, Robinson and Davies¹⁵ have reported an association constant of 1.0 for thallos perchlorate on the basis of conductivity data.

In calculating $F_1(X)$ for thallos chloride assuming the formation of a perchlorate complex, the activity coefficients employed must again be those of the ions of a strong electrolyte, and thus, for reasons expounded earlier, it was assumed that $f_s = f_{\text{Tl}^+} = f_{\pm(\text{KCl})} = 0.604$ at $\mu = 1.0$. The coefficients for chloride and perchlorate ions were those obtained using Harned's rule.

To obtain values of $F_1(X)$ for $\text{Tl}^+ - \text{Cl}^-$ association from the data in mixed electrolytes, it is necessary to equate the quantity

$$\{[F_0(X) - 1/f_s - K^0_{\text{TlClO}_4} C_{\text{ClO}_4} f_{\text{ClO}_4}] / C_{\text{Cl}^-} f_{\text{Cl}^-}\}$$

with $F_1(X)$. These quantities have been calculated using Robinson and Davies' value of the association constant for thallos perchlorate, and they

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

are listed in column 8 of Table V. A plot of $F_1(X)$ vs. C_x yields an intercept of 4.3, corresponding to K_1^0 for $[\text{TlCl}]$ (aq.).

It is observed that the two values of $F_1(X)$ in column 8 at the lowest chloride concentration are somewhat high but that for the remainder of the solutions, no trend appears in the value of $F_1(X)$. This situation might arise if $(E^{0,1/2})_s$ were too positive or if f_s were too large. Both of these factors would have their greatest effect in the region of low chloride concentration.

The data obtained using gelatin as a maximum suppressor yielded similar results for K_1^0 of thallos chloride association.

For thallos chloride, the value of $\log K_1^0 = 0.46$ determined from data in varying ionic strengths is in agreement with most of the values determined conductometrically which range from 0.48 to 0.52 with one higher value at 0.61, but it is lower than those determined from potentiometric and solubility data which range from 0.59 to 0.68.¹⁶ The value of $\log K_1^0 = 0.64$ determined at constant ionic strength of 1.0 is in excellent agreement with these latter values. The reason for the apparent grouping of association constants by different methods and the reason for the two different polarographic values are not immediately apparent. The latter difference could conceivably be due to liquid junction potentials being handled inadequately. Vlcek corrected his data by means of the Henderson equation. The liquid junction potentials for the chloride data at constant ionic strength were estimated to be 1 millivolt or less, and since these estimations are very approximate, no correction was made.

In conclusion, the polarographic method of studying complex formation does yield for relatively simple systems equilibrium constants comparable to those obtained by other methods when activity coefficients are included.

More complicated systems, where consecutive equilibria occur, have not as yet been studied but will be the subject of a future investigation.

(16) Ref. 10, p. 106.

[CONTRIBUTION FROM THE MELLON INSTITUTE,² PITTSBURGH, PA.]

Sn¹¹⁹ Nuclear Magnetic Resonance Spectra¹

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The Sn¹¹⁹ spectra of a number of organic and inorganic tin compounds have been obtained. Chemical shifts of over 1800 parts per million were found and indirect spin-spin couplings with protons in alkyl groups were observed to be of the order of 50 to 100 cycles per sec. The spectra of mixtures of SnCl₄, SnBr₄ and SnI₄ were examined, and all of the twelve possible mixed tin (IV) halides, including the preciously unreported SnBr₃I, SnBr₂I₂ and SnBr₃I, and SnClBrI₃, SnClBr₂I and SnCl₂BrI, were found to be present in the concentrations expected for random halogen exchange. The average lifetimes of the halide molecules in the mixtures were found to be between 10⁻² and 10 seconds. Solvent effects upon the Sn¹¹⁹ chemical shifts of various tin compounds were observed and the Sn¹¹⁹ chemical shift of SnCl₂·2H₂O in aqueous solution was found to be dependent upon the concentration of added hydrochloric acid.

Introduction

As part of a program in this Laboratory for the study of the nuclear magnetic resonance (n.m.r.)

(1) Presented in part at the 133rd meeting of the American Chemical Society in San Francisco, April 15, 1958.

spectra of compounds of the Group IV b elements, C¹³ spectra^{3,4} and Si²⁹ spectra⁵ have been investigated

(2) Multiple Fellowship on Silicones sustained by Dow Corning Corporation and Corning GlassWorks.

(3) P. C. Lauterbur, *J. Chem. Phys.*, **26**, 217 (1957).