PROTON MAGNETIC RELAXATION IN ACIDIFIED

AQUEOUS SOLUTIONS CONTAINING Cr(III)

by

Dale N. Manos

Submitted in Partial Fulfillment of the Requirements

For the Degree of

Master of Science

in the

Chemistry

Program

Richard C. Phillips   _August 16/1976_
Adviser   Date

August 19, 1976
Dean of Graduate School   Date

YOUNGSTOWN STATE UNIVERSITY

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ABSTRACT

PROTON MAGNETIC RELAXATION IN ACIDIFIED

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Nuclear magnetic relaxation rates of protons in
acidic solutions of Cr(III) have been measured as a function
of hydrogen ion concentration at $28^{o}C$ and 60.00 Mhz in $HClO_4$
from 0.001 M to 10 M and in HCl and H_2SO_4 from 0.5 M to 10 M.
The scalar coupling constant was determined for each acid
from experimental proton chemical shifts. The proton relaxa-
tion rates are controlled by both relaxation processes, T_{2b},
and proton-exchange rates.

In weak acid solutions that proton-exchange is due to
an uncatalyzed hydrolysis reaction. In solutions of moderate
acidity (0.5 M to 6 M) the increase in the observed proton
relaxation is due to an acid-catalyzed proton-exchange be-
tween the Cr(III) ions and the solvent. The increase in pro-
ton relaxation rates in that region is controlled by the
proton-exchange correlation time given by $\tau_b = (k_b a_\pm)^{-1}$ where
$a_\pm$ is the mean acid activity. The rate constant for acid-
catalyzed proton-exchange, k_b, was determined for each acid.
The relative magnitudes of those rate constants were used as
evidence of a specific acid-catalysis of proton-exchange in

$HClO_4$, HCl and H_2SO_4. In addition to the specific acid- catalyzed proton-exchange, a general acid catalyzed exchange was proposed for H_2SO_4 where the general acid-catalyst is presumably HSO_4^-. At higher acid concentrations the proton relaxation rates become relaxation controlled (T_{2b}) for HCl. At high concentrations (above 6 M) of $HClO_4$ and H_2SO_4 the relaxation rates are controlled by the T_{2b} and some other process(es). We have rationalized that process(es) by proposing that the electron-spin relaxation time and/or the proton residence time decrease at the highest acid concentrations.

ACKNOWLEDGEMENTS

I would like to express acknowledgement of Dr. R. C. Phillips for the many discussions, suggestions and support offered in the course of this research. Dr. Phillips's guidance and expertise were indispensable.

Drs. J. A. Reeder and S. M. Schildcrout, who served as thesis committee members, are also acknowledged for their comments and aid in producing the present thesis.

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LIST OF SYMBOLS (CONT.)

$t_{\frac{1}{2}}$	Half-life exchange time	hr
T	Absolute temperature	^{o}K
T_1	Spin-lattice relaxation time	sec
$(T_1)_{tr}$	Spin-lattice translational diffusion time	sec
T_2	Corrected phase memory relaxation time	sec
T_{2a}	Proton relaxation time in acidified aqueous solutions	sec
T_{2b}	Proton relaxation time in the Cr(III) first coordination sphere	sec
T_{2h}	Proton relaxation time	sec
$(T_2)_{tr}$	Phase memory translational diffusion relaxation time	sec
T_2'	Relaxation time in Cr(III) solutions	sec
T_2''	Relaxation time due only to Cr(III) ions in solution	sec
z	Paramagnetic ion coordination number	none
β	Bohr magneton	erg gauss^{-1}
γ_I	Proton magnetogyric ratio	erg gauss^{-1}
γ_s	Electron magnetogyric ratio	erg gauss^{-1}
$\gamma_{\pm}$	Mean activity coefficient	none
$\Delta\nu_{\frac{1}{2}}$	Half-height linewidth	hz
$\Delta\omega$	Proton chemical shift	hz
η	Viscosity	g cm^{-1} sec^{-1}
λ	Wavelength	nm
μ	Electron magnetic moment	erg gauss^{-1}

LIST OF SYMBOLS (CONT.)

Σ_i	Summation of proton concentrations	mol l^{-1}
τ_b	Proton residence time in the Cr(III) first coordination sphere	sec
τ_c	Dipolar correlation time	sec
τ_e	Spin-exchange correlation time	sec
τ_r	Rotational correlation time	sec
τ_s	Electron-spin relaxation time	sec
ω_I	Nuclear precessional frequency	rad sec^{-1}
ω_s	Electron precessional frequency	rad sec^{-1}

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CHAPTER I

INTRODUCTION

Studies of paramagnetic first transition series
metal ion-solvent interactions have often employed nuclear
magnetic resonance (NMR) techniques as a probe into solu-
tion dynamics and structure. A unique advantage of NMR as
a tool for investigation of kinetics is that the NMR exper-
iment does not perturb the exchange rate (or equilibrium).
The resonant nuclei which exchange between the paramagnetic
ion first coordination sphere (where the relaxation effect
is greatest) and the bulk solution may be observed directly
in the two environments.

Relaxation of resonant nuclei may be represented by
two relaxation time constants, the spin-lattice (or thermal)
and the phase memory (or spin-spin) relaxation times. The
spin-lattice relaxation time (T_1) is associated with a loss
of energy to other internal degrees of freedom and approach
of the spin system to thermal equilibrium. The phase memory
relaxation time (T_2) is associated with a decay time during
which the in-phase components of nuclear spin become random-
ly oriented. Those relaxation processes are primarly due to
a proton-electron interaction produced at the proton by
neighboring spins, allowing a rapid energy exchange between
the spin states.

Various investigations of proton relaxation times as
a function of temperature in nonacid or slightly acid (0.1 M

H^+) aqueous Cr(III) solutions show that the proton relaxation times (T_1 and T_2) decrease with increasing temperature from $0°$ to $30°C$, and above $30°$ the rate begins to level off.[1-4] Bloembergen and Morgan[5] point out that the rate of proton-exchange between the Cr(III) ions and the solvent water molecules increases with temperature causing the decrease of relaxation times in aqueous Cr(III) solutions. At those acid concentrations (0.1 M or less) the proton-exchange mechanism is postulated to proceed by the acid hydrolysis step,

$$Cr(H_2O)_5HOH^{+3} + HOH \rightleftharpoons Cr(H_2O)_5OH^{+2} + H_3O^+. \qquad (1)$$
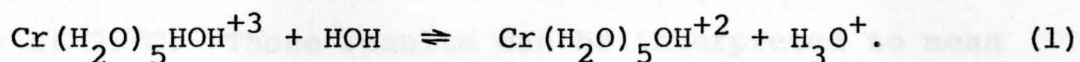
Melton and Pollack[4] suggest reaction (1) is a concerted proton transfer in which a coordinated water molecule is connected through a Grotthus chain of water molecules to the coordinated OH^- ion and proton-exchange occurs via a proton jump across hydrogen bonds.

Swift and Stephenson[6] give another mechanism at higher acidities (1.1 to 1.8 M HNO_3) to explain the observed decrease in T_2 with increasing hydrogen ion concentration. The net effect of that proposed concerted acid-catalyzed proton-exchange mechanism which involves protonation of the $Cr(H_2O)_6^{+3}$ ion followed by a deprotonation is:

$$Cr(H_2O)_5HOH^{+3} + H^*OH_2^+ \rightleftharpoons Cr(H_2O)_5HOH^{*+3} + H_3O^+. \qquad (2)$$
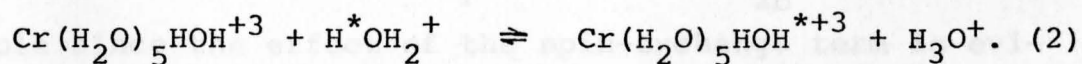
In a subsequent NMR study of proton relaxation rates in acidic Cr(III) solutions Swift and co-workers[7] report an acid-catalysis of proton relaxation rates in $HClO_4$,

H_2SO_4, H_3PO_4 and acetic acid. The proton relaxation rates, $1/(P_bT_2)$, in references 6 and 7 were treated as being solely dependent on the proton residence time in the $Cr(H_2O)_6^{+3}$ ion first coordination sphere, τ_b, which was set equal to a linear function of the acid molarity,

$$1/(P_bT_2) \quad = \quad 1/\tau_b \quad = \quad k_1 + k_2[H^+] . \qquad (3)$$

Nolle and Morgan[8] at 40.00 Mhz and Melton and Pollack[4] at 60.00 Mhz find the ratio of T_1/T_2 to be significantly greater than unity in 0.1 M $HClO_4$ solutions of Cr-(III) at 25°C. Those results can be interpreted to mean that in general the observed relaxation is at least in part relaxation controlled and specifically spin-exchange controlled. Luz and Shulman[9] measure a proton chemical shift in 0.1 M $HClO_4$ solutions of Cr(III) at 28°C and those data support the rationale that spin-exchange relaxation contributes to the observed phase memory relaxation rates.

Previous studies of weakly acidic Cr(III) solutions show that $1/(T_2)$ increases with temperature and reaction (1) is the postulated proton-exchange mechanism.[4] At low acidity (0.1 M H^+) the ratio of T_1/T_2 greater than unity indicates that the contribution to the proton relaxation rate, $1/(T_2)$, from the relaxation controlled mechanism (T_{2b}) is not negligible since the effect of the spin-exchange term is evident. At moderate acidity a rationale for the increase in proton relaxation rates with increasing acidity is based on the proton-exchange mechanism of reaction (2) only.[6]

The present work presents the results of NMR phase memory proton relaxation experiments in aqueous $HClO_4$, HCl and H_2SO_4 solutions of Cr(III) over a large range of acid concentrations (0.1 M to 10 M H^+). That range of acid concentrations is employed to elucidate the proton relaxation mechanism(s) in moderate acid (0.5 to 6 M) and high acid (above 6 M) solutions of Cr(III). It was felt that studying a large range of acid concentrations would yield a better understanding of proton-exchange processes at lower acidities. It is also necessary to study the proton relaxation rates over a large acid concentration range to determine the contribution of T_{2b} to those rates. If T_{2b} contributes signifigantly to the observed relaxation rates, as implied by previous studies,[4,8,9] then T_{2b} should be taken into account to correctly determine the proton-exchange parameters. The present study should afford a method such that the contribution from T_{2b} to the relaxation rates may be estimated. At high acidities where the proton-exchange rates are expected to be very high, the observed proton relaxation rates should be relaxation controlled and not exchange controlled.

In addition measurment of the proton chemical shifts, which have only been measured in 0.1 M $HClO_4$,[9] should determine the specific contribution of spin-exchange to the observed proton relaxation rates. As stated, previous studies have shown that the T_1/T_2 ratio is signifigantly greater than unity so that spin-exchange relaxation must

exist at lower acidities and may contribute to the relaxation at acidities greater than 0.1 M.

At the acidities employed in the present study it is necessary to use mean acid activities rather than molalities to represent the proton residence time, τ_b, as a rapidly increasing function of hydrogen ion concentration.

A model based on a solvated (hexacoordinate) Cr-(III) ion which is compatible with our results and those in the literature is utilized to interpret the relaxation rate data. The parameters and equations which determine NMR correlation times controlling proton relaxation in each acid (HClO$_4$, HCl and H$_2$SO$_4$) are reviewed.

CHAPTER II

THEORY

The Bloembergen-Solomon Equation

The reduction of the experimental phase memory re-
laxation time (T_2), which is caused by the addition of para-
magnetic ions to water, has been theoretically explained by
an electron-nuclear dipole-dipole interaction equation in-
itally given by Bloembergen, Purcell and Pound,[10] followed
by a more rigorous derivation from Solomon.[11] Bloembergen[12]
has formulated an additional relaxation mechanism of scalar
coupling between electron spin of the paramagnetic ion and
proton spin, $A\overline{I}\cdot\overline{S}$, to explain the chemical shifts of protons
in paramagnetic ion solutions. The equation which combines
the dipolar (dd) and scalar interaction (ex) is:

$$\frac{1}{(T_{2b})} = \frac{c_1}{r^6} \left[7\tau_c + \frac{13\tau_c}{1 + \omega_s^2 \tau_c^2} \right] \text{(dd)}$$

$$+ c_2 \, (A/h)^2 \left[\tau_e + \frac{\tau_e}{1 + \omega_s^2 \tau_e^2} \right] \text{(ex)}. \qquad (4)$$

Where

$$c_1 = \frac{4}{15} \pi^2 \gamma_I^2 \gamma_s^2 h^2 S(S+1) \qquad (5)$$

and

$$c_2 = \frac{4}{3} \pi^2 S(S+1). \qquad (6)$$

S is the electron-spin quantum number, γ_I and γ_S are the proton and electron magnetogyric ratios, respectively. The ion-proton internuclear distance is r, and ω_S is the electron precessional frequency.

The spin-exchange coupling constant, (A/h), is expressed as:[13]

$$\frac{\Delta\omega}{\omega_I} = \frac{2 \pi P_b g \beta S(S+1)}{3 \gamma_I k T} (A/h).$$ (7)

The experimental chemical shift is $\Delta\omega$ and ω_I is the nuclear precessional frequency. The nuclear factor and Bohr magneton are g and β, respectively. The Boltzman constant is k, and T is the absolute temperature.

$$P_b = \frac{z N}{\Sigma_i N_i}$$ (8)

where z is the coordination number of the paramagnetic ion of concentration N and $\Sigma_i N_i$ is the concentration of all exchangeable protons from water and acid in solution.

Correlation Times

The correlation time for dipolar interaction is

$$\tau_c^{-1} = \tau_r^{-1} + \tau_s^{-1} + \tau_b^{-1}$$ (9)

and for the isotropic spin-exchange correlation time one has

$$\tau_e^{-1} = \tau_s^{-1} + \tau_b^{-1}.$$ (10)

For a sphere of radius a diffusing in a fluid of

viscosity η the rotational correlation time is[10]

$$\tau_r = 4 \pi \eta a^3 / 3 k T .$$ (11)

The electron-spin relaxation time is τ_s, and τ_b is the residence time of a proton in the first coordination sphere of the Cr(III) ion.

Relaxation Rate Equations

The observed relaxation rates in this type system may depend on both the relaxation time of protons in the first coordination sphere of the paramagnetic ion and the rate of proton-exchange between that environment and the solvent.[14] Swift and Connick[15] considered the limiting equations governing relaxation in aqueous solutions of dilute paramagnetic ions. Combining their equations (10c) and (10d) gives a formula which takes into account proton chemical exchange and first-sphere relaxation (T_{2b}). Relaxation rates present only in the solvent, $1/(T_{2a})$, with no paramagnetic ions in solution are subtracted from the relaxation rates in solutions containing paramagnetic ions, $1/(T_2')$, so that the proton relaxation rate due only to the paramagnetic ions, $1/(T_2'')$, remains

$$\{1/(T_2') - 1/(T_{2a})\} = 1/(T_2'')$$ (12)

The subscripts a and b refer to the solvent and the first coordination sphere, respectively, after the notation of McConnell.[16] The relaxation time in the paramagnetic ion

first coordination sphere is T_{2b}, see equation (4), and τ_b is the lifetime for proton-exchange between the first coordination sphere of the ion and the solution.

Phase memory relaxation times (T_2) were calculated from the half-height line widths $(\Delta\nu_{\frac{1}{2}})$ where

$$T_2 = 1/(\pi \Delta\nu_{\frac{1}{2}}), \tag{13}$$

for a Lorentzian absorption signal.

CHAPTER III

EXPERIMENTAL

Solution Preparation

Reagent grade chemicals were used in the preparation of all solutions. Water was triply distilled in glass from a basic potassium permanganate solution. The extremely hygroscopic Cr(III) perchlorate (Alpha) was used without further purification, but was dried under vacuum at the boiling temperature of toluene with magnesium perchlorate as dessicant. That drying resulted in a salt of about 3 waters of hydration (as shown by subsequent volumetric analysis) which was convient to weigh.

To insure a uniform concentration of Cr(III) ions, N, in a series of experiments with a particular acid, a stock solution of $Cr(ClO_4)_3$ was prepared in 1.00 M $HClO_4$. At that concentration $HClO_4$ prevented formation of acid hydrolysis products in the stock solution. The acidity of the stock solution was verified by potentiometric titration against standard sodium hydroxide. An Orion model 801 pH meter and a standard glass electrode were used. The first derivative of the relative mv versus ml of sodium hydroxide titrant gave the acid endpoint.

The stock solution was analyzed for Cr(III) concentration by conversion of the Cr(III) ions to dichromate. An aliquot of Cr(III) was boiled with ammonium persulfate and silver nitrate as catalyst. The solution gradually changed

from a light purple-blue to yellow. Excess $(NH_4)_2S_2O_8$ was destroyed by continued boiling. Stock Cr(III) thus oxidized was titrated with ferrous ammonium sulfate. Diphenlyamine sulfonic acid sodium salt was the indicator and phosphoric acid was added to supply an acidic medium and to complex the ferric ions produced.

The acid solutions were prepared from $HClO_4$ (J. T. Baker), HCl (Fisher) and H_2SO_4 (Dupont). The composition of each solution used in NMR experiments was known by weight percent and molarity. Those solutions contained weighed volumes of the stock solution (10.00 ml), acetone (2.00 ml), the appropriate acid and enough distilled water to bring the final volume to 50.00 ml.

The Cr(III) ion concentration in the $HClO_4$ series was 0.0136 M. The HCl and H_2SO_4 series were 0.0108 M in Cr(III). $HClO_4$ was added to the volumetric flasks in an amount such that the HCl and H_2SO_4 samples were 0.500 M in $HClO_4$. That was done to prevent hydrolysis during solution preparation. Proton relaxation at low $HClO_4$ concentrations was studied in 0.0200 M Cr(III) solutions. Sodium hydroxide was added to some of those solutions to raise the pH. Acidity was measured with a digital pH meter.

Acetone, which has a single peak, was the internal reference. It comprised 3 to 4 mole percent of the protons in solution. Tert-butyl alcohol and p-dioxane were tried as internal references. The former proved insoluble in acid solutions. The broadened and shifted water signal overlapped

the dioxane peak making that compound an unsatisfactory internal reference.

Solutions identical in acidity and reference composition (acetone), but without Cr(III), were prepared for use in NMR and visible spectroscopic measurments. Their NMR spectra gave the proton relaxation due only to acidified water (T_{2a}). The chemical shift was measured relative to the acetone internal standard as a function of total acid concentration. The chemical shift of the water solutions subtracted from those shifts of similar solutions containing Cr(III) yielded the shift of the proton peak due to the Cr(III) ions. Visible spectra were obtained from a Cary Model 14 recording spectrometer using Cr(III) solutions in the sample beam and those of closely matched acidity in the reference beam.

Precautions Against Complex Ion Formation

Chromium(III) forms complexes with chloride and sulfate ions. The Cr(III) solutions containing HCl and H_2SO_4 became green on standing. Complexation was observed after 48 hours in both of those acid systems at the highest concentrations ($\sim$ 10 M). Swift and co-workers[7] noted complexation in H_2SO_4 - Cr(III) solutions but reported the NMR data were reproducible from freshly prepared samples at room temperature. Plane and Taube[17] found the half-time for formation of a Cr(III) chloro-complex to exceed 35 hours in 1.134 M $Cr(ClO_4)_3$, 0.847 M $HClO_4$ and 4.25 M chloride ions at $27^\circ C$. The samples in the present investigation were maintained at

room temperature and the NMR measurments were made within 5 hours of sample preparation. With those precautions, complex ion formation in the two acid systems (HCl and H_2SO_4) should be at a minimum.

Excess Anion Experiments

The possibility of an anion effect was examined using $NaClO_4$ (G. F. Smith) and NaCl (J. T. Baker). Both salts were dissolved in distilled water and filtered, that was necessary for the $NaClO_4$ which contained black particles. After solvent evaporation on a hotplate, the salts were recrystalized from solution and dried in a vacuum oven at $120^{\circ}C$. The range of salt concentrations was 0.499 M to 3.230 M for $NaClO_4$ and 0.082 M to 3.055 M for NaCl. Those experiments were conducted in solutions 0.0136 M in Cr(III) and 2.00 M in $HClO_4$.

NMR Measurments

Precision-bore NMR tubes, supplied by the Wilmad Glass Co., were cleaned prior to use with hot 6 M HCl and throughly rinsed with distilled water and acetone. Dissolved O_2 was removed from the samples by a freeze-pump-thaw technique; the tubes were then sealed under vacuum.

A Varian DA-60 NMR spectrometer operating in the high-resolution mode was used to record proton NMR spectra. The sample temperature was maintained at $(301\pm2)^{\circ}K$ by the

magnet heat exchanger. Radiofrequency power levels were well below saturation and the sweep rate was slow enough not to affect the chemical shift. Phase detection was carefully adjusted for each spectrum to insure operation in the absorption mode.

CHAPTER IV

RESULTS AND DISCUSSION

Proton Relaxation At Various Acidities

Figure 1 displays the proton relaxation rate, $1/(NT_2)$, spanning 0.001 to 10 M $HClO_4$ in solutions of Cr-(III). Division by the molar Cr(III) ion concentration, N, normalizes the proton relaxation rates to unit Cr(III) ion concentration. For the sake of clarity in discussing those results, let the data in figure 1 be separated in the following way. The region from 0.001 M to 0.01 M $HClO_4$ is designated as low acidity. From 0.01 M to about 0.5 M $HClO_4$ is the intermediate region. From 0.5 M to 6 M $HClO_4$ is of moderate acidity and above 6 M is the high acid region. Swift and Stephenson[6] find similar results for the behavior of $1/(T_2)$ as a function of HNO_3 molarity (0.001 to 1.8 M) in Cr(III) solutions at 10°C.

Below 0.01 M $HClO_4$ the proton relaxation rate increases as the hydrogen ion concentration decreases. That region contains the hydrolysis product $Cr(OH)^{+2}$ and possibly other higher hydrolysis species.[4] Due to the uncertainty of species present at those low acid concentrations no analysis of that region was attempted.

A constant proton relaxation rate is found at intermediate acidity. That region is identified with the acid hydrolysis proton transfer step of reaction (1). The rate of reaction (1) is not dependent on hydrogen ion concentration
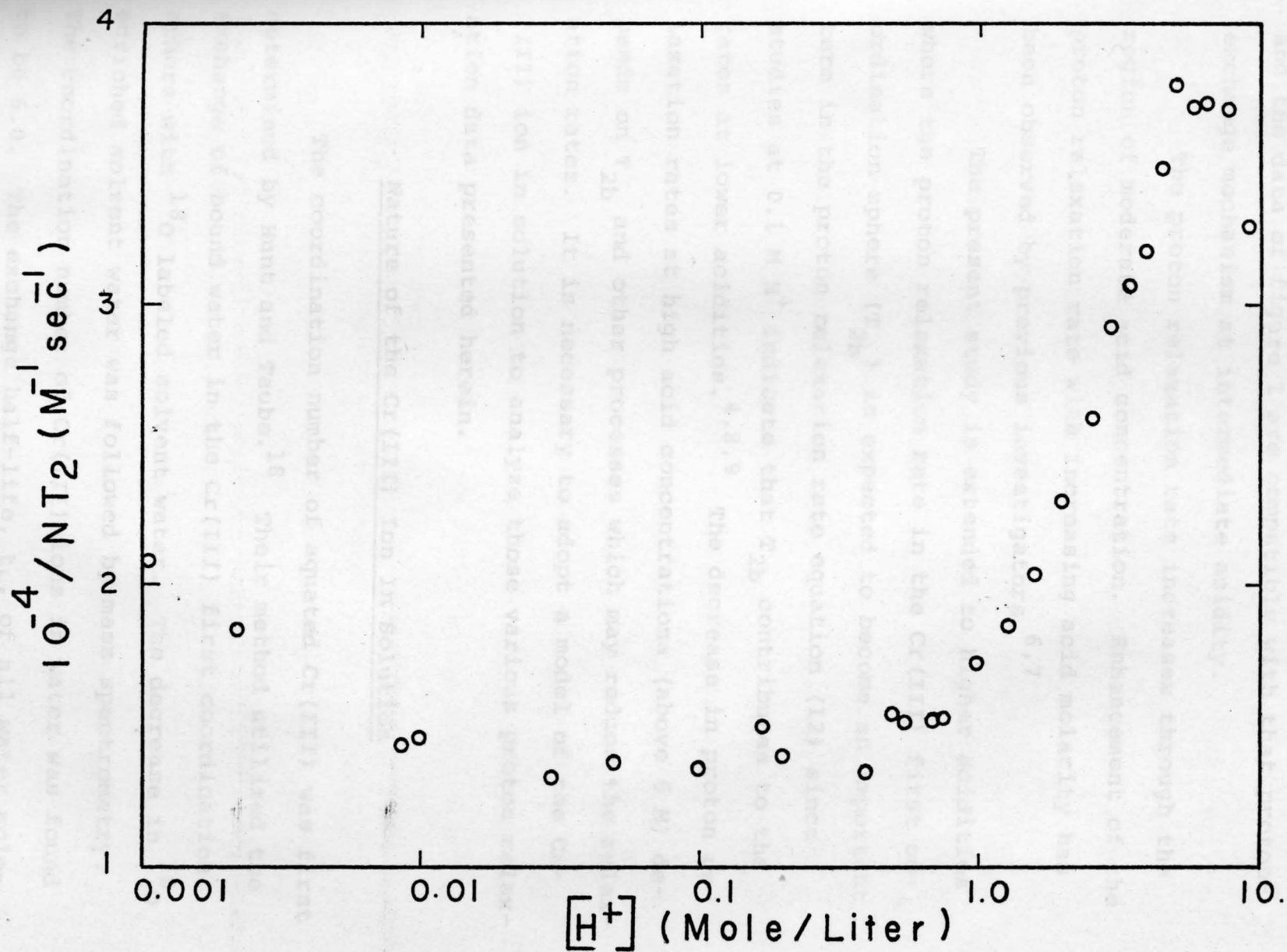
Fig.1. Proton relaxation rate normalized to unit Cr(III) ion concentration, versus HClO$_4$ molarity.

and the data of figure 1 are compatible with that proton-exchange mechanism at intermediate acidity.

The proton relaxation rate increases through the region of moderate acid concentration. Enhancement of the proton relaxation rate with increasing acid molarity has been observed by previous investigators.[6,7]

The present study is extended to higher acidities where the proton relaxation rate in the Cr(III) first coordination sphere (T_{2b}) is expected to become an important term in the proton relaxation rate equation (12) since studies at 0.1 M H^+ indicate that T_{2b} contributes to the rates at lower acidities.[4,8,9] The decrease in proton relaxation rates at high acid concentrations (above 6 M) depends on T_{2b} and other processes which may reduce the relaxation rates. It is necessary to adopt a model of the Cr(III) ion in solution to analyze those various proton relaxation data presented herein.

Nature of the Cr(III) Ion In Solution

The coordination number of aquated Cr(III) was first determined by Hunt and Taube.[18] Their method utilized the exchange of bound water in the Cr(III) first coordination sphere with ^{18}O labeled solvent water. The decrease in ^{18}O enriched solvent water was followed by mass spectrometry. The coordination number of Cr(III) ions in water was found to be 6.0. The exchange half-life, $t_{\frac{1}{2}}$, of all water molecules initally present in the Cr(III) first coordination

sphere was measured. In 1.47 m $Cr(ClO_4)_3$ and 0.13 m $HClO_4$ at

at $25^{\circ}C$ $t_{\frac{1}{2}}$ was 40 hours. After that initial study, verifica-

tions of the hexacoordination and the very long exchange

half-life of first coordination sphere water molecules have

appeared in the literature.[17,19-21]

Laswick and Plane[22] separated the species $Cr(H_2O)_6^{+3}$

by ion-exchange chromatography from neutral boiled solutions

of $Cr(ClO_4)_3$ and showed that the visible spectra of the frac-

tion associated with $Cr(H_2O)_6^{+3}$ have two absorbance maxima

at 408 nm and 576 nm with molar absorptivities of 15.6

1/mol cm and 13.4 1/mol cm, respectively. A study of the

absorbance versus Cr(III) concentration in 2.00 M and 4.43 M

$HClO_4$ is shown in figure 2. We note that the absorbance is

linear with Cr(III) concentration and find the molar absor-

ptivities to be 13.9 1/mol cm at 408 nm and 12.2 1/mol cm at

576 nm. Those lower values probably are better molar absorp-

tivities for octahedral Cr(III) in water since Laswick and

Plane may not have completely separated all nonoctahedral

species (which have higher molar absorptivities) from the

$Cr(H_2O)_6^{+3}$ fraction. The acid present in our solutions

should suppress formation of the nonoctahedral species which

are produced by boiling nonacid Cr(III) solutions. Chromium-

(III) solutions at other acidities were found to have similar

spectral properties. NMR experiments in which the $HClO_4$ con-

centration was fixed and the amount of Cr(III) ion was var-

ied, proved the proton relaxation time (T_2) increases

linearly with Cr(III) ion concentration. Furthermore, as
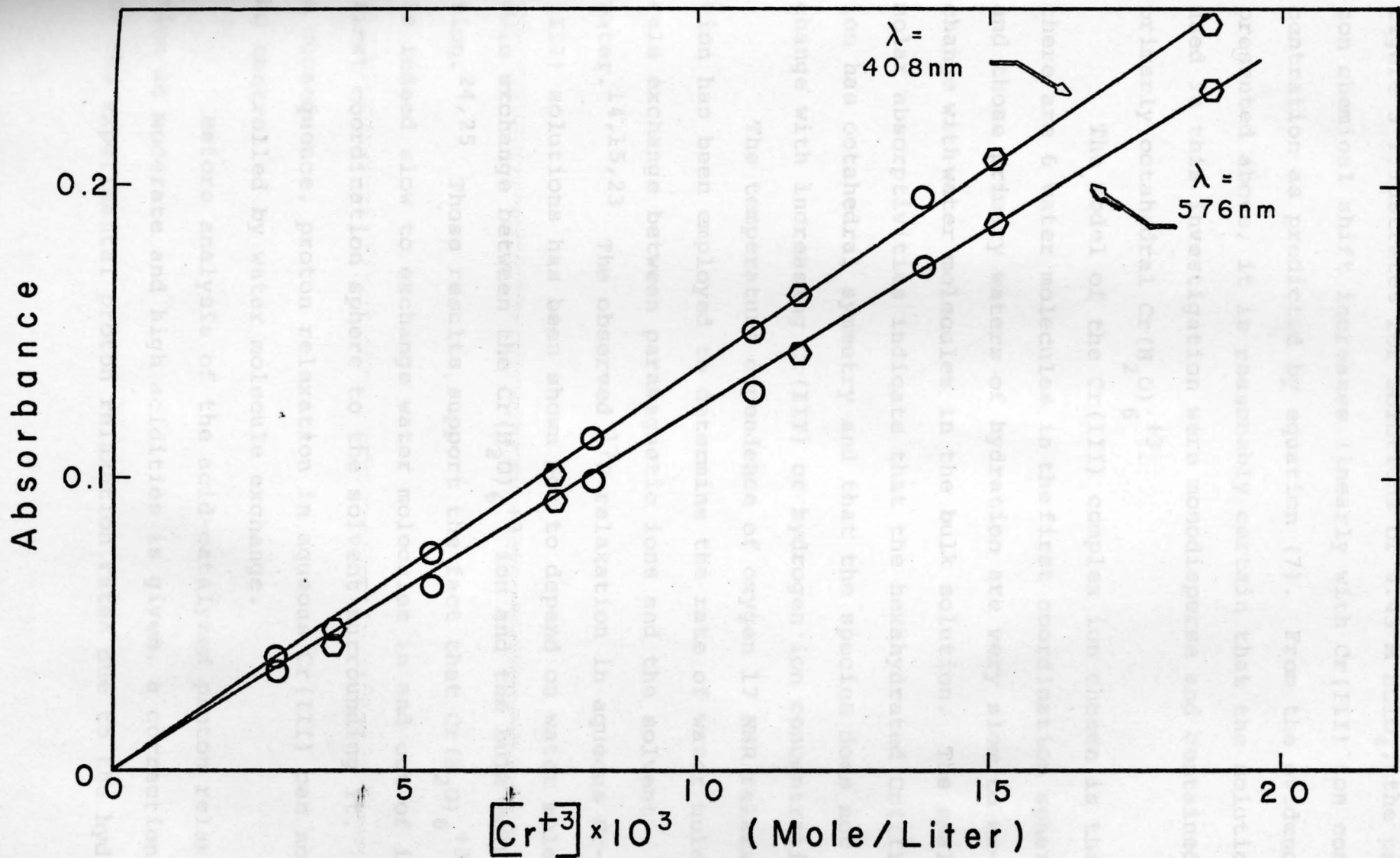
Fig.2. Absorbance versus Cr(III) concentration in 2.00 molar HClO$_4$ (hexagons) and 4.43 molar HClO$_4$ (circles), at the two visible absorbance maxima of 408 nm and 576 nm. The slope at each wavelength is the molar absorptivity.

figure 3 illustrates for solutions of 4.43 M $HClO_4$, the proton chemical shift increases linearly with Cr(III) ion concentration as predicted by equation (7). From the evidence presented above, it is reasonably certain that the solutions used in this investigation were monodisperse and contained primarly octahedral $Cr(H_2O)_6^{+3}$.

The model of the Cr(III) complex ion chosen is that there are 6 water molecules in the first coordination sphere and those primary waters of hydration are very slow to exchange with water molecules in the bulk solution. The small molar absorptivities indicate that the hexahydrated Cr(III) ion has octahedral symmetry and that the species does not change with increasing Cr(III) or hydrogen ion concentration.

The temperature dependence of oxygen 17 NMR relaxation has been employed to determine the rate of water molecule exchange between paramagnetic ions and the solvent water.[14,15,23] The observed ^{17}O relaxation in aqueous Cr-(III) solutions has been shown not to depend on water molecule exchange between the $Cr(H_2O)_6^{+3}$ ion and the bulk solution.[24,25] Those results support the fact that $Cr(H_2O)_6^{+3}$ is indeed slow to exchange water molecules in and out of its first coordination sphere to the solvent surrounding it. As a consequence, proton relaxation in aqueous Cr(III) can not be controlled by water molecule exchange.

Before analysis of the acid-catalyzed proton relaxation at moderate and high acidities is given, a correction of the experimental proton relaxation rates due to the hydro-
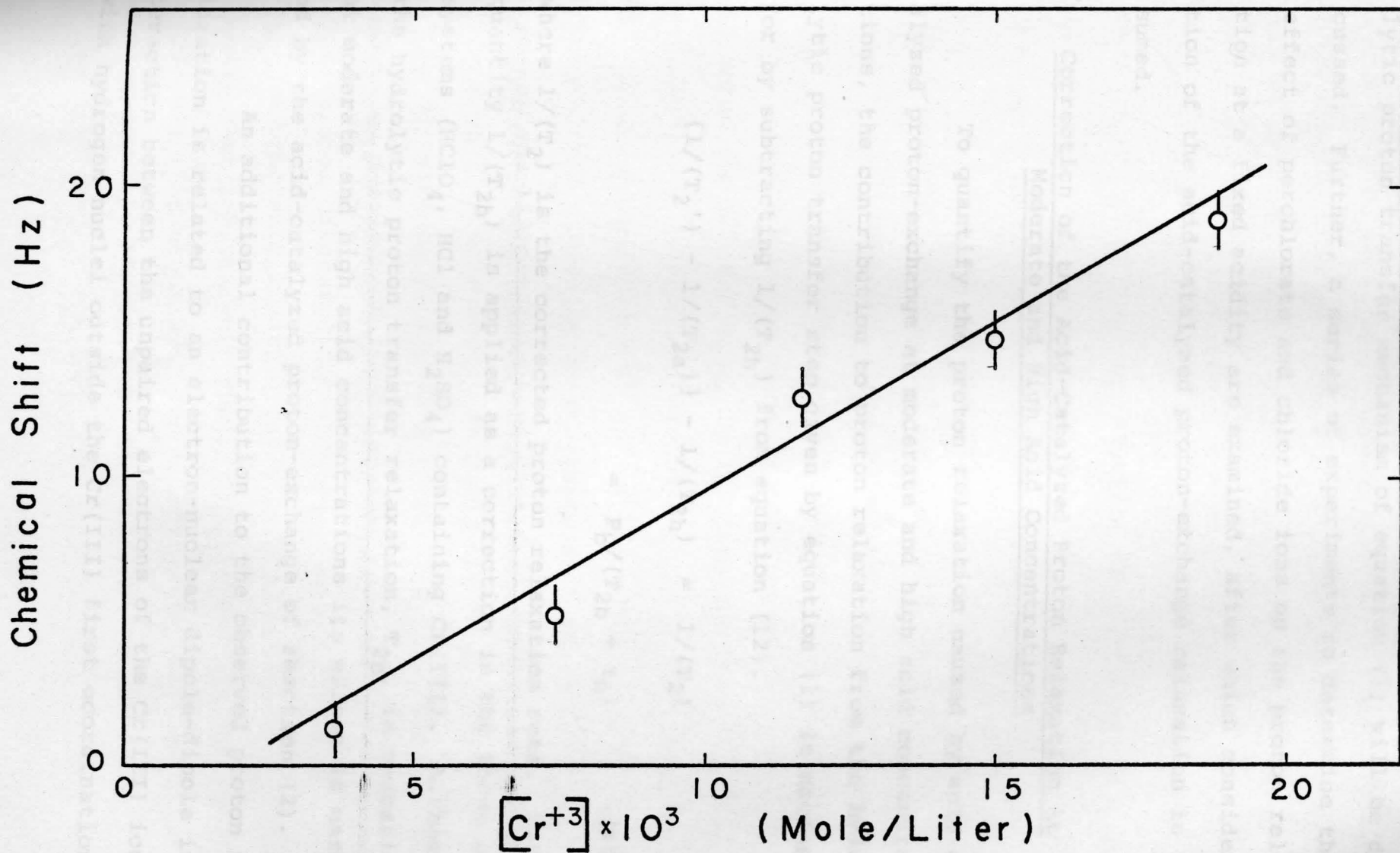
Fig. 3. The chemical shift in hertz versus Cr(III) ion concentration in 4.43 molar HClO$_4$.

lytic proton transfer mechanism of equation (1) will be discussed. Further, a series of experiments to determine the effect of perchlorate and chloride ions on the proton relaxation at a fixed acidity are examined, after which consideration of the acid-catalyzed proton-exchange relaxation is resumed.

Correction of the Acid-Catalyzed Proton Relaxation At Moderate and High Acid Concentrations

To quantify the proton relaxation caused by acid-catalyzed proton-exchange at moderate and high acid concentrations, the contribution to proton relaxation from the hydrolytic proton transfer step given by equation (1) is accounted for by subtracting $1/(T_{2h})$ from equation (12).

$$\{1/(T_2') - 1/(T_{2a})\} - 1/(T_{2h}) = 1/(T_2)$$

$$= P_b/(T_{2b} + \tau_b) \qquad (14)$$

where $1/(T_2)$ is the corrected proton relaxation rate. The quantity $1/(T_{2h})$ is applied as a correction in the three acid systems ($HClO_4$, HCl and H_2SO_4) containing Cr(III). Although the hydrolytic proton transfer relaxation, T_{2h}, is operative at moderate and high acid concentrations its effect is masked by the acid-catalyzed proton-exchange of reaction (2).

An additional contribution to the observed proton relaxation is related to an electron-nuclear dipole-dipole interaction between the unpaired electrons of the Cr(III) ions with hydrogen nuclei outside the Cr(III) first coordination

sphere. That effect has been formulated as a diffusion of rigid spheres in a continuous medium of viscosity η. The formula given by Abragam[26] is

$$1/(T_1)_{tr} = \frac{16 \pi^2 N_p \mu^2 \gamma_I^2 \eta}{15 k T} \qquad (15)$$

where $(T_1)_{tr}$ is the NMR spin-lattice translational diffusion relaxation time. The concentration of Cr(III) ions per cm^3 is N_p and μ is the effective electron magnetic moment.

In a similar context Melton and Pollack[4] calculated $(T_1)_{tr}$ and $(T_2)_{tr}$ for solutions containing Cr(III) ions. The translational diffusion terms were found to be nearly equal at 28^oC. Abragam's equation (15) was employed to estimate $(T_2)_{tr}$. In the present analysis, solution viscosities were estimated for HCl and H_2SO_4 at 25^oC and for $HClO_4$ at 20^oC from data in a standard reference.[27]

The contribution to the proton relaxation rates from translational diffusion in the three acid systems, except H_2SO_4 at the highest concentrations (viscosities), is calculated to be 2 to 4 percent. In H_2SO_4 the contribution becomes 5.1 to 8.9 percent from 7.53 M to 10.57 M. The $1/(T_{2h})$ correction as carried out in the present analysis contains translational diffusion to an extent of 3 to 4 percent; i.e., T_{2h} is a composite of the hydrolytic proton transfer step and translational diffusion. The $1/(T_2)_{tr}$ contribution should become signifigant only at the highest H_2SO_4 concentrations, but a correction for that effect would not change the qualitative features of the corrected data and no quantitative

interpretation is attempted for the high acid concentration region. Therefore, subtraction of the translational diffusion effect is omitted in correcting the proton relaxation rates of the three acid systems since $(T_2)_{tr}$ is contained implicitly in T_{2h}. The remaining corrected proton relaxation rates, $1/(P_bT_2)$, are displayed in figures 4 through 6.

Excess NaClO$_4$ and NaCl

To demonstrate that proton relaxation is solely dependent on the acid species (or hydrogen ion concentration) and not anions only, excess anion was added to various acidic Cr(III) solutions. The results of the investigation of added $NaClO_4$ and NaCl in 2.00 M $HClO_4$ and 0.0136 M Cr(III) are shown in figure 7. The proton relaxation rate is plotted versus total anion molarity. The anions ClO_4^- (circles), and Cl^- (squares), were added using $NaClO_4$ and NaCl, respectively. Triangles are the proton relaxation rate in $HClO_4$ with no added salt. Within experimental error $NaClO_4$ causes a slight decrease in relaxation rate at 3.2 M ClO_4^-. The increase in proton relaxation rate at 2 to 3 M Cl^- may be due to viscosity effects. Swift and Stephenson[6] find T_2 to be virtually independent of excess NO_3^- ion concentration in 1.1 M HNO_3 solutions of $Cr(NO_3)_3$. Those results complement our conclusion that the increase in $1/(P_bT_2)$ at moderate acidities is due to a mechanism dependent on hydrogen ion concentration and independent of ClO_4^- or Cl^- concentration.
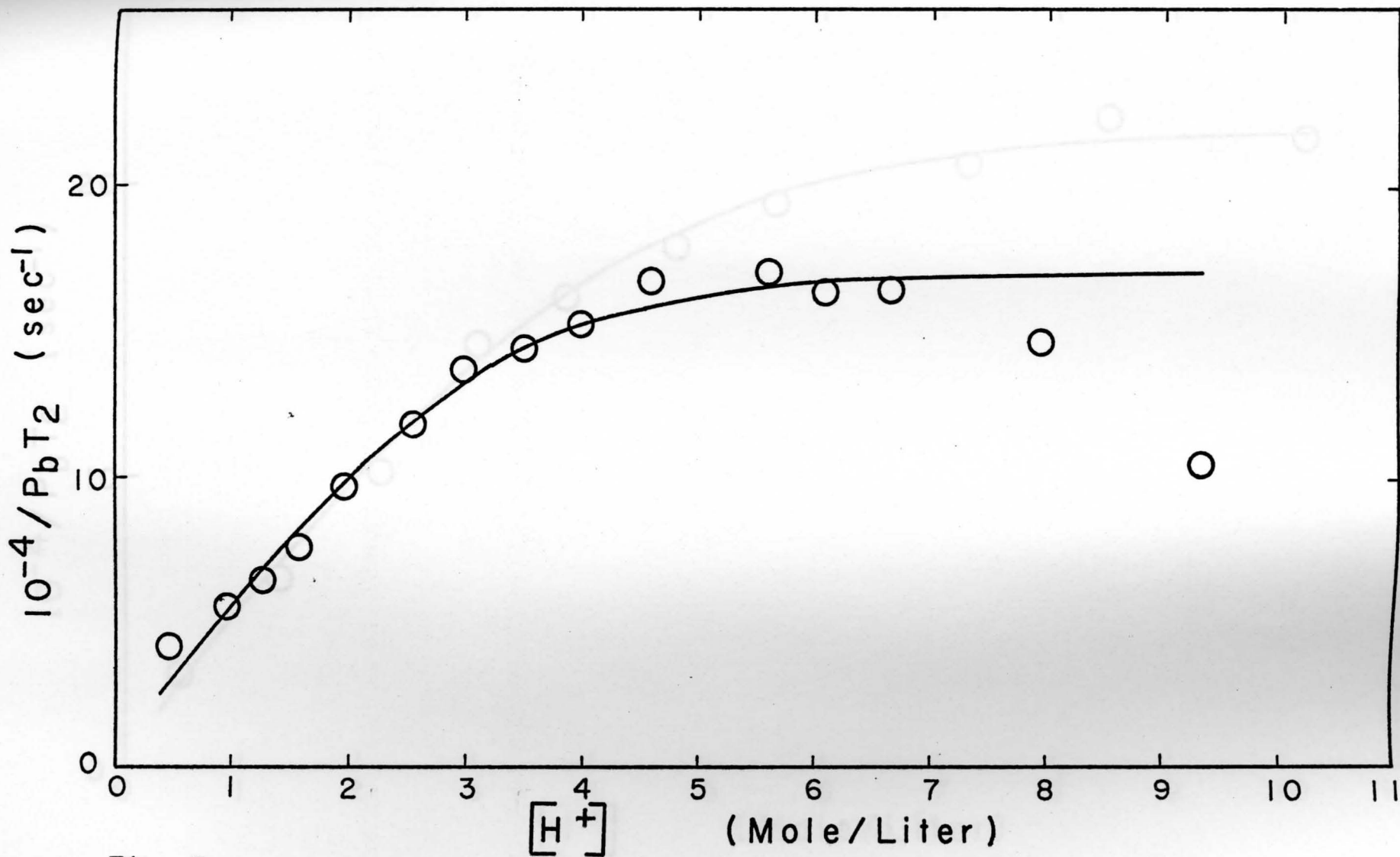
Fig. 4. Proton relaxation rate versus $HClO_4$ molarity. The circles are corrected exper-
imental points. The solid line is generated by the constants listed in Table 2
and equation (16).

Fig. 5. Proton relaxation rate versus HCl molarity, including 0.500 M $HClO_4$. The circles are corrected experimental points. The solid line is generated by the constants listed in Table 2 and equation (16).

Fig. 6. Proton relaxation rate versus H_2SO_4 molarity, including 0.500 M $HClO_4$. The circles are corrected experimental points. The solid line is generated by the constants listed in Table 2 and equation (16).
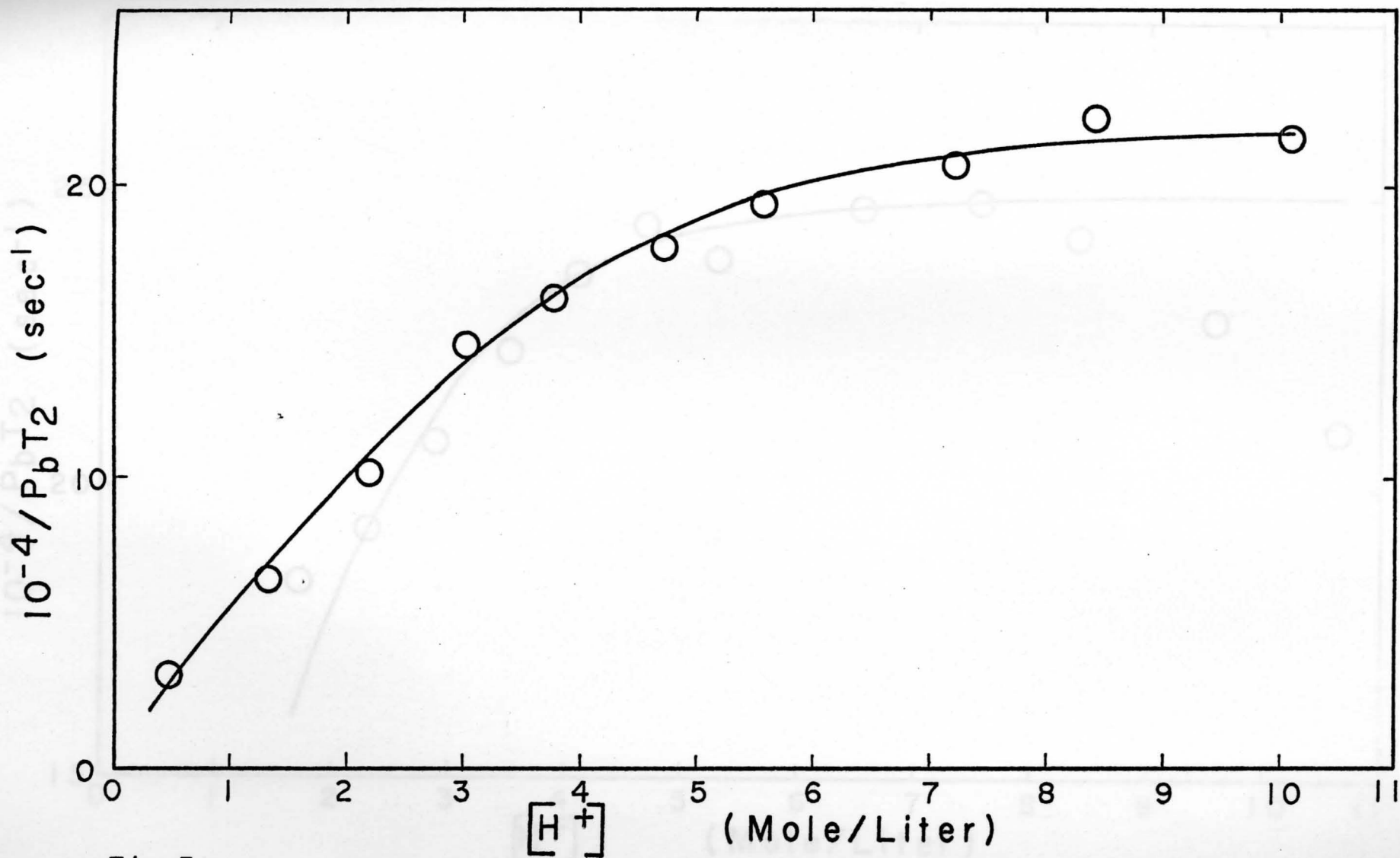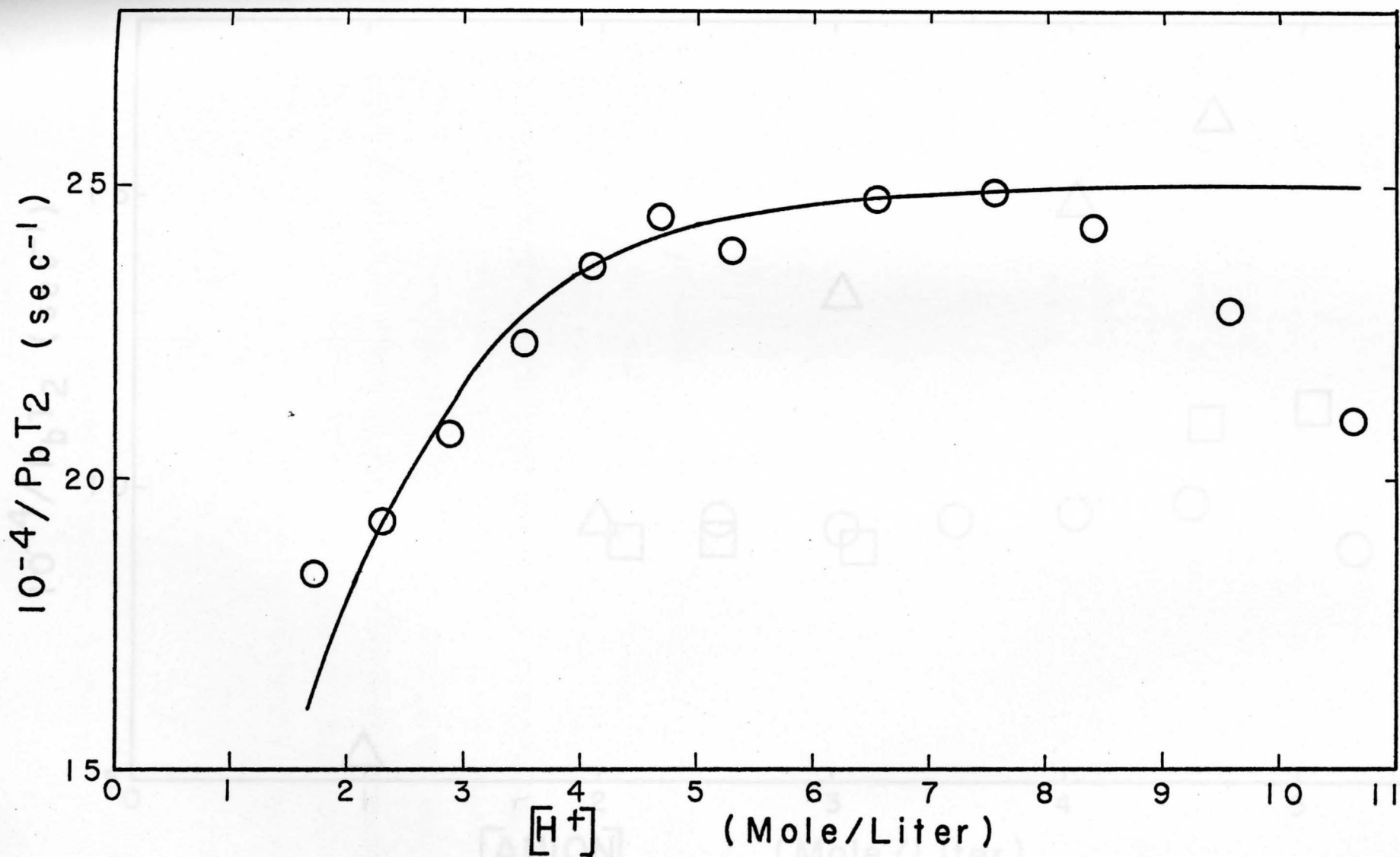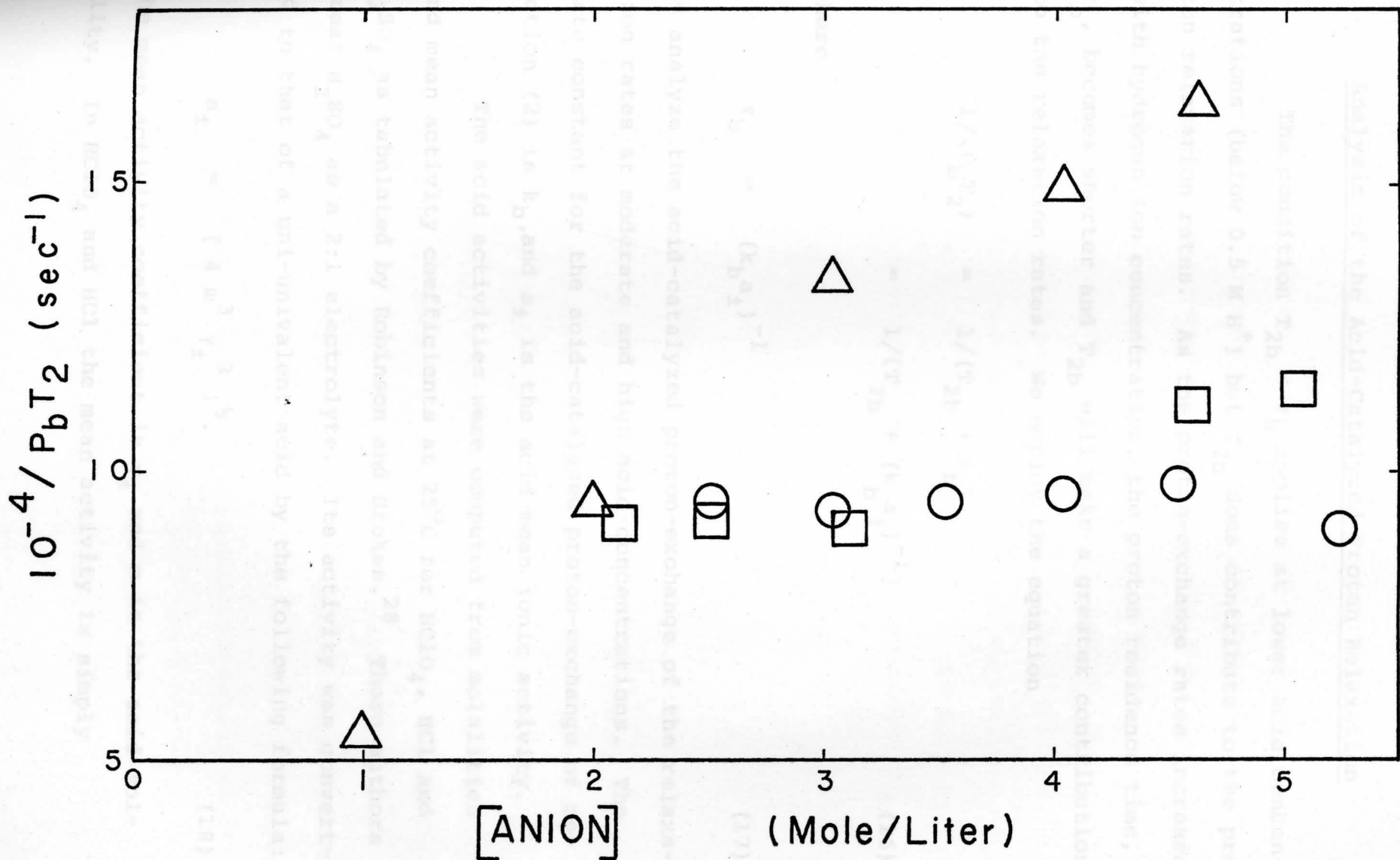
Fig. 7. Proton relaxation rate versus total anion concentration. The triangles are HClO$_4$. The circles are NaClO$_4$ added and the squares are NaCl added to solutions 2.00 M in HClO$_4$.

Analysis of the Acid-Catalyzed Proton Relaxation

The condition $T_{2b} < \tau_b$ applies at lower acid concentrations (below 0.5 M H^+) but T_{2b} does contribute to the proton relaxation rates. As the proton-exchange rates increase with hydrogen ion concentration, the proton residence time, τ_b, becomes shorter and T_{2b} will make a greater contribution to the relaxation rates. We employ the equation

$$1/(P_b T_2) = 1/(T_{2b} + \tau_b)$$
$$= 1/\{T_{2b} + (k_b a_\pm)^{-1}\} \qquad (16)$$

where

$$\tau_b = (k_b a_\pm)^{-1} \qquad (17)$$

to analyze the acid-catalyzed proton-exchange of the relaxation rates at moderate and high acid concentrations. The rate constant for the acid-catalyzed proton-exchange of reaction (2) is k_b, and $a_\pm$ is the acid mean ionic activity.

The acid activities were computed from molalities and mean activity coefficients at 25°C for $HClO_4$, HCl and H_2SO_4 as tabulated by Robinson and Stokes.[28] Those authors treat H_2SO_4 as a 2:1 electrolyte. Its activity was converted to that of a uni-univalent acid by the following formula:

$$a_\pm = (4 m^3 \gamma_\pm^3)^{\frac{1}{2}}. \qquad (18)$$

The mean activity coefficient is $\gamma_\pm$ and m is the acid molality. In $HClO_4$ and HCl the mean activity is simply

$$a_{\pm} = m \, \gamma_{\pm} . \tag{19}$$

Using equation (16) and the corrected experimental proton realaxation rates, first-sphere and other proton relaxation mechanism(s) may be obtained. The quantities T_{2b} and τ_b are used as adjustable parameters in equation (16) to produce the best curve-fit of $1/(P_b T_2)$. However, T_{2b} may be derived independently from equations (4) through (11) and the complex-ion model. That calculation serves to indicate the reliability of the T_{2b}'s and k_b's from the curve-fitting. A discussion of the parameters that apply in computing T_{2b} follows.

Calculation of T_{2b}

The Dipolar Term

The dipolar (dd) and spin-exchange (ex) terms of equation (4) combine to give $1/(P_b T_2)$. The dipolar correlation time, τ_c, is controlled by τ_r since it is shorter than τ_s or τ_b; see equation (9). The correlation time associated with a molecular rotation, τ_r, depends on the radius of the solvated Cr(III) ion and the solution viscosity. Viscosities were taken from the literature.[27] Nightingale[29] gives the hydrated radius of Cr(III) as 4.61×10^{-8} cm. The values of τ_r from equation (11) are in reasonable agreement with those estimated by Morgan and Nolle[30] and Bloembergen and Morgan[5] in a completely different calculation. The electron-spin relaxation time, τ_s, based on ESR data with appropriate

frequency correction to 60.00 Mhz is 2.34 x 10^{-9} sec.[5] The proton residence time, τ_b, is calculated from its assumed dependence on the mean activity of each acid; see equation (16).

The ion-proton internuclear distance, r, given in reference 4 and as estimated from ionic radii is 2.74 x 10^{-8} cm. The dipolar term is 5 to 7 times greater than the spin-exchange term for $HClO_4$ and HCl. Spin-exchange makes a greater contribution to T_{2b} in H_2SO_4 due to the larger chemical shifts in H_2SO_4, assuming the same value of τ_s in the three acids.

The Spin-Exchange Term

The spin-exchange correlation time depends on τ_s or (and) τ_b, see equation (10), whichever is shorter controls τ_e. The coupling constant, (A/h), is determined from experimental proton chemical shifts, the probability of a proton being in the Cr(III) first coordination sphere, P_b, and equation (7). That constant is not dependent on any assumptions involving correlation times. Figures 8 through 10 show the chemical shift in each acid, with and without Cr(III) ions, as a function of total hydrogen ion concentration. The proton chemical shifts are downfield for the Cr(III) solutions relative to those containing only acid. The shifts in $HClO_4$ and HCl are about the same. In H_2SO_4 the chemical shifts are twice as large and further downfield than in $HClO_4$ or HCl. Proton chemical shifts of 0.1 M $HClO_4$ solutions con-
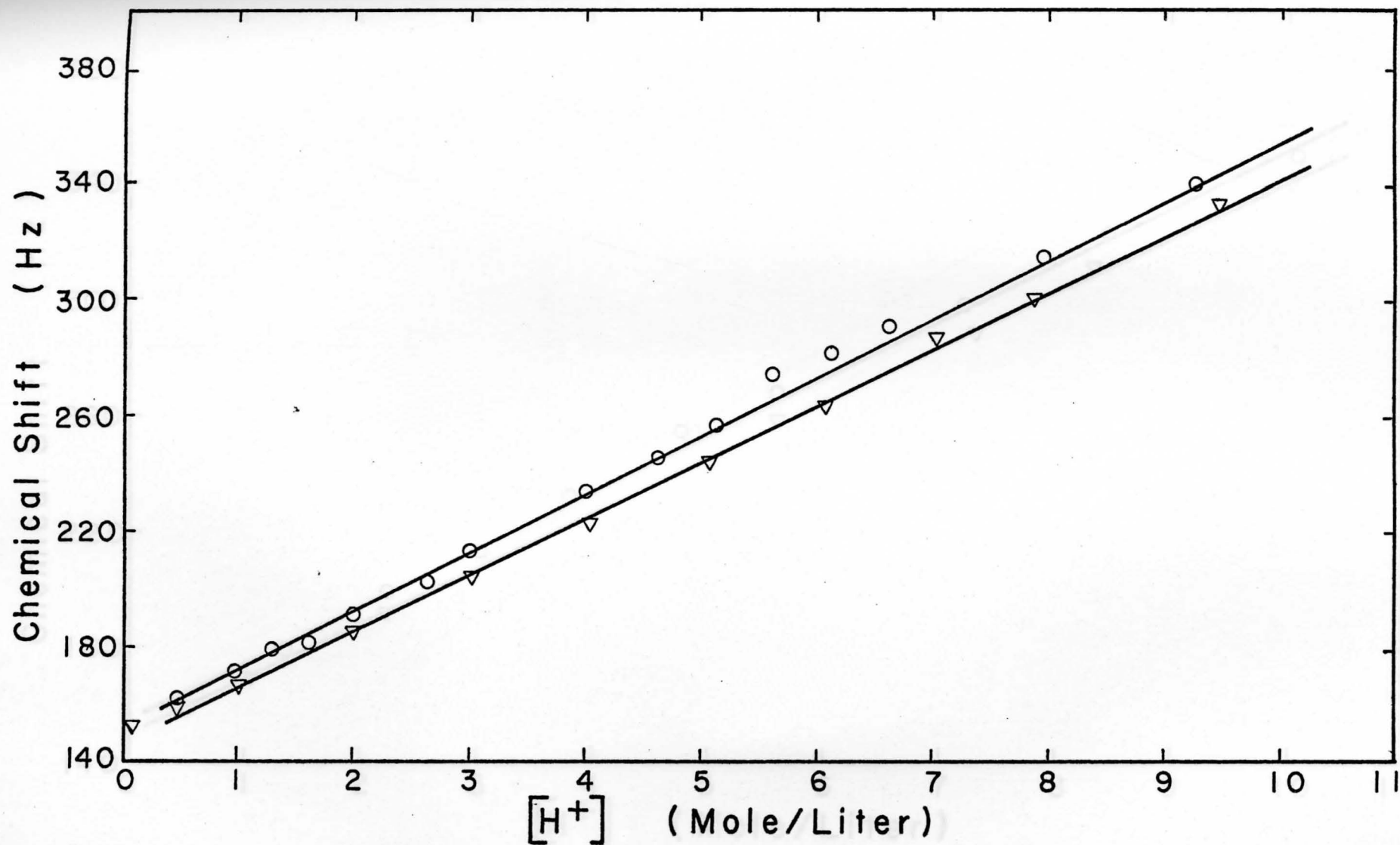
Fig. 8. The chemical shift in hertz versus HClO$_4$ molarity. The triangles are chemical shifts of acid solutions not containing Cr(III). Circles represent the chemical shifts of acidified 0.0136 M Cr(III) solutions.

Fig. 9. The chemical shift in hertz versus HCl molarity, including 0.500 M HClO$_4$. The triangles are chemical shifts in acid solutions not containing Cr(III). Circles represent the chemical shift of acidified 0.0108 M Cr(III) solutions.

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Fig. 10. The chemical shift in hertz versus H_2SO_4 molarity, including 0.500 M $HClO_4$. The triangles are chemical shifts in acid solutions not containing Cr(III). Circles represent the chemical shifts in acidified 0.0108 M Cr(III) solutions.
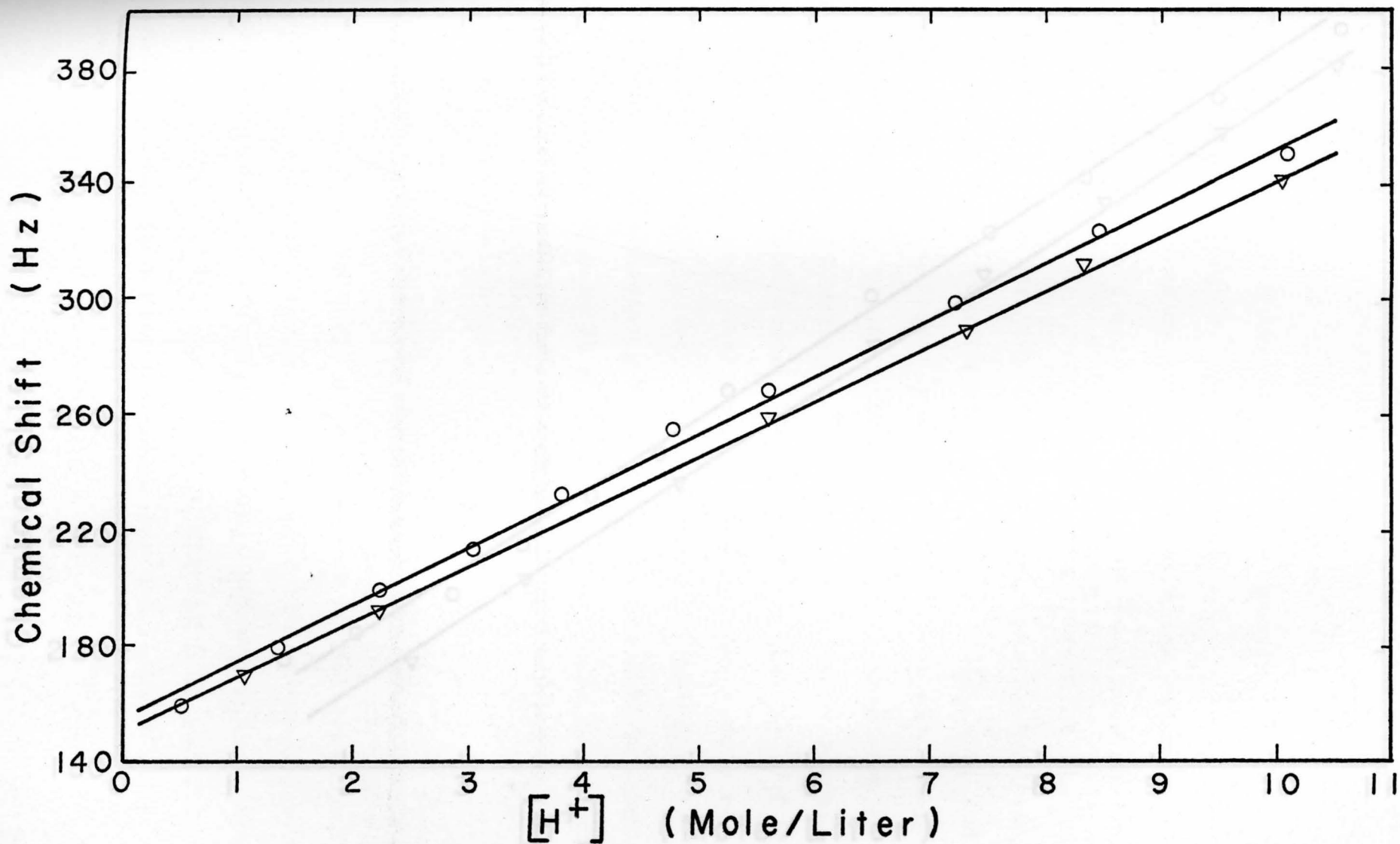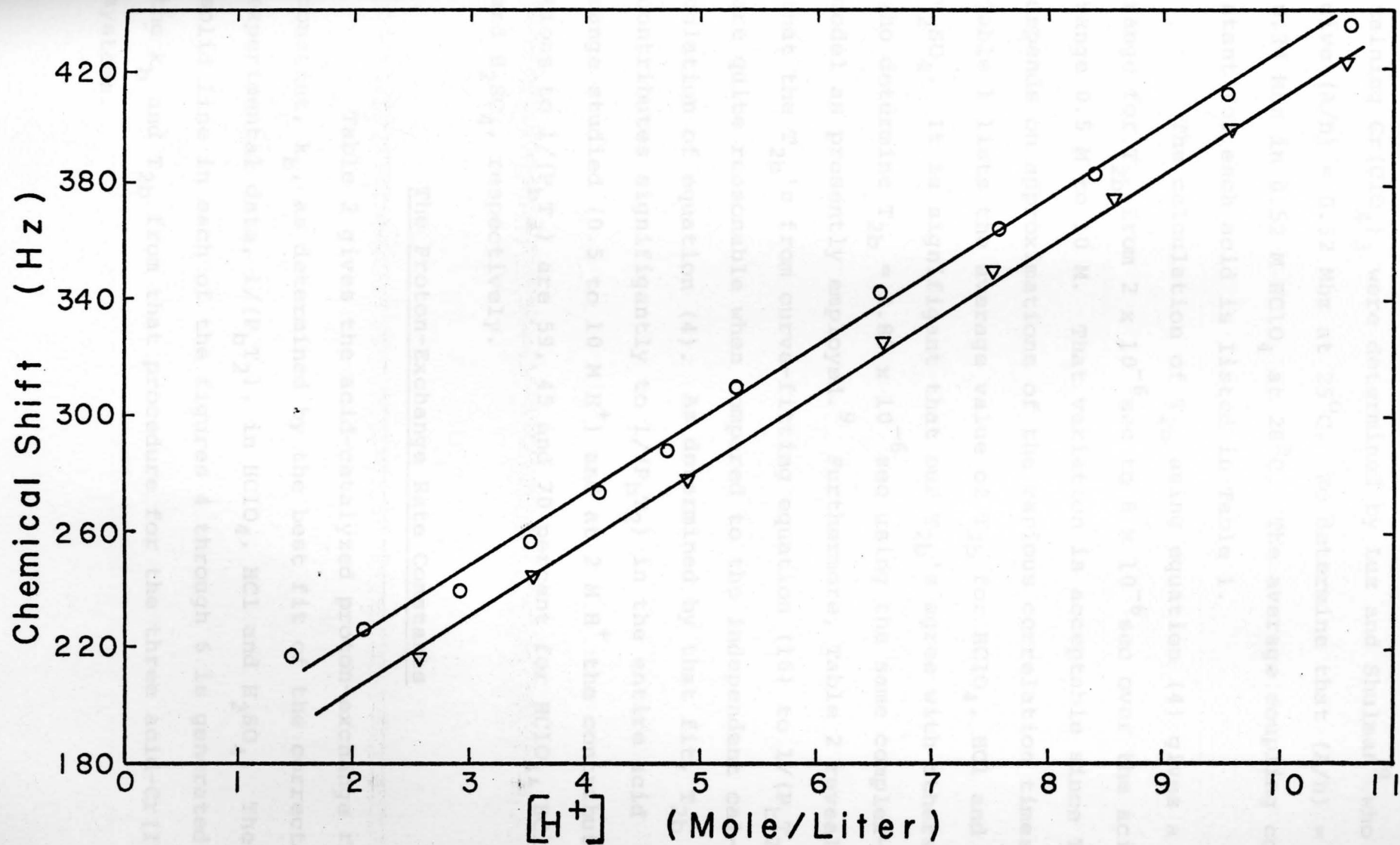
taining $Cr(ClO_4)_3$ were determined by Luz and Shulman[9] who give $(A/h) = 0.32$ Mhz at $25^\circ C$. We determine that $(A/h) = 0.34$ Mhz in 0.52 M $HClO_4$ at $28^\circ C$. The average coupling constant for each acid is listed in Table 1.

The calculation of T_{2b} using equation (4) gives a range for T_{2b} from 2×10^{-6} sec to 8×10^{-6} sec over the acid range 0.5 M to 10 M. That variation is acceptable since T_{2b} depends on approximations of the various correlation times. Table 1 lists the average value of T_{2b} for $HClO_4$, HCl and H_2SO_4. It is signifigant that our T_{2b}'s agree with others who determine $T_{2b} = 3.85 \times 10^{-6}$ sec using the same complex-ion model as presently employed.[9] Furthermore, Table 2 reveals that the T_{2b}'s from curve-fitting equation (16) to $1/(P_bT_2)$ are quite reasonable when compared to the independent calculation of equation (4). As determined by that fit, T_{2b} contributes signifigantly to $1/(P_bT_2)$ in the entire acid range studied (0.5 to 10 M H^+) and at 2 M H^+ the contributions to $1/(P_bT_2)$ are 59, 45 and 70 percent for $HClO_4$, HCl and H_2SO_4, respectively.

The Proton-Exchange Rate Constants

Table 2 gives the acid-catalyzed proton-exchange rate constant, k_b, as determined by the best fit of the corrected experimental data, $1/(P_bT_2)$, in $HClO_4$, HCl and H_2SO_4. The solid line in each of the figures 4 through 6 is generated by the k_b and T_{2b} from that procedure for the three acid-Cr(III) systems.

TABLE 1

AVERAGE VALUES OF (A/h) AND T_{2b}

Acid	(A/h) Mhz	$T_{2b} \times 10^6$ sec
$HClO_4$	0.688	5.78
HCl	0.736	5.92
H_2SO_4	1.73	2.79

TABLE 2

VALUES OF T_{2b} AND k_b FROM CURVE-FITTING EQUATION (16) TO $1/(P_b T_2)$

Acid	$T_{2b} \times 10^6$ sec	$k_b \times 10^{-4}$ sec^{-1}
$HClO_4$	6.02	8.87
HCl	4.63	7.34
H_2SO_4	4.02	189.

The calculation of T_{2b} using equations (4) through (11) gave a range for T_{2b} which is otherwise held constant in the curve-fit procedure. Some variation in T_{2b} is expected based on reasonable approximations of the various correlation times. That variation is not enough to greatly change the quantitative features of our analysis or the rate constants, k_b, derived from the curve-fit procedure.

Specific and General Acid-Catalysis

The determined proton-exchange rate constants for $HClO_4$ and HCl are the same within experimental error. Since those constants are the same and apparently independent of the acid anion, we associate those rate constants with a specific acid-catalyzed proton-exchange. The rate constant for H_2SO_4 is much larger than for $HClO_4$ or HCl. That larger rate constant for H_2SO_4 is identified with a general acid-catalysis of proton-exchange. Specific and general acid-catalysis are observed in the present treatment which includes T_{2b} relaxation in the rate equation, (16). Swift and co-workers,[7] though ignoring T_{2b} in their analysis, note larger proton relaxation rates for acetic acid, H_3PO_4 and H_2SO_4 in Cr(III) solutions compared to the relaxation rate for $HClO_4$. It seems a general acid-catalysis of proton-exchange occurs in solutions of undissociated acids containing Cr(III). The HSO_4^- ion is the undissociated species in H_2SO_4 and is presumably responsible for the general acid-catalysis of proton-exchange in that acid.

Proton Relaxation At High Acid Concentrations

In the present analysis, the high acid concentration limit of $1/(P_bT_2)$ is equal to $1/(T_{2b})$; see equation (16), where the inequality $\tau_b \ll T_{2b}$ holds. That adequately describes the relaxation rates of HCl. The calculations based on our determination of τ_b show at high acid concentrations for $HClO_4$ and H_2SO_4 that T_{2b} controls the relaxation rate equation, (16). Extrapolation of the exchange rates to those high acid concentrations shows that the exchange rates become so rapid that τ_b becomes $\ll T_{2b}$ and $< \tau_s$. At those high acidities τ_s and τ_b contribute to τ_e, and τ_e becomes smaller. A decrease in τ_e leads to a smaller spin-exchange relaxation rate and thus a decrease in the proton relaxation rates, as observed. That argument is based on the reasonable assumption that there is a constant contribution from dipolar relaxation to T_{2b} at all acid concentrations. A decrease in τ_b may not be the only or the most important effect in reduction of $1/(P_bT_2)$ in $HClO_4$ and H_2SO_4. There is electron-spin resonance (ESR) evidence that τ_s is slightly reduced with increasing $HClO_4$ concentration and that τ_s is shorter in H_2SO_4 than $HClO_4$.[31]

Figure 11 shows the fraction of water (P_a) outside the first coordination sphere of the Cr(III) ions as a function of total acid concentration for $HClO_4$, HCl and H_2SO_4. The water concentration decreases more sharply with increasing acid concentration in $HClO_4$ and H_2SO_4 than in HCl for which a
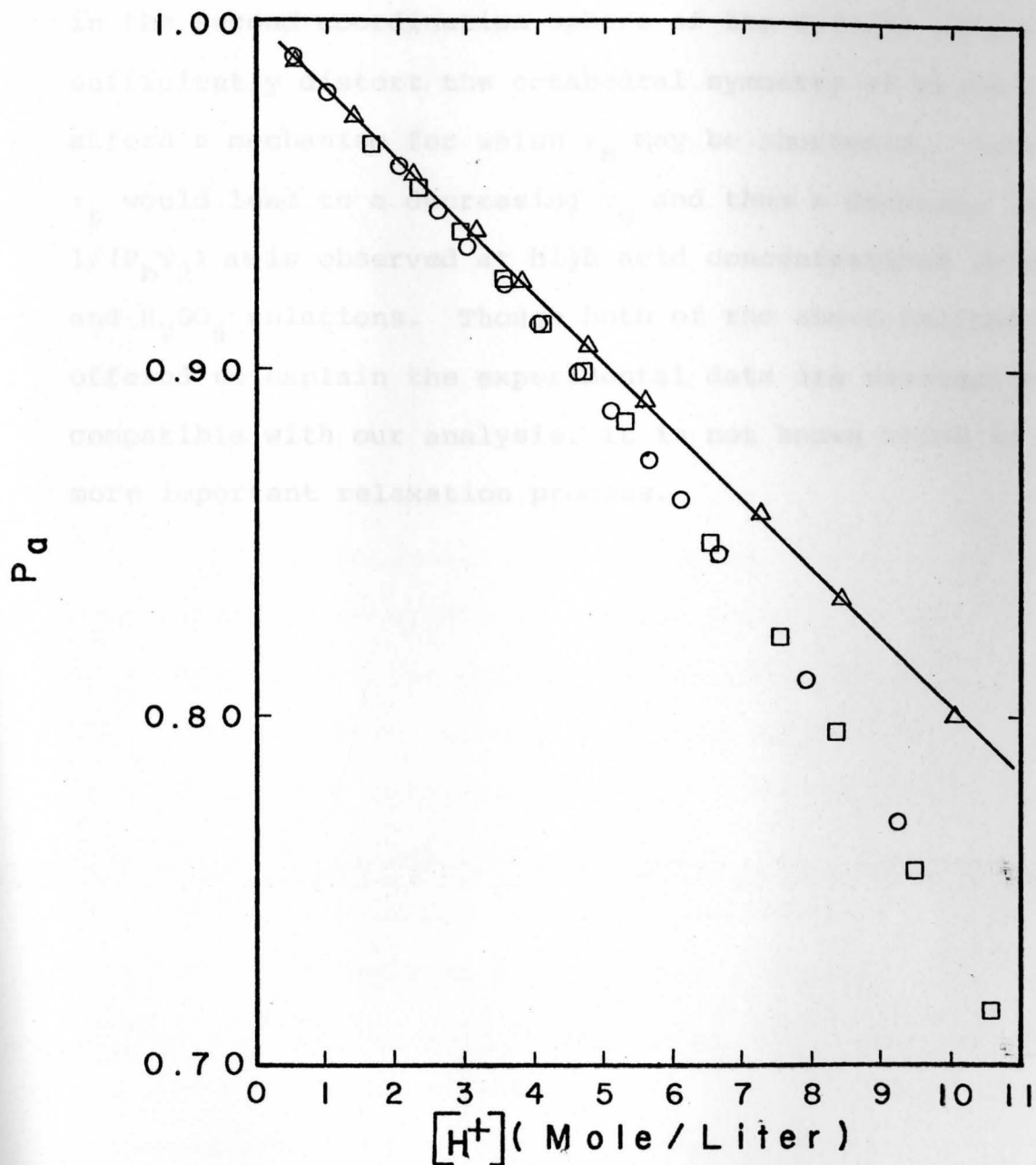
Fig. 11. The fraction of water outside the first coordination sphere (P_a) versus total acid concentration. Circles, triangles and squares represent $HClO_4$, HCl and H_2SO_4, respectively.

linear decrease occurs. That decrease in water concentration (or increase in anion concentration) is compatible with the experimental τ_s data.[31] An increase in anion concentration in the second coordination sphere of the Cr(III) ions should sufficiently distort the octahedral symmetry of those ions to afford a mechanism for which τ_s may be shortened. Decreasing τ_s would lead to a decreasing τ_e and thus a decrease in $1/(P_b T_2)$ as is observed at high acid concentrations in $HClO_4$ and H_2SO_4 solutions. Though both of the above rationales offered to explain the experimental data are reasonable, and compatible with our analysis, it is not known which is the more important relaxation process.

CHAPTER V

SUMMARY AND CONCLUSIONS

The acid dependence of proton relaxation rates in
aqueous $HClO_4$, HCl and H_2SO_4 solutions containing Cr(III)
ions was determined via high-resolution NMR measurments at
60.00 Mhz and 28°C. Four distinct regions of relaxation were
observed and those regions are the low (0.001 to 0.01 M H^+),
intermediate (0.1 to 0.5 M H^+), moderate (0.5 to 6 M H^+) and
high (above 6 M H^+) acid concentrations. No analysis of the
low acid concentration region was attempted where various
hydrolysis species may exist.

Proton relaxation in the region of intermediate acid
concentrations is attributed to the proton-exchange controll-
ed relaxation via the hydrolysis mechanism given by equation
(1). The relaxation rates due to that mechanism were sub-
tracted from the relaxation rates at moderate and high acid
concentrations. That correction takes into account relaxa-
tion rate contributions from other relaxation processes.

In the region of moderate acid concentrations, the
present experiments with excess ClO_4^- and Cl^- anions show
that the proton relaxation rates in that region are due to
a process dependent on the concentration of acid species (or
hydrogen ion) and not anions. The increase in relaxation
rates at moderate acid concentrations is attributed to an in-
crease in exchange rates of protons between the first coor-
dination sphere of the Cr(III) ions and protonated water

molecules in the bulk solution. The net mechanism for that exchange process is given by equation (2).

From our analysis, the corrected proton relaxation rates, $1/(P_bT_2)$, should become constant at the highest acid concentrations studied for $HClO_4$ and H_2SO_4. The relaxation data show that there is in fact a decrease in $1/(P_bT_2)$ at those high acid concentrations. We offer the following rationales to explain that decrease in $1/(P_bT_2)$ for $HClO_4$ and H_2SO_4. Since the relaxation is controlled by T_{2b} at high acidities, for a constant τ_s, τ_b contributes to the spin-exchange correlation time, τ_e, and makes the spin-exchange relaxation rate smaller. A smaller τ_e (and smaller spin-exchange contribution) leads to a decrease in $1/(P_bT_2)$. In addition, τ_s is expected to decrease at high anion concentrations. That process in itself is compatible with the decrease in $1/(P_bT_2)$ at the highest $HClO_4$ and H_2SO_4 concentrations. The data do not warrant a choice between those two rationales, and in fact, both processes may contribute to the observed decrease in the relaxation rates at high concentrations of $HClO_4$ and H_2SO_4.

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