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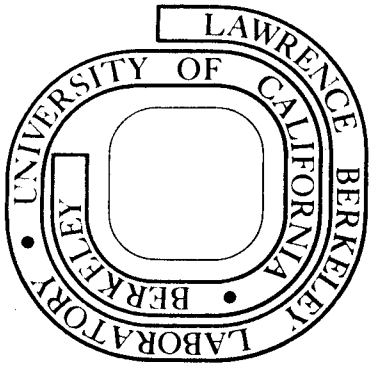

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MUONIUM CHEMISTRY IN LIQUIDS

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Muonium Chemistry in Liquids

ABSTRACT

The muonium atom can properly be considered a light isotope of hydrogen. Its fast chemical reactions in liquids can be studied experimentally by virtue of the depolarizing effect of the hyperfine coupling upon the μ^+ nucleus, an effect which is quenched by rapid chemical reactions. Analytical formulae for the amount of μ^+ depolarization are derived for the simplest case, in which the μ^+ is placed in a diamagnetic compound in a single rate-determining chemical reaction. Data for muonium reacting with iodine in methanol solution are fitted to these formulae to obtain a rate constant of $(14\pm2) \times 10^{10}$ liter/mole-sec, about three times faster than the analogous reaction of the hydrogen atom in similar media.

I. INTRODUCTION

Chemical reactions of hydrogen atoms constitute some of the most elementary processes in physical chemistry. The theory of the absolute rates of such reactions has often been clarified by measurements of "isotope effects", differences in the reactions of the three naturally occurring isotopes of hydrogen: protium, deuterium and tritium.[1-3] The positronium atom has been thought of as an ultralight isotope of hydrogen, but the analogy is poor, since chemical binding of positronium is a qualitatively unique process.[4] We wish to suggest to the chemistry community that there is a "true" light isotope of hydrogen available for study in the form of the muonium atom. The "nucleus" of muonium (Mu) is the positive muon (μ^+), an unstable elementary particle with a lifetime of 2.20 μsec and a mass 0.1126 times that of the porton. Muonium (μ^+e^-) atoms almost always form when positive muons are stopped in matter,[5,6] and usually react soon thereafter to form chemical bonds with molecules of the medium[6]. This paper treats only the simplest type of chemical reaction of the Mu atom, in which a single (rate-determining) step places the μ^+ in a diamagnetic environment.

Sections II and III provide the historical and experimental background for a discussion of the μ^+ depolarization technique. In Section IV, a convenient theoretical structure is developed which relates the chemical reactivity of muonium to several observable effects on the μ^+ polarization. In section V this theory is applied to experimental data for a simple case, and a chemical rate constant is extracted; the result is compared with the corresponding H atom value in Section VI. In Section VII the present and projected status of muonium chemistry studies is evaluated.

II. MUONS, MUONIUM AND DEPOLARIZATION

The muon has enchanted particle physicists for years as the inexplicable "heavy electron," all of whose properties except lifetime and mass are identical to those of electrons (or, in our case, positrons). Indeed, the negatively charged muon acts exactly like a heavy electron, forming "muonic atoms" in which the μ^- orbits tightly about the nucleus, well inside any electronic orbits.[7] Muonic hydrogen, consisting of a proton and a μ^-, chemically resembles a neutron and is a poor analogue of atomic hydrogen in any conventional chemical sense. The positive muon, on the other hand, is in a practical sense much more like a light proton than a heavy positron. Its mass is much closer to that of a proton than to that of a positron, and it does not annihilate with electrons. Furthermore, when it forms an atom, the nucleus is still some 207 times as heavy as the orbiting electron; unlike the positronium atom, which has no proper nucleus, the Mu atom thus has almost exactly the same size and binding energy as the H atom, and to high precision satisfies the Born-Oppenheimer picture of a nearly massless electron adiabatically screening a heavy, quasistationary nucleus. From a chemical point of view, then, muonium differs from hydrogen only in mass and in small corrections for nuclear motion or possible effects of its different nuclear magnetic moment.

The weak interaction is both the source and the demise of muons. Most muons originate in pion (π) decay, along with a muonic neutrino (ν_μ) or antineutrino, depending upon the charge. Here we will be concerned only with positive muons. Thus the reaction in which our μ^+ is born is

$$\pi^+ \rightarrow \mu^+ + \nu_\mu .$$

A striking feature of weak interactions is "parity violation," an example of which is the fact that all neutrinos have negative helicity -- that is, their spins always point in the direction opposite to their momentum. Since the pion has zero spin, the muon's spin must cancel that of the neutrino; simultaneously, the momenta of the muon and neutrino must be equal and opposite in the pion's rest frame; thus the muon from pion decay is forced to have negative helicity as well. This is of great significance experimentally, for it insures that a muon beam coming off in a given direction from pion decay at rest will be nearly 100% polarized opposite to its momentum.

The muon later decays in the reaction

$$\mu^+ \rightarrow e^+ + \nu_e + \bar{\nu}_\mu .$$

Here again the unique helicity of the neutrino leads to a parity violation; in this case the (easily detected) decay positron has a tendancy to come off along the spin of the muon, in a pattern of the form $(1 + a\cos\theta)$, where a is the decay asymmetry and θ is the angle between the μ^+ spin and e^+ emission direction.[6,7] The decay asymmetry has an average value of about 1/3, giving a rather sensitive indication of the degree and direction of polarization of the muon spins. This effect was first observed in 1957,[8] at which time it

was noticed that the degree of polarization of the stopped muons depended strongly upon the stopping medium. Such environment-dependent depolarization was the subject of intermittent but enthusiastic theoretical study in the decade following its first observation, mainly because of a continuing series of experiments using the asymmetric decay of the muon to measure its magnetic moment[9], its anomalous magnetic moment[10], and the hyperfine splitting of muonium[11], in an elegant test of quantum electrodynamics. It was vital to understand the interactions of the stopped muon with its environment in these experiments, and this proved nontrivial.

A series of Russian theoretical papers[12,13] finally pointed the way to a better understanding of the process of "fast" depolarization of positive muons in condensed matter -- the result of brief formation of muonium atoms, in which the hyperfine coupling of the muon with the electron leads to rapid motions of the muon spin. The depolarization is incomplete only because of chemical reactions of the Mu atom which place the muon in a diamagnetic environment, a feature of the process which was early recognized[14] to provide an opportunity for study of the chemistry of muonium.

III. EXPERIMENTAL METHOD

Several approaches have been taken to studying the effects of the stopping medium upon the muon's apparent initial polarization[6]. Each relies upon the asymmetric decay and the coupling of the μ^+ spin to an external magnetic field through its magnetic moment. We will not attempt a comprehensive review here, but only describe briefly the "transverse field" technique used in the measurements to be discussed. For a detailed description of this technique, the reader should consult Refs. [6], [9] and [15].

In this method, a beam of polarized positive muons is stopped in a liquid target in a uniform magnetic field perpendicular to the μ^+ spin polarization direction. After the muons stop and stabilize in a diamagnetic environment, their spin precess in the plane perpendicular to the magnetic field at the free muon Larmor frequency,

$$\omega_\mu = 2\pi \gamma_\mu B, \text{ where } \gamma_\mu = 13.6 \text{ MHz/kG} \quad .$$

Eventually the muon decays, at which time the decay positron is most likely to be detected by a scintillation counter in the plane of precession if the μ^+ spin is pointing in its direction. The e^+ detection probability thus oscillates in time as the muon polarization sweeps past the counter. A high resolution clock is started by the signal in one counter array as the muon enters the target, and stopped by the signal in the positron counter, if and when the decay positron is detected. The resultant measured time intervals are binned into a time histogram which is equivalent to the detection probability as a function of time. This distribution falls off exponentially due to the decay lifetime of the muons, and has a superimposed oscillation whose

phase and amplitude are a measure of the direction and magnitude of the apparent initial muon polarization. An example of such an experimental time histogram is shown in Fig. 1 for muons stopping in CCl_4, where virtually no depolarization occurs.

The quantity measured in this way is called the residual polarization (P_{res}) of the μ^+ in its final (diamagnetic) environment; P_{res} depends markedly upon the chemical characteristics of the stopping medium (as mentioned earlier) due to the reactivity of muonium, the depolarizing agent. It is the role of the theory developed here and in Ref. [16] to relate P_{res} to the concentration of reagent in solution, allowing extraction of bimolecular rate constants for thermal chemical reactions of Mu atoms.

IV. THE MUONIUM MECHANISM OF μ^+ DEPOLARIZATION

Why does P_{res} often differ from unity? Several attempts have been made[16,17,18] to answer this question in a very general way; the goal of this paper is not to supplant those attempts, but to achieve a more concise and lucid explanation for a simple example by using a somewhat different theoretical approach. We exclude radical formation[16] and other complications to the depolarization mechanism, and concentrate on the details of the depolarizing influence of the Mu atom.

As noted earlier, a μ^+ slowing down in matter ultimately captures an electron to form the ground-state muonium atom, μ^+e^- (gas-phase ionization potential $\sim$13.5 eV). It is only after the formation of Mu (typically within $\sim 10^{-10}$ sec of the time of entry of the μ^+ into the target)[6] that effective depolarization of the μ^+ spin begins, due to the combined effect of the hyperfine interaction between μ^+ and e^- spins and the precession of the coupled spin system in an applied magnetic field. Our first task, then, is to describe this motion in some detail.

A. Time Dependence of the μ^+ Spin in Muonium

The polarized muon generally captures an unpolarized electron from the medium[6], so that Mu is formed in two spin states with equal probability: $|A\rangle = |\rightleftarrows\rangle$ and $|B\rangle = |\rightleftarrows\rangle$, where $\rightleftarrows$ refers to the μ^+ spin and $\rightarrow$ or $\leftarrow$ refers to the e^- spin direction. We have used an unusual notation to emphasize that the original spin direction is perpendicular to the magnetic field. Later we will want to use $\hat{z}$, the field direction, as a quantization axis, defining $\hat{x}$ as the initial muon spin direction. First, however, we can equally well describe

any spin state in terms of its total angular momentum along the original spin direction, using the notation $|F,M\rangle_\perp$. In this basis $|A\rangle = |1,+1\rangle_\perp$, which would be a stationary state of the hyperfine Hamiltonian in zero field[6]; but the state describing the other half of the ensemble is a superposition of two zero-field eigenstates: $|B\rangle = (|1,0\rangle_\perp + |0,0\rangle_\perp)/\sqrt{2}$. Thus, even in zero field, it would oscillate between $|\rightleftarrows\rangle$ and $|\leftrightarrows\rangle = (|1,0\rangle_\perp - |0,0\rangle_\perp)/\sqrt{2}$ at the hyperfine frequency $\nu_o = 4463$ MHz, which may be thought of as the frequency of precession of the muon in the field of the electron's magnetic moment. As a result of this fast "hyperfine oscillation," half of the free muonium ensemble appears to be completely depolarized within $\sim 10^{-10}$ sec[6].

In the presence of a finite transverse field, neither of states $|A\rangle$ and $|B\rangle$ is an eigenstate of the Zeeman Hamiltonian[5,6], and the motion of the spins becomes more complex. In order to describe it, we first express $|A\rangle$ and $|B\rangle$ in the basis $|F,M\rangle_\parallel$ labelled according to total angular momentum along the field direction, $\hat{z}$. The basis $|F,M\rangle_\parallel$ is obtained from the basis $|F,M\rangle_\perp$ by a simple rotational transformation of $\pi/2$ about the $\hat{y}$ axis. The resultant expressions for the initial state vectors are

$$|A(0)\rangle = \frac{1}{2}|1,+1\rangle_\parallel - \frac{1}{\sqrt{2}}|1,0\rangle_\parallel + \frac{1}{2}|1,-1\rangle_\parallel \qquad (1a)$$

$$|B(0)\rangle = \frac{1}{2}|1,+1\rangle_\parallel + \frac{1}{\sqrt{2}}|0,0\rangle_\parallel - \frac{1}{2}|1,-1\rangle_\parallel . \qquad (1b)$$

Next we change basis again to express the initial states in terms of the $|m_\mu, m_e\rangle$ states referred to the $\hat{z}$ quantization axis. Again we will

use a mnemonic notation using arrows to denote spin direction. This step is a simple exercise in manipulating Clebsch-Gordan coefficients; the results are

$$|A(0)\rangle = \frac{1}{2}\left(|\Uparrow\uparrow\rangle - |\Uparrow\downarrow\rangle - |\Downarrow\uparrow\rangle + |\Downarrow\downarrow\rangle\right) \tag{2a}$$

$$|B(0)\rangle = \frac{1}{2}\left(|\Uparrow\uparrow\rangle + |\Uparrow\downarrow\rangle - |\Downarrow\uparrow\rangle - |\Downarrow\downarrow\rangle\right) \tag{2b}$$

Finally we expand our states in the Zeeman eigenstates $|i\rangle$ corresponding to energy eigenvalues $E_i = \hbar\omega_i$. These are given in terms of $|m_\mu, m_e\rangle$ by[5,6]

$$|1\rangle = |\Uparrow\uparrow\rangle \tag{3a}$$

$$|2\rangle = s|\Uparrow\downarrow\rangle + c|\Downarrow\uparrow\rangle \tag{3b}$$

$$|3\rangle = |\Downarrow\downarrow\rangle \tag{3c}$$

and

$$|4\rangle = c|\Uparrow\downarrow\rangle - s|\Downarrow\uparrow\rangle \tag{3d}$$

where

$$c = \frac{1}{\sqrt{2}}\left[1 + \frac{x}{\sqrt{1+x^2}}\right]^{1/2}, \tag{4a}$$

$$s = \frac{1}{\sqrt{2}}\left[1 - \frac{x}{\sqrt{1+x^2}}\right]^{1/2}, \tag{4b}$$

and

$$x = (\omega_e + \omega_\mu)/\omega_o = \frac{B}{B_o}.$$

Here, $\omega_o = 2\pi\nu_o$ is the hyperfine frequency in muonium (2.8×10^{10} rad/sec); $\omega_e = (m_e/m_\mu)\omega_\mu = 207\,\omega_\mu$ is the electron Larmor frequency. One can think of $B_o = 1585$ G as the field at the electron due to the muon's magnetic moment. Having made this final transformation of basis, we can write down the time dependence by inspection, since each eigenstate has the simple exponential dependence $\exp(i\omega_i t)$.

The time dependence of the state vectors is thus

$$|A(t)\rangle = \frac{1}{2} e^{i\omega_1 t} |1\rangle - \alpha e^{i\omega_2 t} |2\rangle + \frac{1}{2} e^{i\omega_3 t} |3\rangle + \beta e^{i\omega_4 t} |4\rangle \quad (6a)$$

$$|B(t)\rangle = \frac{1}{2} e^{i\omega_1 t} |1\rangle + \beta e^{i\omega_2 t} |2\rangle + \frac{1}{2} e^{i\omega_3 t} |3\rangle + \alpha e^{i\omega_4 t} |4\rangle \quad (6b)$$

where $\alpha \equiv \frac{(s+c)}{2}$ and $\beta \equiv \frac{(s-c)}{2}$, and the frequencies are given by[5,6,19]

$$\omega_1 = \frac{\omega_o}{4} + \omega_- \quad (7a)$$

$$\omega_2 = -\frac{\omega_o}{4} + \sqrt{\frac{\omega_o^2}{4} + \omega_+^2} \quad (7b)$$

$$\omega_3 = \frac{\omega_o}{4} - \omega_- \quad (7c)$$

$$\omega_4 = -\frac{\omega_o}{4} - \sqrt{\frac{\omega_o^2}{4} + \omega_+^2} \quad (7d)$$

Here $\omega_\pm \equiv \frac{1}{2}(\omega_e \pm \omega_\mu)$.

In order to relate the time dependence of the state vectors to the motion of the muon polarization, we must take the expectation value of the muon's Pauli spin operator: $\vec{P}_\mu = \langle \vec{\sigma}_\mu \rangle$. For this, it is most convenient to work in the basis $|m_\mu, m_e\rangle$, where the effect of the Pauli matrices is simply defined. We therefore reexpress our state vectors once more in that basis, using the relations (3):

$$|A(t)\rangle = \frac{1}{2} e^{i\omega_1 t} |\Uparrow\uparrow\rangle - (\alpha s\, e^{i\omega_2 t} - \beta c\, e^{i\omega_4 t}) |\Uparrow\downarrow\rangle - (\alpha c\, e^{i\omega_2 t} + \beta s\, e^{i\omega_4 t}) |\Downarrow\uparrow\rangle + \frac{1}{2} e^{i\omega_3 t} |\Downarrow\downarrow\rangle \quad (8a)$$

$$|B(t)\rangle = \frac{1}{2} e^{i\omega_1 t} |\Uparrow\uparrow\rangle + (\beta s\, e^{i\omega_2 t} + \alpha c\, e^{i\omega_4 t}) |\Uparrow\downarrow\rangle + (\beta c\, e^{i\omega_2 t} - \alpha s\, e^{i\omega_4 t}) |\Downarrow\uparrow\rangle + \frac{1}{2} e^{i\omega_3 t} |\Downarrow\downarrow\rangle \quad (8b)$$

We are interested only in the muon polarization in the $(\hat{x}\text{-}\hat{y})$ plane perpendicular to the $(\hat{z})$ field direction; it can be shown, in fact, that if there is no initial polarization along the field, none will develop[6,16]. Thus we can pack all the interesting information into a single complex quantity, using the compact notation

$$\tilde{P}_\mu \equiv P_x^\mu + i\, P_y^\mu \,. \tag{9}$$

This "complex muon polarization" can be evaluated from the definition of the expectation value:

$$\begin{aligned}\tilde{P}_\mu &= \frac{1}{2}\ \langle A(t)|(\sigma_x^\mu + i\,\sigma_y^\mu)|A(t)\rangle \\ &+ \frac{1}{2}\ \langle B(t)|(\sigma_x^\mu + i\,\sigma_y^\mu)|B(t)\rangle\end{aligned} \tag{10}$$

The explicit solution of this equation using expressions (8) for $|A(t)\rangle$ and $|B(t)\rangle$ is tedious but straightforward, and yields the following result:

$$\tilde{P}_\mu(t) = \frac{1}{2}[c^2(e^{i\omega_{12}t} + e^{-i\omega_{34}t}) + s^2(e^{i\omega_{23}t} + e^{i\omega_{14}t})] \tag{11}$$

where $\omega_{ij} \equiv \omega_i - \omega_j$, using the definitions in Eq. (7).

This expression can be rewritten via trigonometric identities and previous definitions as follows:

$$\tilde{P}_\mu(t) = e^{i\omega_- t}\cos\left(\frac{\omega_o}{2}t\right)[\cos(\tfrac{\omega_o}{2}+\Omega)t - i\, v\, \sin(\tfrac{\omega_o}{2}+\Omega)t] \tag{12}$$

where

$$v = c^2 - s^2 = \frac{x}{\sqrt{1+x^2}}$$

and

$$\Omega = \frac{1}{2}(\omega_{23} - \omega_{12}) = \frac{\omega_o}{2}(\sqrt{1+x^2} - 1)$$

The weak-field ($x \ll 1$) limit of Eq. (12) is especially interesting, both for conceptualization and because most experiments are performed in this region:

$$\tilde{P}_\mu(t) \underset{x \to 0}{\to} \frac{1}{2} e^{i\omega_- t}[\cos \Omega t + \cos(\omega_o + \Omega)t] \qquad (13)$$

The motion of the muon polarization can thus be factored into two parts: an overall precession in the x-y plane at the free muonium Larmor frequency ω_-, multiplied into two terms whose time dependences are pure modulations. The modulation frequency Ω is relatively slow; in low field it can be approximated by $\Omega = \omega_-^2/\omega_o$. The other modulation frequency, ω_o, is extremely high, well beyond the time resolution of the experimental apparatus.

The low-field time dependence described in Eq. (13) can be examined conveniently from two points of view: in the limit of very early times ("fast" viewpoint), $\cos \Omega t \approx 1$, and the motion consists of a fast "hyperfine oscillation" modulated by slower muonium precession. Experimentally, the positron detector is fixed in the plane of precession, so that we observe only the x-projection (i.e., the real part) of the muon polarization, so precession is not distinguished from modulation. Fig. 2 shows the time dependence we would expect to observe for <u>free</u> muonium in a 100 G applied field if our apparatus had sufficient time resolution. In reality, the hyperfine oscillations are too fast to see (period = 0.225 nsec), and we observe motion only on a longer time scale. This brings us to the "slow" viewpoint, in which $\cos(\omega_o + \Omega)t$ averages to zero and the motion apparently consists of a muonium precession signal modulated by a "beat frequency" Ω. This "two-frequency muonium precession" has been observed in various inert media[20] and is of considerable interest to solid state physics[20]. Here, however,

we will deal directly with this "slow" viewpoint only in the extreme low-field limit (a few gauss) where the "beating" can be neglected and Mu precession treated as a faster version of the μ^+ precession already mentioned.

The "slow" and "fast" viewpoints each relate to a separate type of application to the study of chemical reactions of Mu atoms. In this paper we are concerned mainly with the "fast" viewpoint in its application to Mu chemistry in the liquid phase; but it is worthwhile to comment briefly on the application of the "slow" viewpoint to Mu chemistry in gases.

B. Muonium Precession and Mu Chemistry in Gases

Precession of muonium atoms on the "slow" timescale described above can be observed in a time spectrum analogous to Fig. 1 if the applied field is appropriately reduced (by a factor of about 103) and if free muonium is exceptionally stable (uncombined for $\gtrsim 10^{-7}$ sec) and unaffected by magnetic interactions such as spin exchange. Muonium precession has only recently been observed in a liquid[21], but it is a familiar phenomenon in some solids[6,19,20] and in inert gases[6,22,23]. In such cases a relatively slow chemical reaction of Mu atoms with scavenger molecules is reflected directly in the exponential decay of the amplitude of the Mu precession signal: like the microwave power absorption in an ESR experiment on transient radicals, the amplitude of the muonium precession is proportional to the probability of the active species remaining uncombined at the time of observation. Although experiments with muons are radically different from ESR transient studies, in many ways they are formally identical. With the most convenient timescale between 10^{-7} and 10^{-6} sec, the Mu precession technique is ideally suited for measuring quite fast reaction rates of free Mu atoms in the gas phase.

Normally a time spectrum like that in Fig. 1 is corrected for any constant background and for the exponential decay of the muons themselves, and the remaining "signal" is fitted to the form

$$S(t) = e^{-\lambda t}\, \tilde{P}_{\mu}(t), \tag{14}$$

where $\tilde{P}_{\mu}(t)$ is given by Eq. (13) (usually in its extreme low-field limit) and λ is a pseudo-first-order chemical reaction rate.

By varying the concentration of the scavenger, one can use this technique to study absolute rate constants for reactions of Mu atoms in gases

as functions of temperature and pressure; the results can be compared with H atom reaction properties with no apparent ambiguity. Unfortunately, very little work has been done to date with Mu in gases, due to the former necessity to use high pressure moderators in order to stop an appreciable fraction of muons[22]. This situation has recently been improved by the development of a nearly monochromatic, low-energy muon beam[24]. The first few measurements using this type of beam have produced exciting results, which will be reported separately[25]. Extensive studies in gases near atmospheric pressure are now being planned.

Despite the tantalizing but sparse early results[22,23] and the inherent advantages of the gas phase for studying the chemical reactions of muonium, liquids remain the most convenient media for such experiments; for this and historical reasons, the overwhelming majority of data on Mu chemistry have been taken in liquids. In this paper, therefore, we concentrate on the theoretical and experimental treatment of liquid-phase Mu chemistry.

C. Residual Polarization and Mu Chemistry in Liquids

The fundamental distinction between studies of Mu chemistry in gases and liquids is that in liquids the muonium precession signal itself is rarely seen, due to the rapidity of chemical reactions in the denser liquids. In all but the most carefully prepared inert solutions[21], no Mu atoms remain uncombined at observation times (typically ~50 nsec after the muon thermalizes), and we can only detect the much slower precession of the μ^+ itself, which by this time is incorporated into a diamagnetic molecule and is magnetically free. The amplitude and phase of this precession, extrapolated back to t = 0 (the time at which muonium is initially formed), constitute all the available information in the form of the residual muon polarization, P_{res}. Thus, ironically, it is via experimental observation of μ^+ precession on the extremely "long" time scale of microseconds that we obtain information about the reactions of Mu atoms on the "fast" time scale of a few hyperfine periods ($\sim 10^{-9}$ sec or less).

Since each Mu atom reacts chemically at a different time, each muon "emerges" from the muonium environment with a different spin direction, so that the residual polarization is generally reduced and rotated with respect to the initial muon polarization. We will keep account of both the magnitude and direction of P_{res} by letting it be a complex quantity, in keeping with the foregoing formulation of $\tilde{P}_\mu(t)$: the real part is the polarization component along $\hat{x}$, the original spin direction, and the imaginary part is the component in the $\hat{y}$ direction, perpendicular to both $\hat{x}$ and the external field. The observable precession signal is the real part of P(t), the exact (complex) time dependent polarization of the entire muon ensemble. As mentioned earlier,

observation of this signal begins long after the rapid motions of the muon spin in muonium have settled down to the slow precession of the free muon spin in a diamagnetic environment; thus, on the time scale of the chemical interactions of the Mu atom, the observations take place at $t \to \infty$, and we can define the observable quantity as

$$P_{obs}(t) = \lim_{t \to \infty} \text{Re } P(t). \tag{15}$$

The experimental precession signal is fitted to the form

$$P_{obs}(t) = |P_{res}| \cos(\omega_\mu t + \phi), \tag{16}$$

which is equivalent to

$$P_{obs}(t) = \text{Re}\{P_{res}\, e^{i\omega_\mu t}\},$$

with the definition

$$\tan\phi = \text{Im}(P_{res})/\text{Re}(P_{res}). \tag{17}$$

Thus we can derive P_{res} from P(t) by dividing out the free μ^+ precession as if it had started at t = 0, and taking the limit:

$$P_{res} = \lim_{t \to \infty} P(t) \exp(-i\omega_\mu t). \tag{18}$$

The theoretical task is thus reduced to a calculation of P(t).

1. Mu Reaction Kinetics and the Ensemble Polarization

Treatment of the reaction kinetics of Mu atoms in the ensemble of events comprising the experimental sample is greatly simplified by the fact that there is literally one Mu atom at a time in the target. Even over an entire run, only about 10^8 muons are stopped in the target, compared to typical reagent concentrations of 10^{19} cm^{-3}. This is as far as one can get from a "steady state" condition in chemical kinetics, and permits the righteous use of pseudo-first-order kinetics in treating the Mu reaction rate λ as a constant proportional to the reagent concentration [X]. The constant of proportionality is just the bimolecular rate constant, k:

$$\lambda = k[X]. \tag{19}$$

Certain qualitative effects of λ upon P_{res} are obvious: if λ is much faster than the hyperfine frequency in muonium ($4.463 \times 10^9 sec^{-1}$) the muon spins will not have moved appreciably before the Mu reacts, and there is no depolarization - - $P_{res} = 1$. Conversely, if λ is much slower than the precession frequency of Mu in the external field, reactions at randomly distributed times will leave the muons with randomly oriented spins, causing complete depolarization due to "dephasing" - - $P_{res} = 0$. This sets a practical lower limit of $\sim 10^8$ ℓ/mole-sec for rate constants which can be studied by this method. For reaction rates in the range $\omega_- < \lambda < \omega_o$, we must proceed with a calculation of P(t) in order to obtain P_{res} from Eq. [18].

The ensemble muon polarization at time t is formally given by

$$P(t) = \sum_q p_q P_q(t), \tag{20}$$

where the label "q" represents the "fate" of a fraction p_q of the muon ensemble, and $P_q(t)$ is the polarization at time t of that fraction. There are only two types of "fates" of interest here: muons still in uncombined Mu atoms at time t, and muons in diamagnetic products following reaction at times $t' < t$. Since the probability of reaction per unit time, λ, is constant, the probability of a Mu atom remaining free until time t is $e^{-\lambda t}$, and the probability of a reaction within dt' of time t' is $\lambda e^{-\lambda t'} dt'$. Thus the still uncombined Mu atoms give a contribution to P(t) of

$$P_1(t) = e^{-\lambda t} \tilde{P}_\mu(t) \ , \tag{21}$$

while those muons which evolve in Mu until time t', react, and then precess as free muons until time t, give a contribution

$$dP_2(t',t) = \lambda e^{-\lambda t'} \tilde{P}_\mu(t') e^{i\omega_\mu (t-t')} dt' .$$

Recall that $\tilde{P}_\mu(t)$ is the complex μ^+ polarization in free Mu atoms (Eq. 11). The latter class of contributions can be summed over $t' < t$ to give the net contribution from all such "fates,"

$$P_2(t) = \int_o^t \lambda e^{-\lambda t'} \tilde{P}_\mu(t') e^{i\omega_\mu (t-t')} dt' . \tag{22}$$

In the limit of "$t \to \infty$" (i.e., for $\lambda t >> 1$), $P_1(t) \to 0$ (i.e., all the Mu atoms eventually react); meanwhile, the term $\exp(-i\omega_\mu t)$ in the definition of P_{res} (Eq. 18) cancels the term $e^{i\omega_\mu t}$ under the integral in $P_2(t)$. Thus Eq. (18) takes the form

$$P_{res} = \lambda \int_o^\infty \tilde{P}_\mu(t') \exp[-(\lambda + i\omega_\mu) t'] dt' . \tag{23}$$

2. An Analytic Expression for the Residual Polarization

Substituting Eq. (11) into Eq. (23), and dropping the prime on t', we have

$$P_{res} = \frac{\lambda}{2}\int_0^\infty e^{-(\lambda+i\omega_\mu)t}\left[c^2(e^{i\omega_{12}t} + e^{-i\omega_{34}t}) + s^2(e^{i\omega_{23}t} + e^{i\omega_{14}t})\right]dt$$

$$= \frac{\lambda}{2}\left\{\frac{c^2}{\lambda+i(\omega_\mu-\omega_{12})} + \frac{c^2}{\lambda+i(\omega_\mu+\omega_{34})} + \frac{s^2}{\lambda+i(\omega_\mu-\omega_{23})} + \frac{s^2}{\lambda+i(\omega_\mu-\omega_{14})}\right\} \quad (24)$$

The experimentally measured quantities are $|P_{res}|$ and ϕ, where $P_{res} = |P_{res}|\, e^{i\phi}$ [recall Eqs. (16) and (17)]. Qualitatively, ϕ is the average angle through which the free Mu atom precesses in the external field before it reacts. Measurements of this parameter are vital in proving the validity of the model for μ^+ depolarization[6,25,26].

3. Qualitative Features of the Residual Polarization

Equation (24) is somewhat unwieldy in its general form. By making some approximations we can make certain physical aspects clear in several limiting cases. Since most experiments are carried out in low field, we consider only the low-field case, $x << 1$, for which $c \approx s \approx \frac{1}{\sqrt{2}}$, $\omega_{12} \approx \omega_{23} \approx \omega_-$ and $\omega_{14} \approx \omega_{34} \approx \omega_o$. Since $\omega_o >> \omega_- \approx 103\omega_\mu$, we can neglect ω_μ and approximate Eq. (24) by

$$P_{res}\ (x << 1) \approx \frac{\lambda}{2}\left\{\frac{1}{\lambda - i\omega_-} + \frac{\lambda}{\lambda^2 + \omega_o^2}\right\}. \quad (25)$$

For the case of an ultrafast reaction ($\lambda >> \omega_o >> \omega_-$), we obtain the expected result, $P_{res} \rightarrow \frac{\lambda}{2}\left(\frac{1}{\lambda} + \frac{\lambda}{\lambda^2}\right) = 1$. That is, if all the Mu atoms react at $t \approx 0$, the polarization has no chance to change from its initial value (see Fig. 2). Over most of the convenient range of reagent concentrations, reactions are slow ($\lambda << \omega_o$), and we obtain

$$P_{res} \approx \frac{\lambda}{2}\left(\frac{1}{\lambda - i\omega_-}\right) = \frac{1}{2}\left(\frac{1}{1 + \omega_-^2\tau^2}\right)\left(1 + i\omega_-\tau\right), \qquad (26)$$

where

$$\tau \equiv \frac{1}{\lambda}$$

is the mean chemical lifetime of a thermal Mu atom. This expression (26) in turn has two interesting limits. First, for $\omega_-\tau << 1$ (reaction faster than Mu precession),

$$P_{res} \rightarrow \frac{1}{2}(1 + i\omega_-\tau), \quad \text{or}$$

$$|P_{res}| \rightarrow \frac{1}{2} \qquad \text{and } \phi \rightarrow \omega_-\tau$$

That is, the hyperfine oscillations average the muon polarization to $\frac{1}{2}$, and the muons get a chance to precess through a small average angle $\omega_-\tau$ while in muonium. This is in keeping with the qualitative interpretation of ϕ, as mentioned earlier. A second limiting situation is $\omega_-\tau >> 1$ (reaction slower than Mu precession), for which

$$P_{res} \rightarrow \frac{i}{2\omega_-\tau}, \qquad \text{or}$$

$$|P_{res}| \rightarrow 0 \qquad \text{and } \phi \rightarrow \pi/2$$

In this case, Mu precession has averaged the polarization almost to zero, while the contribution from the first half-period of precession still dominates the average phase angle.

All these features are apparent in the unlabelled set of curves shown in Fig.3, representing the exact dependence of $|P_{res}|$ and ϕ upon τ for an external field of 100 gauss. Particularly characteristic is the "plateau" in $|P_{res}|$ for intermediate reaction rates, $\omega_o >> \frac{1}{\tau} >> \omega_-$, where the polarization amplitude is averaged to $\frac{1}{2}$ by the hyperfine oscillations, but is not yet appreciably affected by Mu precession. The curves labelled "h=0.5" are discussed below.

4. Hot - Atom Reactions

So far we have discussed only the fates of those muons which thermalize in free Mu atoms. There is also a significant probability that newly-formed Mu atoms will participate in "hot-atom" reactions while still epithermal ($\sim$1 - 10 eV). These reactions are quite interesting in their own right,[6,27] but will be treated purely phenomenologically here. Since such reactions occur at $t \approx o$ [the slowing down time is $\sim 10^{-12}$ sec[6]], there is no opportunity for these muons to be depolarized. The fraction h of muons undergoing hot-atom reactions thus contributes a constant unrotated component h to the overall residual polarization, while the contribution [Eq. (24)] from thermal reactions of Mu atoms must be multiplied by a factor (1 - h) representing the remaining fraction of the ensemble. Thus

$$P_{res}[\text{overall}] = h + (1-h)\, P_{res}[\text{Eq.(24)}]. \qquad (27)$$

For the typical situation of very dilute reagents in solution, hot-atom

reactions are assumed[16,25] to take place only with solvent molecules; thus h is a constant independent of τ.

5. Predicted Dependence of P_{res} upon Reagent Concentration

The labelled curves in Fig. 3 represent the overall residual polarization at 100 G for a hot-atom fraction h = 0.5. Note that ϕ now has a "dip" instead of a "plain", due to the addition of a constant unrotated component to the dwindling rotated component for large τ.

Together with the "plateau" effect in $|P_{res}|$, this "phase dip" is a ubiquitous characteristic of the muonium depolarization mechanism. Both are most visible in low field ($B<<B_o=1585G$), as can be seen from Fig. 4, in which the τ dependence has been converted to an explicit dependence upon reagent concentration [X], using Eq. (19) and assuming a rate constant of $k = 10^{10}$ ℓ/mole-sec, with a hot-atom fraction h = 0.5. As the field increases, ω_{Mu} speeds up, bringing the time scale of depolarization-via-Mu-precession closer to that of depolarization-via-hyperfine-oscillations, and thus narrowing the "plateau" region separating the two effects. Finally, for $B>B_o$, the external field begins to "break" the muon's "contact grip" on the electron's spin, and the Mu atom no longer precesses simply as a spin-1 system whose magnetic moment is dominated by that of the electron. Under the influence of the complicated motions which result (recall Eq. [11]), P_{res} loses both the "plateau" and the large "phase dip" which were characteristic of "slow" Mu precession. In an experimental investigation, measured values of $|P_{res}|$ and ϕ for various reagent concentrations are fitted to curves of this sort to extract values for h and k. We turn now to a discussion of such an experimental fit.

V. EXPERIMENTAL RESULTS: Mu + I_2

Measurements of μ^+ depolarization at the 184 In. Cyclotron in Berkeley have included three experimental curves of P_{res} ($[I_2]$) in methanol solutions at 103G (Fig.5), 1000G (Fig.6), and 4500G (Fig.7). Methanol was chosen as a solvent because of the high solubility of I_2 in CH_3OH and the apparent lack of a fast thermal reaction of Mu with CH_3OH. [26] No phase data are shown for the higher fields of 1000 and 4500 G because phase information is not very meaningful at these fields where $\omega \gtrsim \omega_o$. The curves drawn through the points are the best fits to Eq. (27) using Eqs. (24) and (17) and $\lambda = k[I_2]$. The results are listed in Table I; they are essentially identical to those obtained earlier[26] by fitting the same data with the more general theory derived in Ref. [16] by diagonalizing the spin density matrix. A weighted average gives $k=(14\pm2) \times 10^{10}$ ℓ/mole sec.

The probability h of hot-atom reaction of Mu^* with CH_3OH is treated as an empirical parameter in this discussion. However, the value of $(14\pm2) \times 10^{10}$ ℓ/mole-sec for k(Mu + I_2) calls for physical interpretation here. The thermal reaction involved is presumed to be

$$Mu + I_2 \rightarrow MuI + I, \qquad (28)$$

in perfect analogy to the well-known reaction for the H atom, for which the rate constant in aqueous solution is reported [28] to be 4×10^{10} ℓ/mole sec. If we overlook the different solvents, we can say that Mu reacts with I_2 in solution about 3 times as fast as does H.

VI. COMPARISON OF Mu and H RATE CONSTANTS

As stated earlier, muonium and hydrogen are "isotopes" of the simplest possible atom, chemically similar in every respect except for their masses, which differ by a factor of 8.84. A detailed comparison of chemical reaction rates for Mu and H thus provides a unique opportunity for testing models of dynamic isotope effects in chemical kinetics. Such comparisons between H and D (deuterium) have already revealed differences as large as a factor of 5 in some cases.[2,3] These results are considered indicative of a quantum-mechanical tunneling contribution to the rate.[3] The much lighter Mu atom can be expected to display marked tunneling behavior, further elucidating the role of that process in chemical kinetics. Comparisons of H and T (tritium) have also been made, but since T usually starts out as a hot atom,[1] these studies are somewhat more difficult to interpret.

A. The Kinetic Isotope Effect in Gases

In gases (at normal pressures) the mean free path of a Mu atom is many molecular radii, and the concepts of collison rates and cross sections are well defined. Thus the rate constant for a specific relative velocity of the reagents is proportional to that velocity and the cross section:

$$k(v) \sim v\,\sigma(v) \qquad (29)$$

where σ is generally a function of velocity due to dynamic effects such as activiation energies. Of course, in a thermal process we observe the average

of k(v) over the thermal velocity distribution,

$$k \equiv \langle k(v) \rangle_v \sim \bar{v}\, \sigma_{eff} \,, \qquad (30)$$

where $\bar{v}$ is the mean thermal velocity and σ_{eff} is an effective average cross section. If we temporarily neglect dynamic effects in σ, we can treat σ_{eff} as a constant geometrical cross section. Although this "hard sphere" collision model is clearly inaccurate, it is useful for didatic purposes. For example, the rate constant is then proportional to the mean velocity, $\bar{v}$; if we neglect the motion of the (heavy) scavenger molecules, $\bar{v}$ is in turn proportional to $m^{-1/2}$, where m is the mass of Mu or H. This produces a trivial kinetic enhancement factor of $\sqrt{\frac{m_H}{m_{Mu}}} \approx 3$ in the ratio of the reaction rates, $\frac{k_{Mu}}{k_H}$. This we refer to as the "kinetic isotope effect." Any additional differences in k_{Mu} and k_H are then probably due to "dynamic isotope effects" related to σ_{eff}; recent experiments in the gas phase show tentative evidence for such effects.[23]

B. Isotope Effects in Liquids

In solution, the kinetic situation is much more complicated. Here, each reagent molecule (or atom) is continually surrounded by a "cage" of solvent molecules which severely restrict its thermal motion.[29] When reactants do meet, it is often in a prolonged encounter with high probability of reaction; diffusion itself is then the rate-limiting process. Such reactions are referred to as diffusion controlled (DC). Since diffusion in liquids is mainly by "squeezing" and "tumbling", such rates are largely determined by the geometrical properties of solvent and reagent molecules, with little or no specific mass dependence. Indeed, in the usual formulation,[29,30] DC rate constants (k_{DC}) depend only on the molecular radii and

diffusion coefficients in the media; hence k_{DC} of Mu and H would be identical in the same media. Making the crude approximation that the aqueous diffusion coefficient of the H atom is the same as that of the hydrated electron [31], 5×10^{-5} cm^2/sec, yields a calculated value [29,30] of $k_{DC} \sim 2 \times 10^{10}$ ℓ/mole-sec for the reaction of H + I_2 in water. The reported value [28] is 4×10^{10} ℓ/mole-sec. Since the latter value is evidently just about the fastest rate constant measured for H atoms in aqueous media, [32] it seems reasonable to state that k_{DC} for H atoms in water must be $< 10^{11}$ ℓ/mole-sec.

What about the Mu atom? Many of the measured rates for Mu are at or above this limit, in a variety of solvents.[26] Our calculations (Table I and previous discussion) yield a value of $k=(14\pm2)\times 10^{10}$ ℓ/mole-sec for the reaction of Mu with I_2 in methanol. Since the room-temperature viscosity of methanol is only about half that of water, one might naively expect k_{DC} of Mu (or H) in methanol to be $\sim 8 \times 10^{10}$ ℓ/mole-sec, which is at least consistent with our experimental results. However, activation energies for thermal reactions of the Mu atom have not yet been measured, so we do not know whether such reactions are likely to be diffusion controlled or not.

Is it really reasonable to expect k_{DC} to be the same for Mu and H in the same media? Probably not! There may well be a specific mass dependence, which would be reflected in a "solvent activation energy".[33] In water, for example, a solvation energy of ~4.5 kcals/mole is usually ascribed to the H atom;[34] this value is only slightly larger than the expected value of E_a for diffusion controlled reactions in most solvents.[29,32] In general, one can interpret the solvent activation energy in terms of a potential well of depth $\sim E_a$ and corresponding Boltzmann factor $\exp(-E_a/RT)$. The rate of diffusion thus represents the ease with which the atom is able to escape over (or tunnel through) a periodic potential lattice. Since the zero-point energy of the Mu atom in this potential well would be three times higher than that of the H

atom in the same well, there could be some enhancement in k_{DC} for Mu due to a smaller E_a. It is unlikely that this effect could be much more than a factor of 2 or 3; it could, however, explain the small differences in rate observed for the reactions of H + I_2 and Mu + I_2.

On the other hand, tunneling contributions to the rate will clearly be more important for the much lighter Mu atom than for H. Is the enhanced rate for Mu + I_2 the result of tunneling through the solvent activation activation barrier? If so, then the DC rates would generally depend very strongly upon the solvent media and might even approach the collision frequency of gas-phase kinetics in some cases. Indeed, we have previously reported[26] some Mu atom rates which are orders of magnitude faster than the corresponding H atom rates. At the moment , the role which tunneling plays in the chemical reactions of Mu is only tantalizingly apparent.

VII. CONCLUDING REMARKS

The experimental results and theoretical interpretations presented here are, we believe, the best evidence to date that studies of muonium chemistry in liquids are a practical and exciting reality. We chose the simplest known example in order to emphasize this point; studies of more complicated experimental situations,[26] and the extended theory to treat them,[6,16] depend for their viability upon the proven validity of the simplest case. While these results indicate the reliability of the method, more measurements (e.g., of temperature-and solvent - dependence of the reaction rates) are needed to firmly cement the foundations of muonium chemistry. Such studies are being undertaken at several meson-producing laboratories, in both liquids and gases, and in the next few years this field should be placed on a much firmer footing.

The most exciting goal of these investigations is a better understanding of the physical processes involved in the chemical reactions of the simplest atom - - in particular, a clarification of the role of tunneling. This goal depends upon the availability of precise values for the absolute reaction rates of H and D atoms -- which in some cases are still unreliable. Progress in this field must thus proceed apace with further careful investigations of H atom chemistry.

It is also possible that the μ^+ depolarization technique will find more direct applications in the field of H atom chemistry. For instance, studies of Mu chemistry in liquids are strongly analogous to H atom investigations in which the H atoms are commonly produced by radiolysis

of hydrogenic materials (e.g., water) and followed via their ESR signal.[35] Despite the relative scarcity of muons, the μ^+ depolarization technique has some distinct advantages: first, Mu atoms can be introduced into any medium, including proton-free liquids or highly alkaline solutions in which the OH^- ions seriously quench H atom production by radiolysis; second, since the Mu atoms are introduced from outside with minimal disturbance of the medium, one can conveniently study reactions of Mu with substances which are extremely susceptible to radiation damage from radiolysis; third, with literally one Mu atom in the sample at a time, the various recombination problems which plague most H atom studies are nonexistent. Thus there may be many interesting reactions which can only be studied by muonium methods, and in almost every situation the reactions of Mu will be less complicated than those of H by interference from competing chemical processes. It seems quite likely, therefore, that muonium chemistry studies will soon become a valuable addition to the experimental methods of fundamental physical chemistry.

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Table I: Best fits to proper Muonium mechanism for Mu + I_2 in methanol

Field (gauss)	Hot-atom fraction[(a)]	$k_M \times 10^{-10}$ (1 $mole^{-1}$ sec^{-1})
103	0.54 ± .015	13.1 ± 1.6
1000	0.52 ± .025	15.0 ± 2.4
4500	0.52 ± .02	13.6 ± 1.5

(a) See discussion in text

FIGURE CAPTIONS

Fig. 1. Typical experimental time spectrum showing μ^+ precession in 100 G external field. Data is grouped into 10 nsec bins for graphical clarity; 0.5 nsec bins were used for fitting.

Fig. 2. Time evolution of real part of muon polarization in free muonium in a 100 G transverse field. The fast oscillations at the hyperfine frequency, ω_o, are not directly observable experimentally.

Fig. 3. Theoretical dependence of magnitude and phase of residual muon polarization upon chemical lifetime of free Mu atoms, for 100 G external field. Unlabelled curves represent the situation with no hot atom reactions (h=0).

Fig. 4. Theoretical dependence of residual polarization upon reagent concentration when the rate constant is 10^{10} ℓ/mole-sec. In each case the hot atom fraction h=0.5. See text for discussion of B_o=1585G.

Fig. 5. Experimental data and best fit for dependence of residual polarization upon concentration of I_2 in methanol at 103 gauss. Leftmost points are for pure methanol (P_{res}=h) and are therefore actually infinitely far off-scale to the left.

Fig. 6. Experimental data and best fit for P_{res} as a function of I_2 concentration in methanol at 1000 G. Leftmost point is again for pure methanol and represents the pure hot atom fraction, h.

Fig. 7. Experimental data and best fit for P_{res} as a function of I_2 concentration in methanol at 4500 G. Leftmost point is for pure methanol.

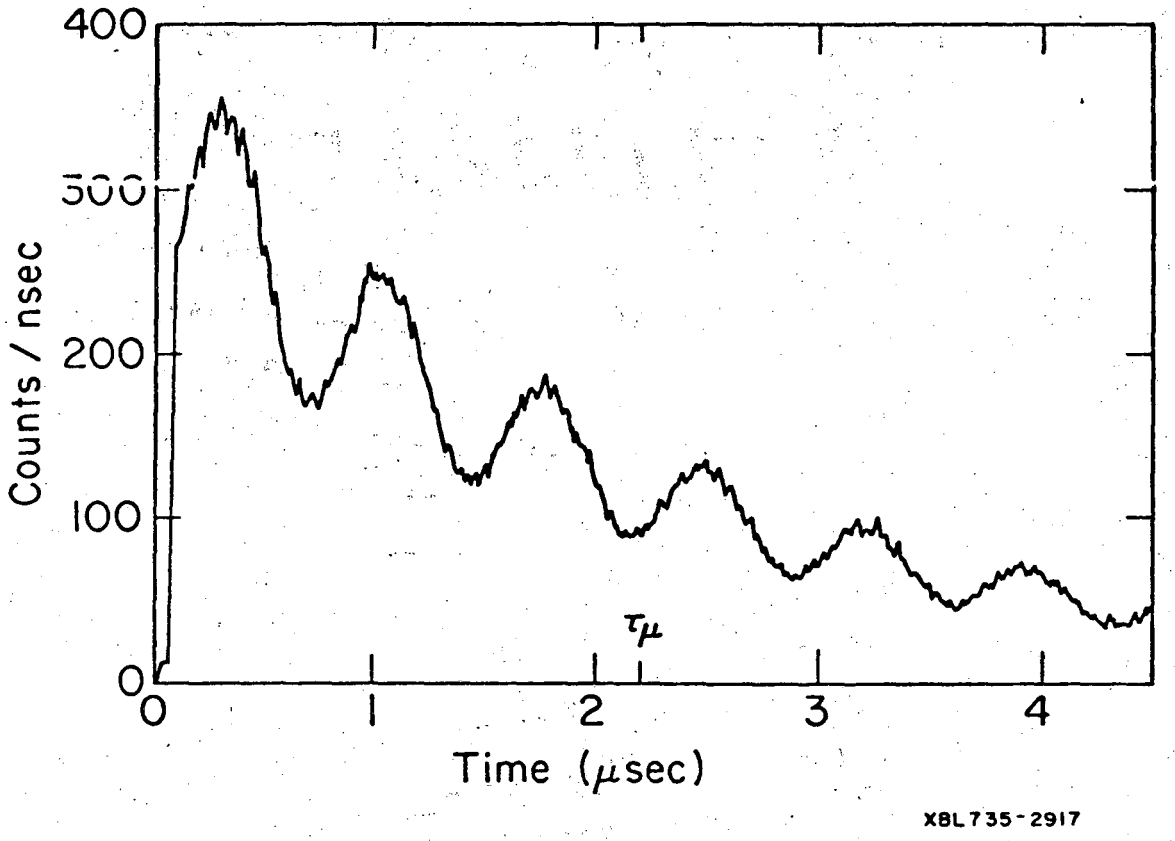
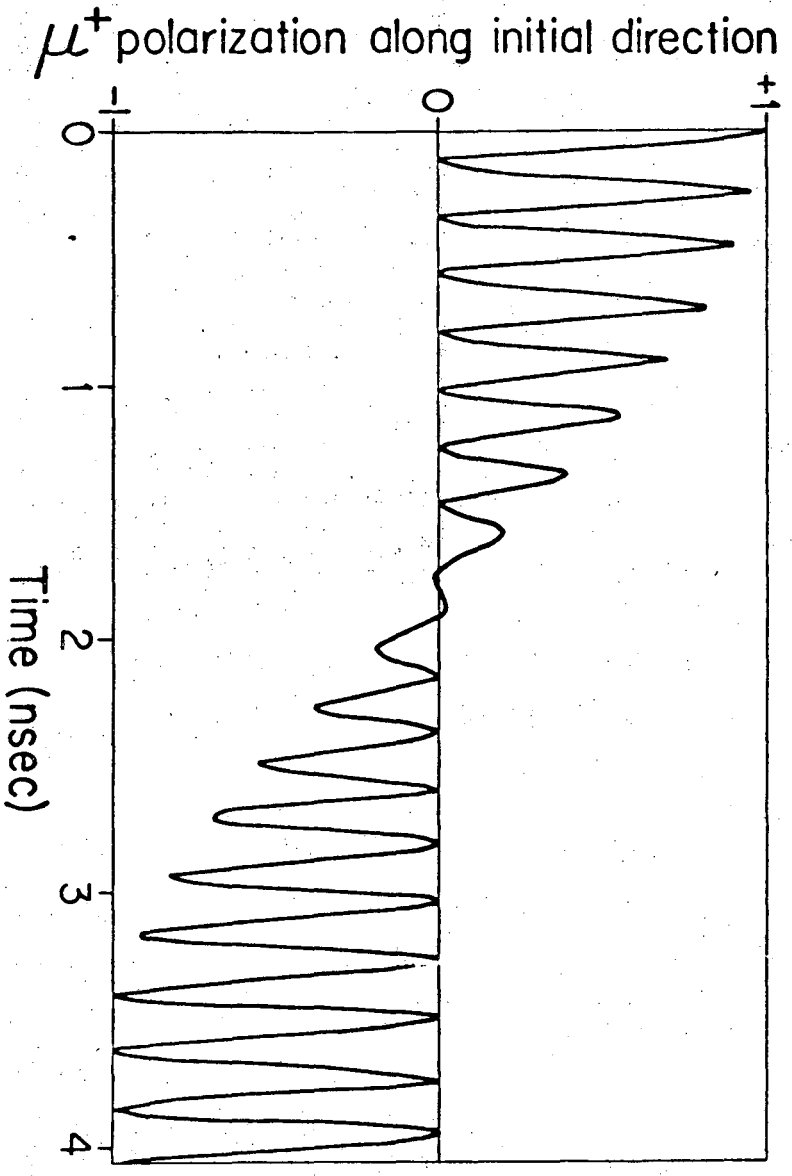


Fig. 1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0
+1
0
1
2
3
4
Time (nsec)

Fig. 2

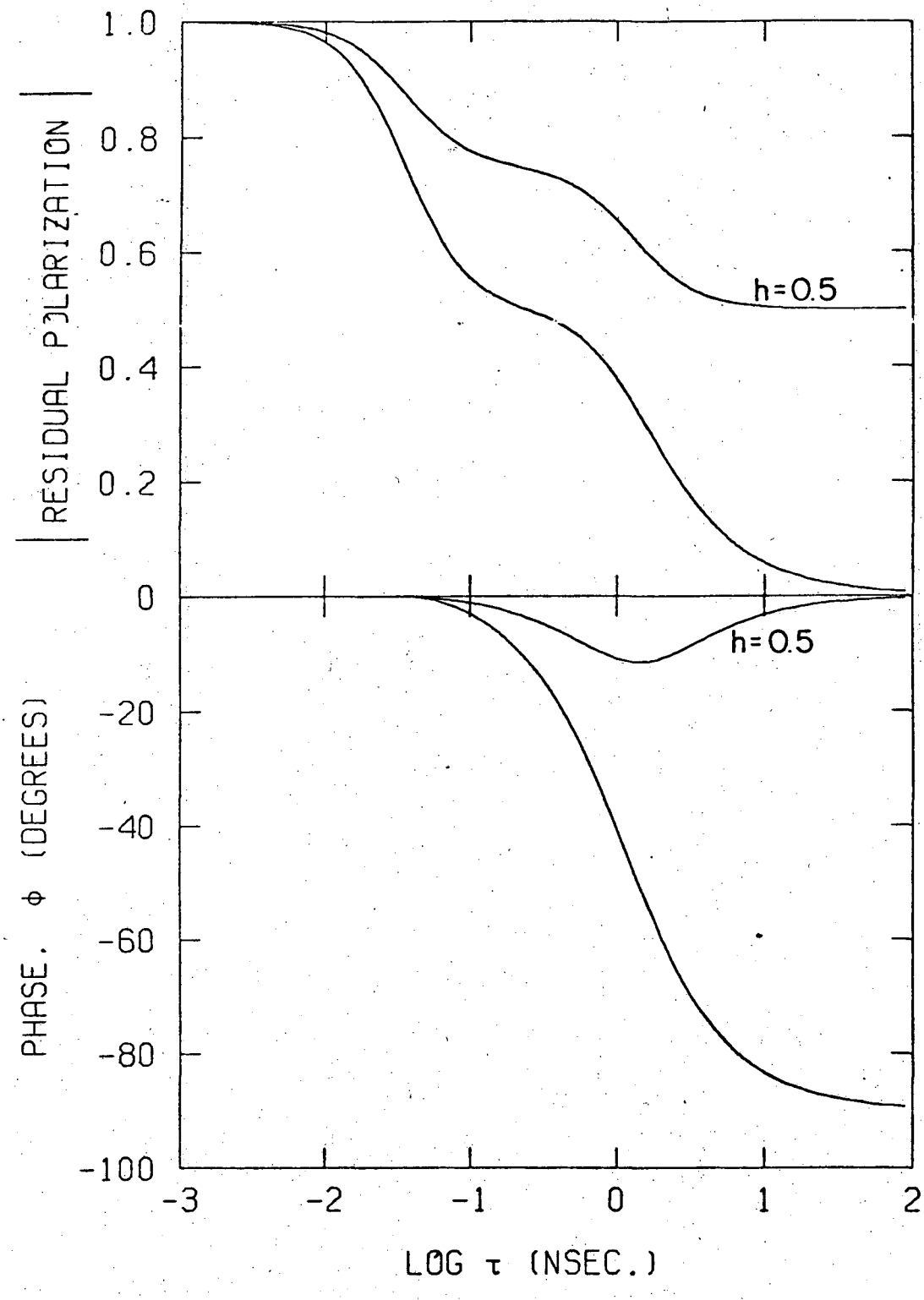
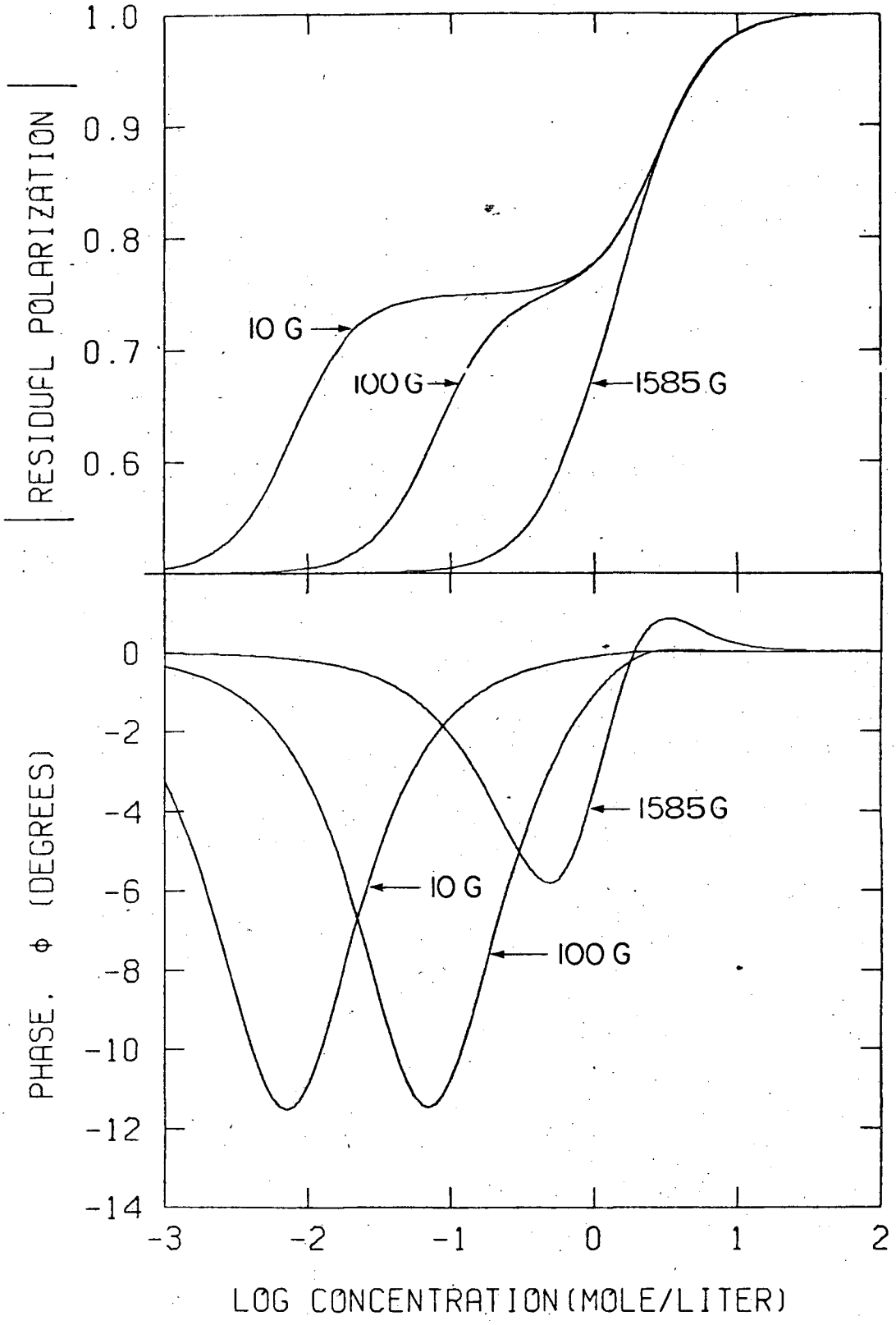


Fig. 3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0.8
0.7
0.6
RESIDUFL POLARIZATION
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1585 G
0
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-6
-8
-10
-12
-14
PHASE, Φ (DEGREES)
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1
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LOG CONCENTRATION (MOLE/LITER)

Fig. 4

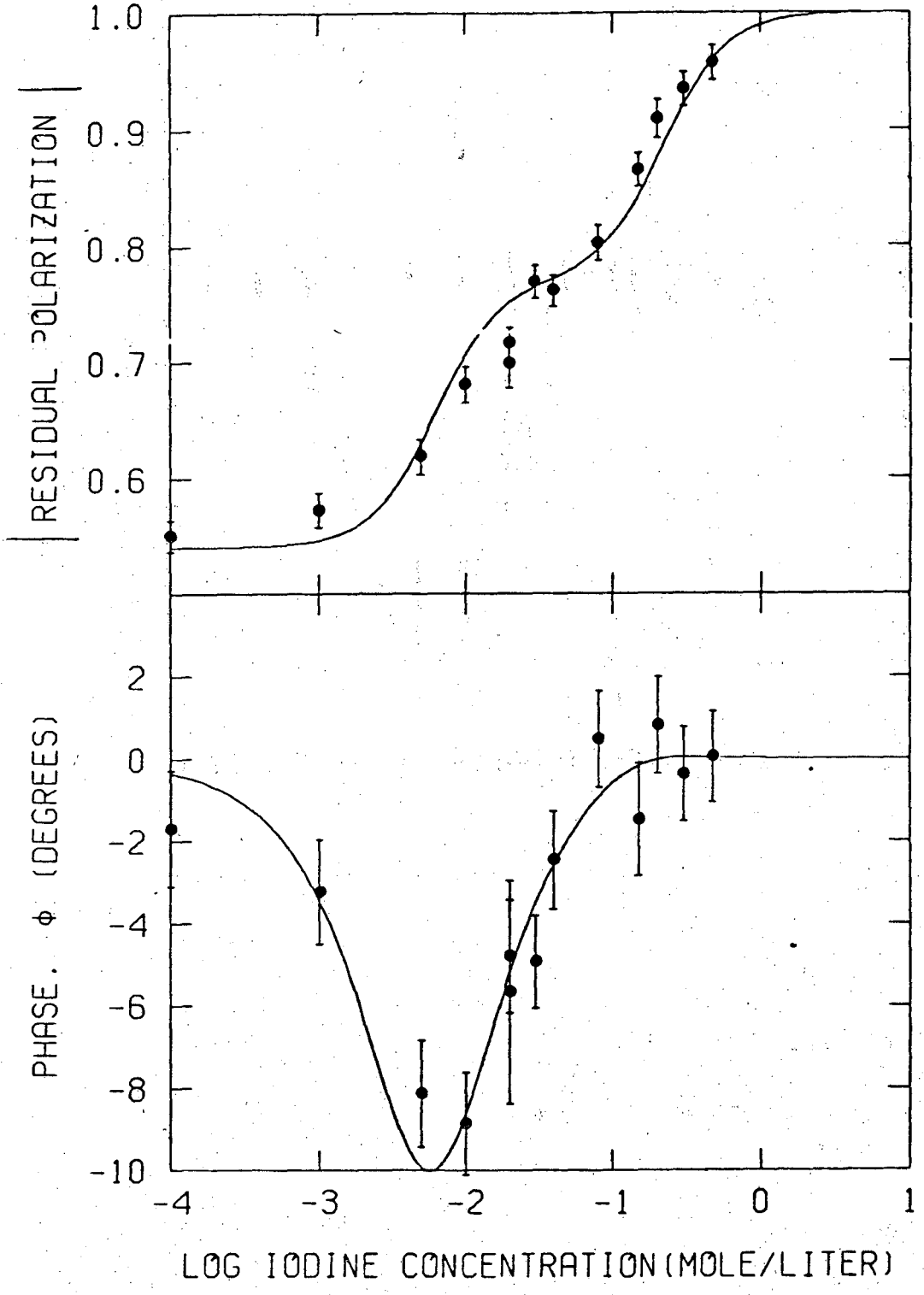
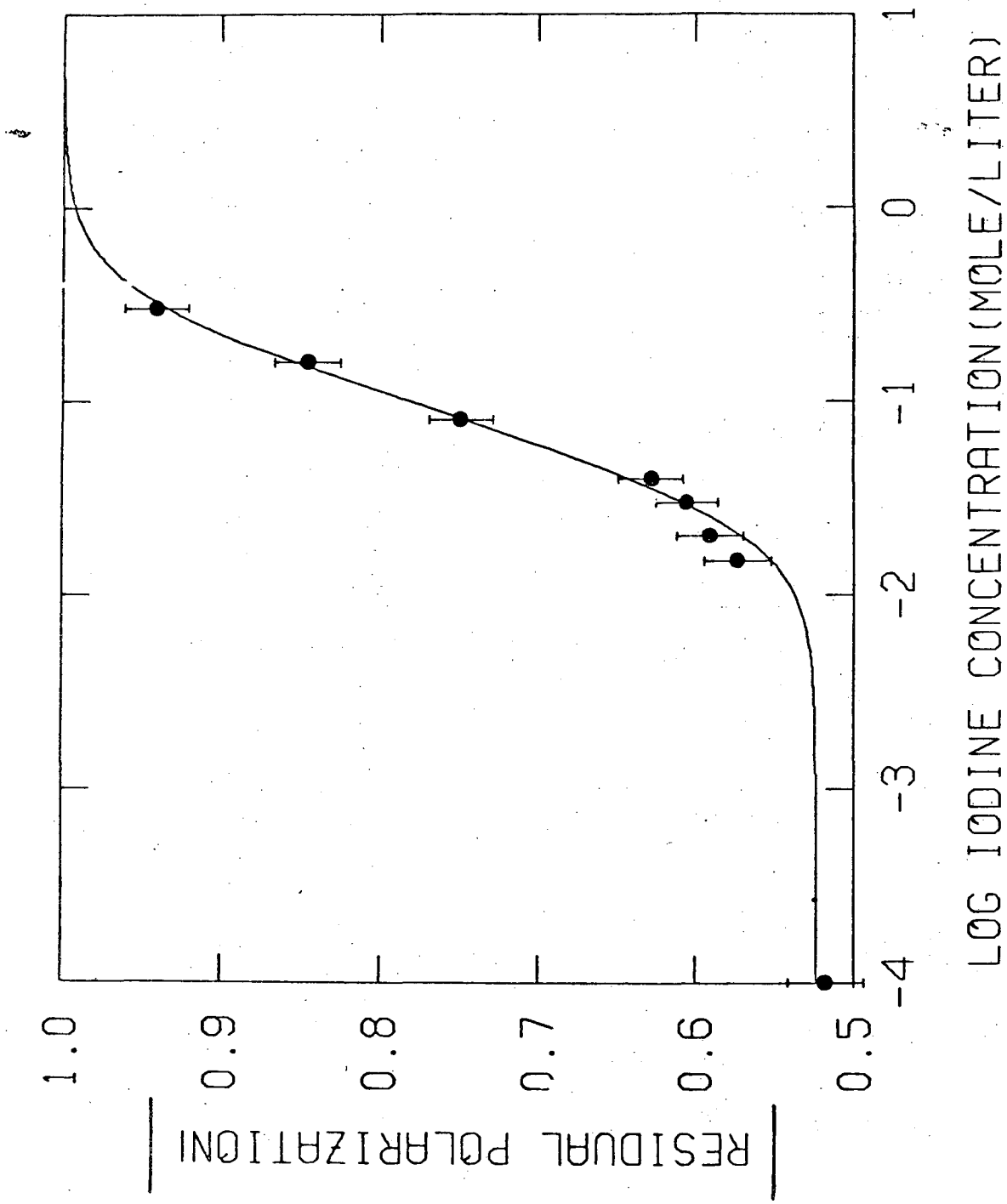


Fig. 5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1
LOG IODINE CONCENTRATION (MOLE/LITER)

Fig. 6

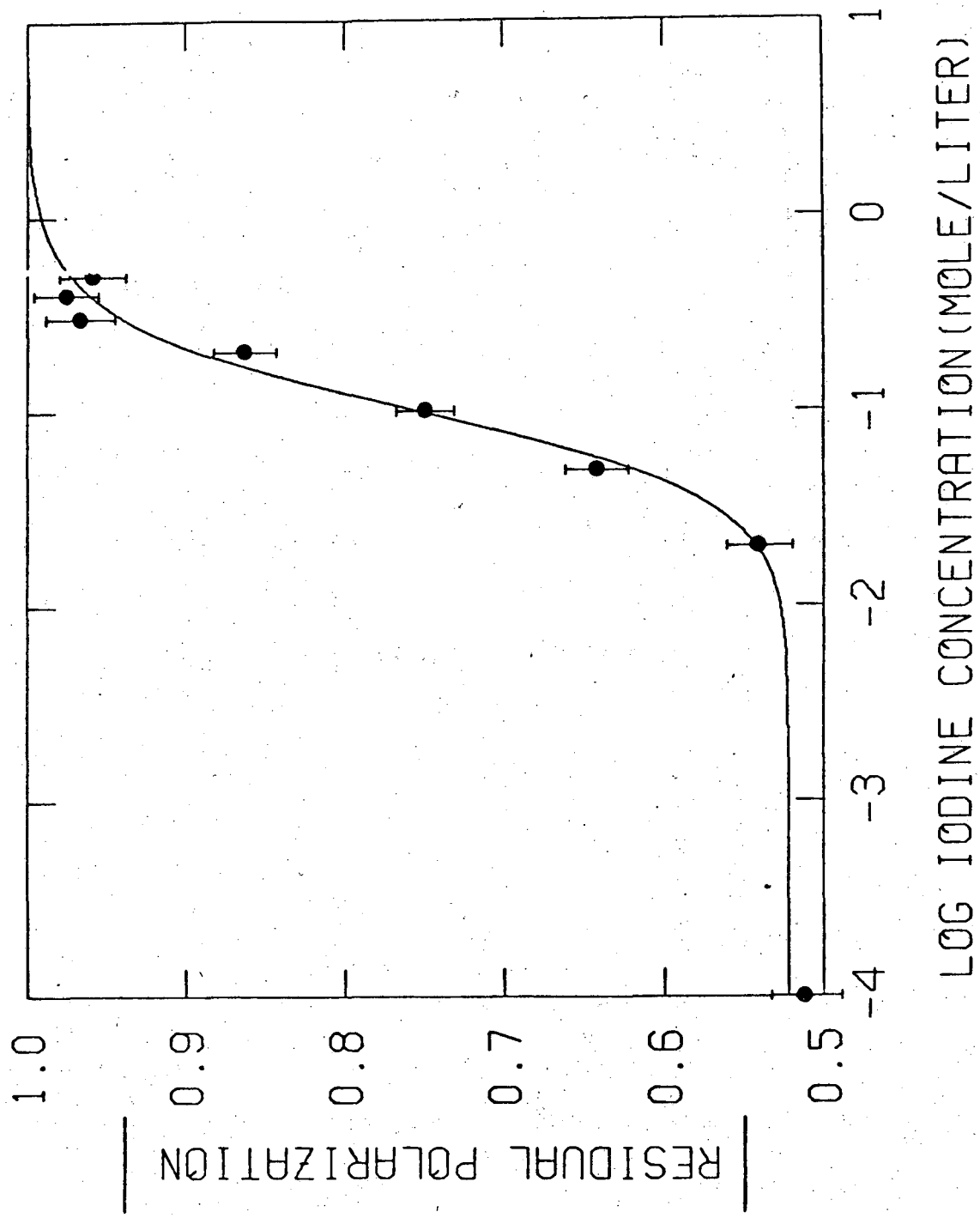

Fig. 7

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