

POSITRONIUM FORMATION IN ORGANIC LIQUIDS
AND STUDIES OF MICELLE, LIPOSOME AND POLYMER SYSTEMS
BY POSITION ANNIHILATION TECHNIQUE,

by

Belkacem, Djermouni,,

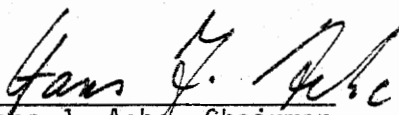
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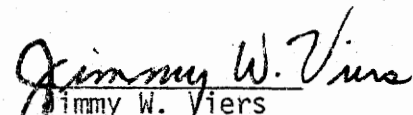
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To My Father's Memory

To My Mother
To My Family
To My Friends
Love.

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INTRODUCTION

There are certain nuclear processes which are largely affected by the chemical environment in which they occur. These processes include: the Mössbauer effect, angular correlation of cascade radiation, depolarization of muon and muonium and finally the positron - electron annihilation process. All these processes involve transformations of nuclei of elementary particles which are affected by the molecular and crystalline environment. As an example, the positron-electron pair known as "Positronium" was found to be an excellent probe for the investigation of chemical and physical processes in matter; this is because its lifetime and the mechanism of its decay process are determined by the chemical and physical state of the environment. Therefore these four nuclear processes can serve as nuclear probes, and can provide very important information about the properties of the environment and their changes.

In the first part of this thesis, several series of experiments were carried out in order to understand more accurately the detailed mechanisms responsible for the positronium formation in organic liquids.

In the second part, the positron annihilation technique was applied to the study of micellar systems, biomembranes systems and polymers. The technique is shown to be a very powerful tool in several cases superior to conventional methods for the investigation of these systems.

CHAPTER I: BASIC PRINCIPLES OF POSITRONIUM

A. Positron:

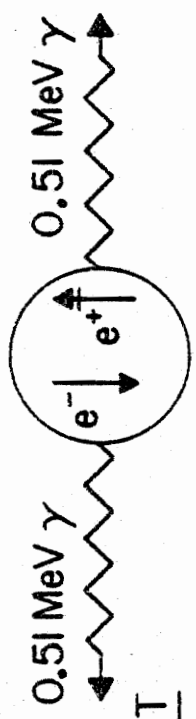
One of the most significant predictions made from Dirac's¹ relativistic quantum mechanics of the electron was the existence of some positively charged states of the electron. The positive particle called "positron" was detected, two years later, by Anderson² in cloud chamber tracks of cosmic radiation. The positron is the anti-particle of the electron. It has the same mass and electric charge as the electron, but the sign of its charge is positive. Its spin, like that of the electron, is $\frac{1}{2}\hbar$; it belongs to the class of leptons and obeys the Fermi-Dirac statistics.

The next discovery was that positrons annihilate^{3,4}; a positron may annihilate upon collision with an electron and produce electromagnetic radiation. Distinct selection rules for the conservation of energy, momentum and parity govern the number of quanta emitted in a collision of a free positron with an electron.⁵

If the spins of the electron and the positron are anti-parallel, that is, a singlet 1S_0 interaction, two γ quanta are emitted, each having the energy $m_0c^2 = 0.511$ MeV (where m_0 is the rest mass of the positron or electron and c is the velocity of the light). The two photons are emitted in nearly opposite directions (figure 1).

If the spins are parallel, that is, triplet 3S_1 interaction, three γ quanta are emitted. The distribution of the angle between the three γ quanta and the distribution of the annihilation energy of 1.02 MeV over the three γ quanta are more complicated than in the two quanta annihilation (figure 2 and 3).

POSITRON ANNIHILATION
BY TWO PHOTON EMISSION



SINGLET
J=0

ANNIHILATION RATE

$$\lambda_s^0 = Z N \pi r_0^2 c (\text{sec}^{-1})$$

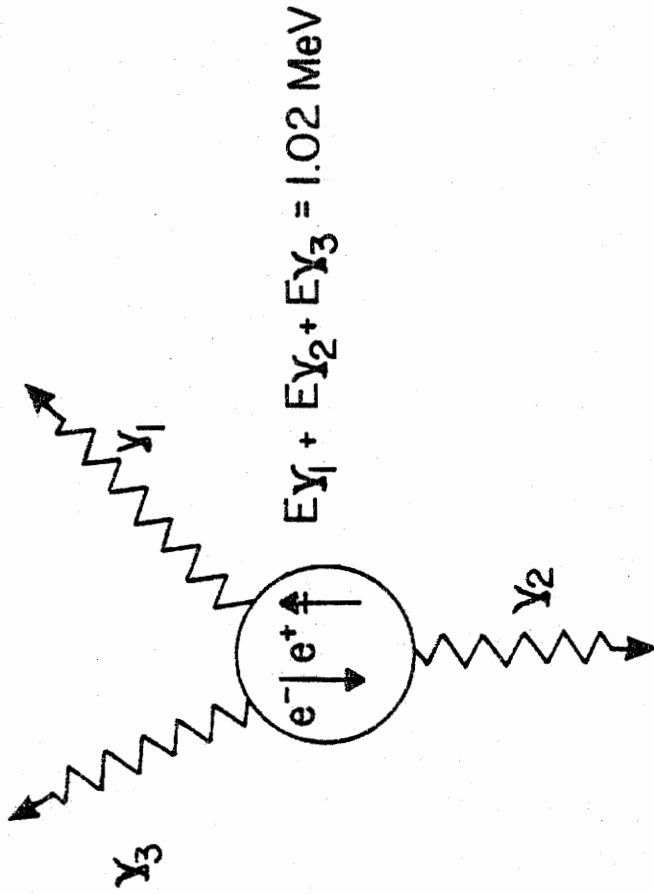
TYPICAL: GAS (NTP)

$$\tau_s^0 \approx 10^{-7} \text{ sec.}$$

LIFETIMES: CONDENSED PHASE

$$\tau_s^0 \approx 10^{-10} \text{ sec.}$$

Figure 1. Two-quantum Annihilation of a Positron (schematic)



TRIPLET $J=1$

ANNIHILATION RATE

$$\lambda_T^0 = \frac{\lambda_S^0}{1115} = \frac{ZN\pi r_0^2 c}{1115} \text{ [s}^{-1}\text{]}$$

Figure 2. Three-quantum Annihilation of a Positron (schematic)

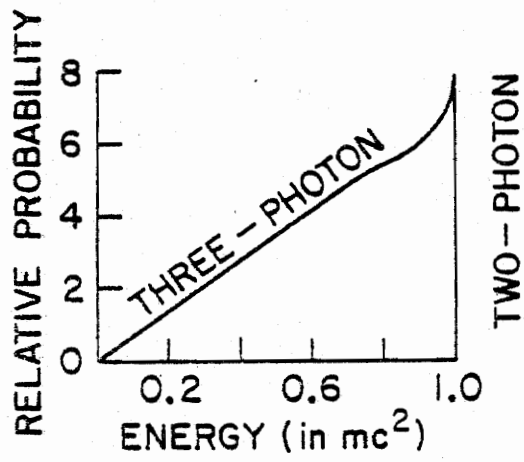


Figure 3. γ -Energy of a Positron-Electron Annihilation

The cross-section for the two γ annihilation of a free positron and a free electron was calculated by Dirac¹:

$$\sigma_{2\gamma} = \sigma_D = \frac{\pi r_0^2}{\gamma+1} \left[\frac{\gamma^2+4\gamma+1}{\gamma^2-1} (\text{Ln} (\gamma + \sqrt{\gamma^2-1}) - \frac{\gamma+3}{\sqrt{\gamma^2-1}}) \right] \quad (1)$$

where $\gamma = 1/\sqrt{1-\beta^2}$; $\beta = v/c$ is the velocity of the positron (the electron is considered to be at rest); and $r_0 = e^2/m_0c^2 = 2.8 \times 10^{-13}$ cm is the classical radius of the electron and positron.

When $\beta \ll 1$, equation (1) becomes:

$$\sigma_D = \frac{\pi r_0^2}{\beta} + \frac{\pi r_0^2}{v} \cdot c \quad (2)$$

The rate of free annihilation, which occurs mainly by the two-photon process from the singlet 1S_0 state, depends on σ_D and the positron-electron overlap in this state. This leads to the expression

$$\gamma_S = NZ\pi r_0^2 \cdot c \text{ sec}^{-1} \quad (3)$$

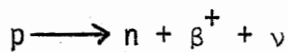
where N is the atomic density and Z the atomic number of the substrate. Ore and Powell⁶ were the first to calculate the ratio of the two photon to three photon annihilation rate.

$$\frac{\lambda_S}{\lambda_t} = 1115 \quad (4)$$

The singlet state has a total angular momentum $J = 0$, the Z component of the angular momentum, m , is 0. The triplet state has $J = 1$ and $m = 0; \pm 1$. Thus the statistical weight of triplet (three quantum states) to singlet (one quantum state) is three to one and the ratio of the cross-section of the two annihilation modes is given by:

$$\frac{\sigma_{2\gamma}}{\sigma_{3\gamma}} = \frac{\sigma_s}{\sigma_t} = \frac{2J_s + 1}{2J_t + 1} \cdot \frac{\lambda_s}{\lambda_t} = \frac{1}{3} \cdot 1115 = 372 \quad (5)$$

Positrons are formed as a result of a nuclear decay process. The emission of a positron occurs from a nucleus that is proton rich in relation to its more stable isobars. This radioactive process results from the transformation of a proton, p , within the nucleus into a neutron, n , a positron, β^+ (or e^+) and a neutrino, ν , with an accompanying decrease in the atomic number (Z) of the parent nucleus by one:



A neutrino is emitted simultaneously with the positron and the energy spectrum of emitted positrons is continuous rather than having a discrete value. The positron energy spectrum⁷ for sodium 22 is shown in figure 4.

Positrons formed as a result of a nuclear decay process have kinetic energies of several hundred eV to a few MeV, which they lose by successive collisions with atoms and molecules of the medium. Tao and Green⁸ have estimated that a highly energetic positron interacting with a compound such as water will be slowed down to the first ionization potential of water in 7 psec. The total time needed to thermalize the positron was estimated to be in the range of 100 psec. Besides undergoing free annihilation, positrons may interact with an electron and form a relatively stable bound system called "Positronium".

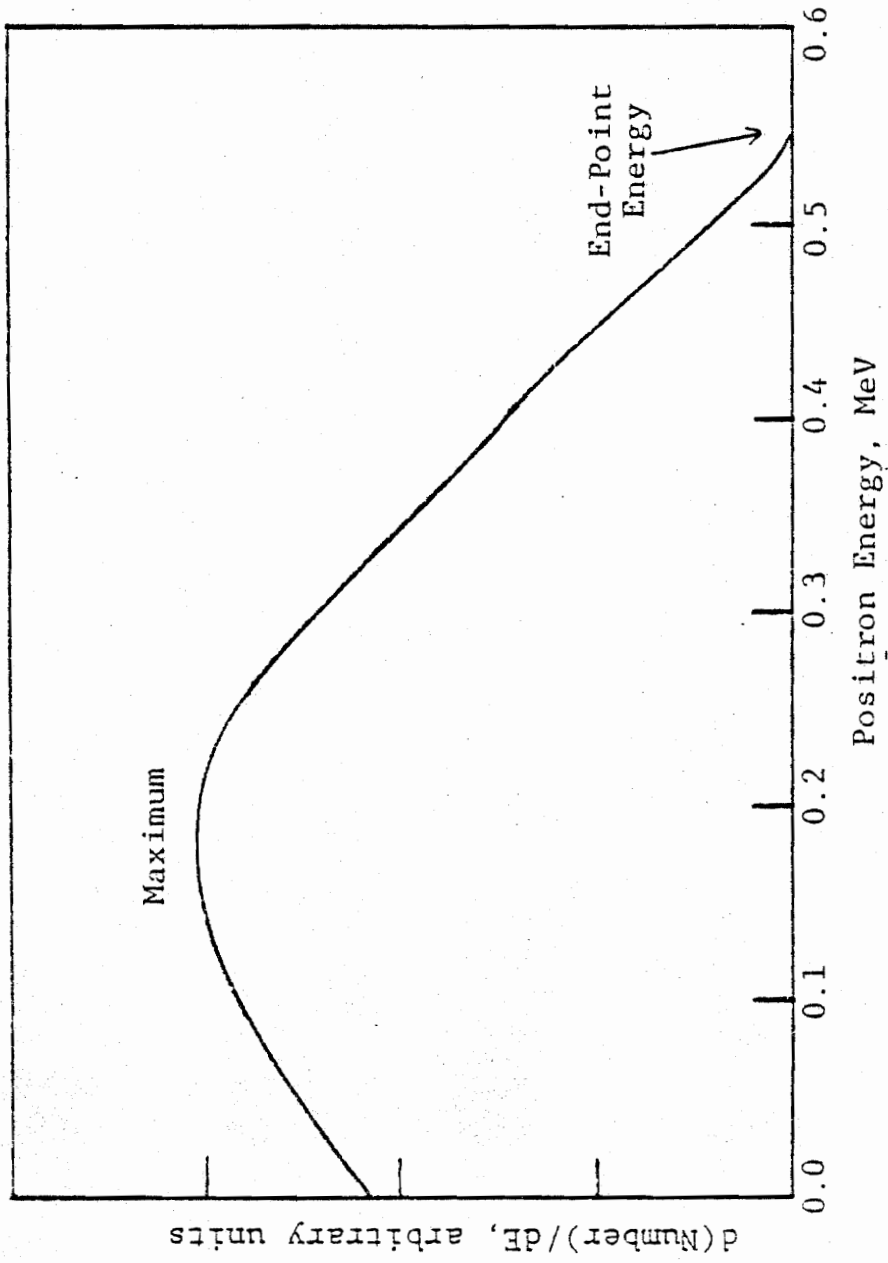


Figure 4. Energy Spectrum of Positrons Emitted From Sodium-22

B. Positronium:

The possible existence of a bound state between a positron and an electron was first postulated by Mohorivic⁹, as early as 1934, and named by Ruark¹⁰ who also calculated the ionization potential of ortho-positronium ($I_p = 6.8$ ev). However, the first experimental evidence for the existence of the positronium atom was reported by Deutsch^{11, 12}. The positronium atom can be regarded as an analogue of the hydrogen atom in which the proton is replaced by a positron;^{13,14} therefore, it represents the lightest isotope of the hydrogen atom and many of its characteristics, such as binding energy, radius etc... are well described by the simple Bohr theory (figure 5).

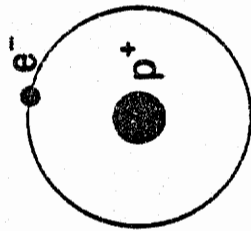
Positronium exists in two ground states: singlet and triplet states with particle spins anti-parallel and parallel, respectively. The singlet state is called para-positronium (p-Ps) and the triplet state ortho-positronium (o-Ps); (figure 6).

The wave functions of the ground states of (para and ortho) positronium can be expressed as follows¹⁴

$$\begin{array}{ll}
 \psi_{0,0} = \frac{1}{\sqrt{2}} [\tau_{-}(1) \tau_{+}(2) - \tau_{-}(2) \tau_{+}(1)] & J = 0, m = 0 \quad 1S_0 \\
 \psi_{1,1} = \tau_{-}(1) \tau_{+}(1) & J = 1, m = +1 \\
 \psi_{1,0} = \frac{1}{\sqrt{2}} [\tau_{-}(1) \tau_{+}(2) + \tau_{-}(2) \tau_{+}(1)] & J = 1, m = +0 \\
 \psi_{1,-1} = \tau_{-}(2) \tau_{+}(2) & J = 1, m = -1
 \end{array} \quad \left. \vphantom{\begin{array}{l} \psi_{1,1} \\ \psi_{1,0} \\ \psi_{1,-1} \end{array}} \right\} 3S_1 \quad (7)$$

statistically, ortho-positronium should be formed in 75% of the atoms and the remaining 25% correspond to para-positronium.

HYDROGEN-ATOM

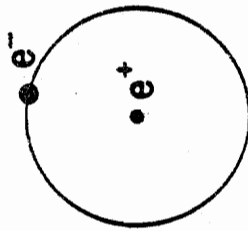


REDUCED MASS: $\approx m_e$

BOHR RADIUS: 0.53 \AA

IONIZATION POT.: 13.6 eV

POSITRONIUM



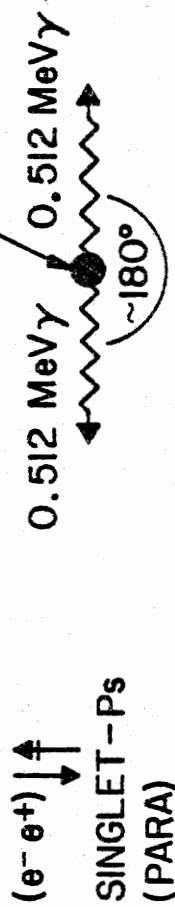
$\frac{m_e}{2}$

1.06 \AA

6.8 eV

Figure 5. Characteristics of Hydrogen and Positronium Atoms

POSITRONIUM ANNIHILATION



$\tau_S^0 = 1.25 \times 10^{-10}$ sec. (FOR FREE PARA-Ps)



$\tau_T^0 = 1.4 \times 10^{-7}$ sec. (FOR FREE ORTHO-Ps)

Figure 6. Positronium Annihilation

C. Model for Positronium Formation

1. The "Ore Model":

The theory of the formation of the positronium in the gas phase was first developed by Ore¹⁵ in 1949. According to this author, the positronium formation takes place in an energy range of a few eV.

The formation of positronium can be represented as follows:



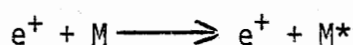
A positron collides with a molecule, M, of the medium and as a result the positron abstracts an electron from it and forms positronium.

If the ionization potential, V, of the molecule, M, is greater than 6.8 eV, the bonding energy of the positron and the electron in the ground state of the positronium atom, the formation of positronium is an endothermic reaction with a threshold energy $Q = (V - 6.8)$ eV i.e. only positrons having a kinetic energy $E_{kin} \gg (V - 6.8)$ eV can form positronium. This determines the lower energy limit, $(V - 6.8)$ eV, for positronium formation.

However, if the positron has a kinetic energy greater than the ionization potential of the molecule M, the probability of ionization of the molecule M will predominate over the positronium formation, e.g.



If the kinetic energy of the positron is greater than the first excitation potential, E^* , of M, electronic excitation of the molecule would compete with positronium formation



This leads to the conclusion that, in gases, the major part of the positronium is formed from positrons with kinetic energies between the first electronic excitation potential of the molecule M (upper limit) and $(V - 6.8)$ eV (lower limit). This energy range, in which the Ps formation is most probable is called "Ore gap". The "Ore Model" is mainly based on the following assumptions:

1. All positrons reach the upper energy limit for Ps formation, E_{\max} , without being annihilated.
2. There is a statistical distribution of the kinetic energy of the positrons in the range E_{\max} and $E = 0$.
3. All positrons whose kinetic energies lies within the "Ore gap" will form positronium.

It follows that the fractions of these positrons is given by:

$$p^0 = \frac{E_{\max} - E_{\min}}{E_{\max}} \quad (10)$$

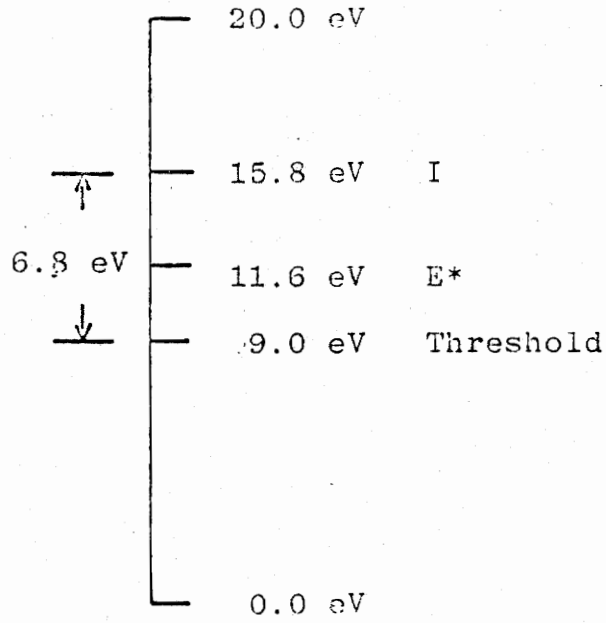
$E_{\max} - E_{\min}$ = width of the "Ore gap".

Depending on the nature of the upper limit (first excitation potential or ionization potential of the molecule M), one obtains P^0 , the fraction of Ps formed:

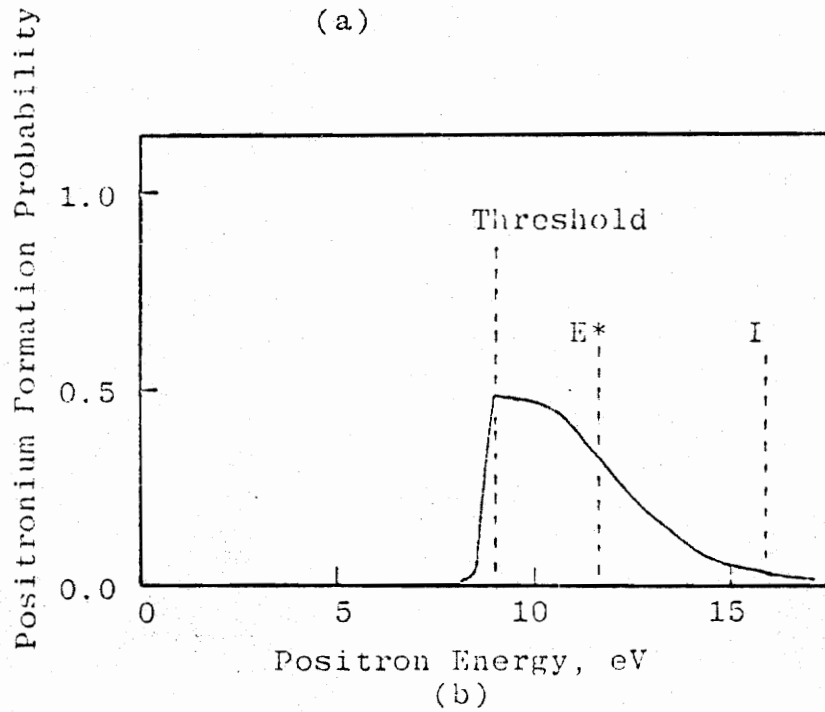
$$6.8/V > P^0 > (E^* - (V - 6.8))/E^* \quad (11)$$

Figure 7a shows an energy diagram of the "Ore gap" in gaseous argon and figure 7b shows a plot of the probability of Ps formation versus the kinetic energy of the positrons in Argon gas¹⁶.

The formation probability has been measured in a large variety of gases and was found to be in the range of 30%¹⁷. The binding energy



(a)



(b)

Figure 7. (a) Energy Diagram of the Ore Gap and (b) Hypothetical Positronium Formation Probability in the Gaseous Argon

of the positron in positronium is less than the ionization potential of many molecules; therefore, positrons with energies below the "Ore gap" will exist. Besides free annihilation another alternative for these positrons is to bind to molecules M and form a molecule complex



The positron complex can also be formed above or within the "Ore gap"; in the latter case, this reaction process will compete with positronium formation.

The "Ore Model" was used successfully to explain the positronium formation in simple gases. However, this model was found to be limited for explaining positronium formation in multi-atomic gases and condensed phases.

2. Modified Ore Model:

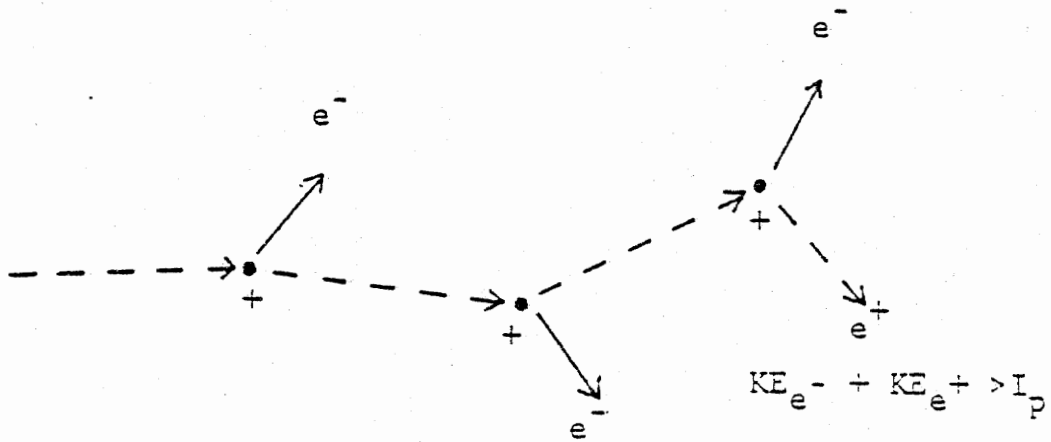
The energetic o-Ps, which is formed in the Ore gap with kinetic energies varying between 6.8 eV and thermal energies has, as any "hot" atom, two alternatives: 1. It may undergo chemical reactions while still hot, followed by a rapid annihilation of the positron in the resulting reactions products; or 2. Lose its kinetic energy via collisions becoming a thermalized Ps atom and reacting as such. The "hot" reactions between the substrate and the "hot" Ps atom have to take place shortly after the birth of the Ps before it becomes thermalized. As a result, the lifetime of the positrons involved in positronium atoms taking part in "hot" reactions will become indistinguishable from that of the free positrons or p-Ps, i.e. it will appear as a part of the short-lived component. The only evidence for the occurrence of such

hot reaction is the reduction of the number of Ps - atoms reaching thermal energies. These "hot" reactions of Ps are considered in the "Modified Ore model". In this model it is considered, also, that the number of o - Ps formed is not related quantitatively to the Ore gap.

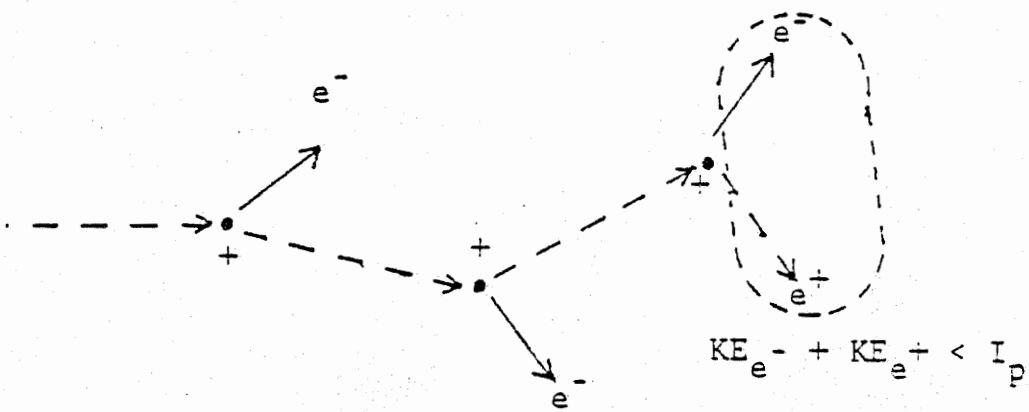
3. The "Spur Model"

When an energetic particle such as a positron is emitted by a radioactive isotope, it is slowed down by collision with the surrounding molecules causing ionization and electronic excitation of the molecules in the medium. The electrons, ions, free radicals and excited molecules formed during the slowing down process of the positron constitute a spur. Many of these generated particles have long lifetimes compared to the lifetime of positron or positronium. As an example, the mean-life of the "solvated electrons" has been found to be in the range of a microsecond. Therefore there is a distinct probability for the slow positron to interact with an electron in the spur and form positronium (figure 8). Based upon these results, Mogensen¹⁸ suggested a new model for the positronium formation, particularly in the condensed phase. The positronium formation may take place as a reaction between the positron and one of the electrons in the spur. The fraction of positronium formation P is determined by the probability that the positrons may not be able to escape capture by electrons.

If r is the distance between a thermalized positron and a thermalized electron in a medium with a dielectric constant ϵ , the probability for them to escape combination has been calculated from the Onsager¹⁹ equation and is given by



(a)



(b)

Figure 8. Formation of the Spur During the Last Path of the Positron
 (a) No Positronium Formed (b) Positronium is Formed

$$1 - P = \exp(-r_c/r) \quad (13)$$

$$p = 1 - \exp(-r_c/r) \quad (14)$$

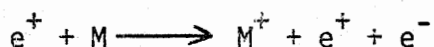
where $r_c = e^2/\epsilon kT$ is the critical distance at which the potential between the electron and the positron is equal to the thermal energy kT . T is the absolute temperature, k the Boltzman constant and e the electron charge. If the value of r is known, P can be calculated and vice versa.

The positronium formation may take place as a reaction between the positron and an electron in the spur. However, this process must compete with other processes such as the recombination of the electrons and the positive ions, diffusion of the electrons out of the spur and reactions in the spur of the electrons (or positrons) with the solvent molecules or scavengers. Also, recent results by Mogensen²⁰ showed that the presence of an external field decreases the P_s formation; that is because some of the positrons and electrons which contributed to the P_s formation are pulled out of the spur by the field.

This model explains some of the experimental results but not all of them.

4. The Modified Spur Model:

Tao²¹ combined both the, "Ore Model" and "Spur Model", in one which he named "Modified Spur Model". This author considers a slowed down positron of the spur in a condensed molecular medium and suggests two distinct reactions. The first reaction will take place when the total kinetic energy of the positron-electron pair is greater than the potential energy between them (figure 8a):



The positron and electron are free to move with respect to each other. During their motion through the densely packed molecules of the medium, the two particles (e^+ and e^-), in the spur, lose their kinetic energies rapidly. Therefore, there is a great possibility that the slowed down positron is under the Coulombic potential of a slowed down electron in the spur, which can result in the formation of positronium atom.

The second reaction occurs when the total kinetic energy of the positron-electron is less than the potential energy between them.



In this case the positron and the electron are under the attractive potential of each other and form Ps. This model agrees with the "Ore Model" and "Spur Model" and shows that the two theories could be complementary; however it does explain the experimental results only semi-quantitatively.

D. Positronium Reactions:

Quantum mechanics predicts that the annihilation lifetime of the positron is basically determined by the degree of overlapping of positron and electron wave functions, which lead to the determination of the intrinsic lifetime of o-Ps of 1.4×10^{-7} sec. However in a condensed medium the lifetime of o-Ps is reduced, due to its interactions with surrounding molecules.

In order to describe the various reaction types between o-Ps atoms and molecules Ache²² et al. have more recently discussed these reactions in a scheme which is based on simple gas kinetic principles.

As shown in figure 9, the basic assumption is that in a collision between o-Ps and another molecule a long lived collision complex may be formed, in which the electron density at the position of the positron is increased. The average time that the o-Ps spends in this complex will depend on the stability of this complex. If only weak forces (Van de Waals) are involved, the Ps will spend a very short amount of time in this environment, and the positron experiences the effect of the increased density for only a short time. As a result, the average lifetime of the Ps differs slightly from the intrinsic lifetime of the o-Ps. On the other hand if this Ps collision complex is relatively stable, then the positron will be in an environment of high electron density for a longer time and its lifetime will be decreased. Moreover, this complex can be just a transition state leading to electron transfer from Ps to substrate, i.e., oxidation of Ps. The result of this latter process is a free positron, whose lifetime in condensed phase is shorter than that of the o-Ps. If the substrate is paramagnetic, the collision can result in a spin conversion from ortho to para, whose intrinsic lifetime is only 1.25×10^{-10} sec. (since the intrinsic lifetime of the latter is very short, its reactions can be neglected). As a conclusion, one can state that all interactions of the o-Ps with matter result in a shortening of its lifetime.

In order to determine accurately the reactivity of thermal o-Ps toward various substrates, one has to develop these qualitative predictions to a quantitative method which allows the calculation of the chemical rate constants for the reactions between o-Ps and substrate.

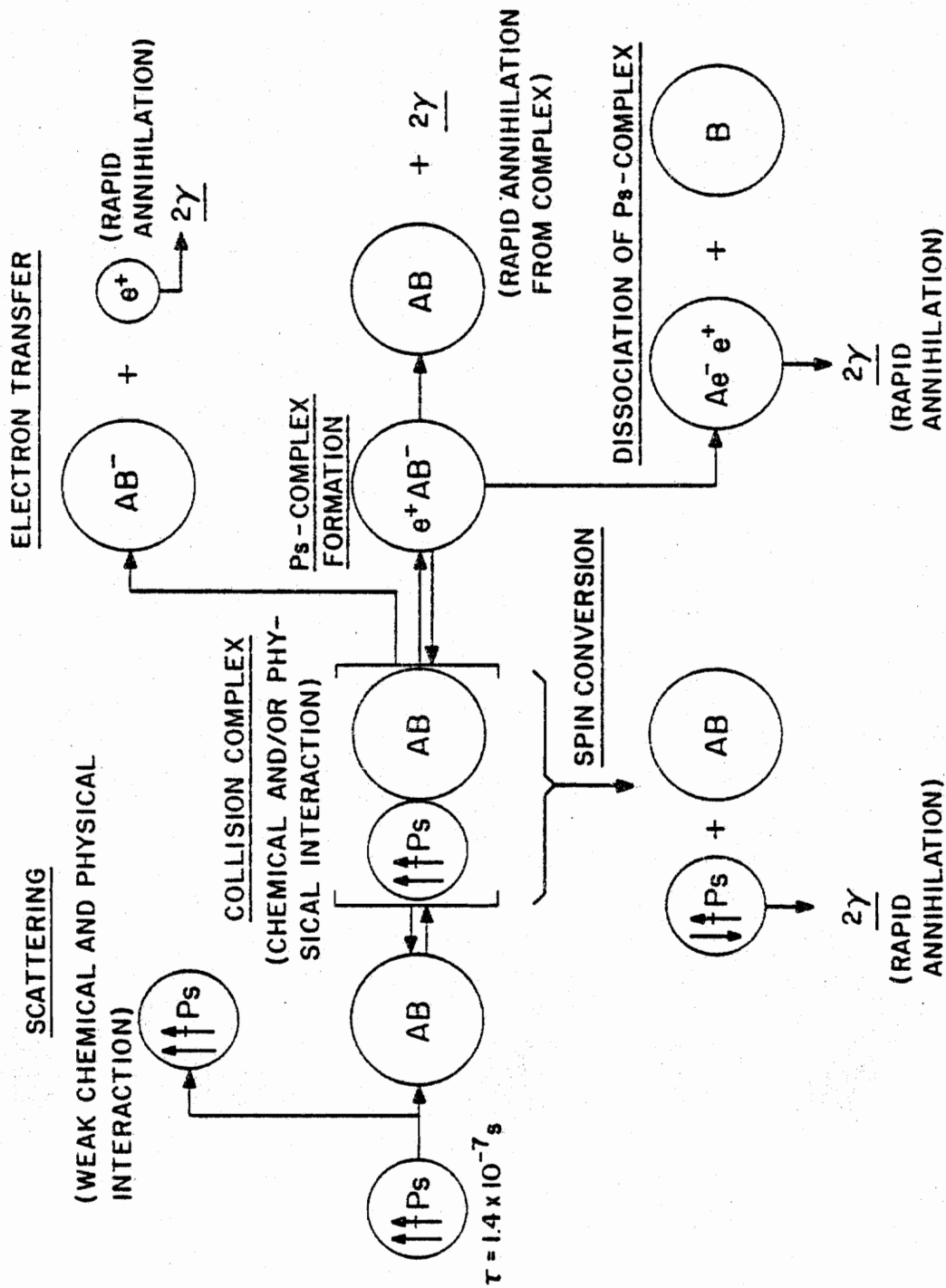
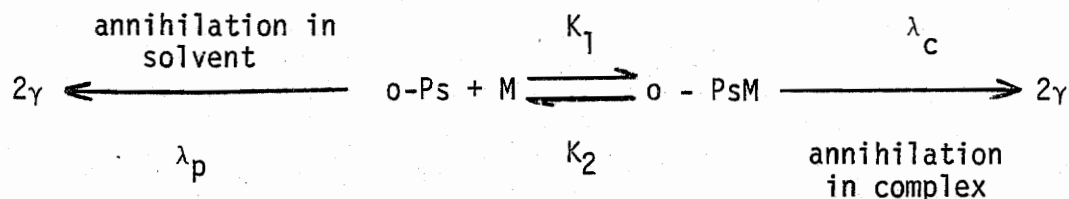


Figure 9. Reactions of Ortho-Positronium

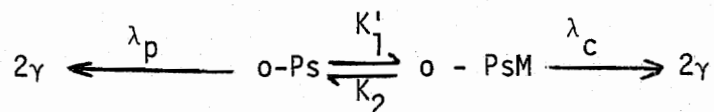
The first step for quantitative evaluation of the chemical rate constants is to set up a reaction scheme which considers the various interactions between the reactants.



It is assumed that M is diamagnetic, i.e. spin conversion is excluded, and the reaction between o-Ps and molecule M is only due to o-Ps - molecule complex formation PsM, from which annihilation takes place, or if oxidation occurs it will proceed via the o-PsM complex as the rate determining step.

According to the postulated reaction scheme, the following reactions have been considered: 1. Reactions of Ps with M to form a Ps complex PsM (rate constant k_1); 2. Decomposition of PsM (rate constant k_2); 3. Positron annihilation in complex (decay constant λ_c); 4. Annihilation of Ps in solvent (decay constant λ_p).

Since the concentration of the substrate M remains essentially constant throughout the experiments the mechanism can be simplified to:



$$k_1' = k_1 [M]$$

$$d[\text{Ps}]/dt = -(k_1' + \lambda_p) [\text{Ps}] + k_2 [\text{PsM}]$$

$$d[\text{PsM}]/dt = k_1' [\text{Ps}] - (k_2 + \lambda_c) [\text{PsM}]$$

From these differential equations, the populations of the various states in which the positron exist, o-Ps and PsM, can be deduced as a function

of time. From these values and the positron annihilation constants for these states, the time-dependent two-photon annihilation rate $R_{2\gamma}$ can be calculated. It is expressed by:

$$R_{2\gamma} = A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t).$$

A_1 and A_2 are scaling factors, related to the number of positrons annihilating at rates λ_1 and λ_2 . λ_1 is a composite of the annihilation of p - Ps and includes the annihilation rates of positron compounds formed as a result of "hot" Ps reactions.

Since the concentration of the substrate M is very small, the following assumption can be made: $(K_2 + \lambda_c) \ll K_1 [M]$. Thus λ_2 is given by the following expression:

$$\lambda_2 = \lambda_p + \frac{K_1 \lambda_c}{K_2 + \lambda_c} [M]$$

$$K_1 \lambda_c / (K_2 + \lambda_c) = K_{\text{obsd}}$$

By determining λ_p , which is identical (in dilute solutions) with λ_2 measured in the pure solvent and knowing the substrate concentration, [M], the apparent constant for Ps reactions is given by

$$K_{\text{obsd}} = \frac{\lambda_2 - \lambda_p}{[M]}$$

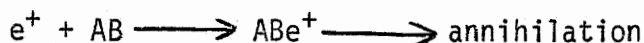
The K_{obsd} represents the average values obtained from a series of measurements taken at different substrate concentrations [M].

E. Inhibition of Thermal Ortho-Positronium:

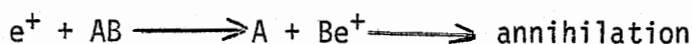
In accordance with the Ore model, inhibition¹⁴ of positronium formulation could occur by two different mechanisms: inhibition of Ps formation by positron capture and inhibition of Ps formation by

rapid slowing down of positrons to energies below the Ore gap. Inhibition can be further subdivided into: 1. self-inhibition, which determines the probability of positronium formation in a pure compound and 2. inhibition due to additives:

1. non-dissociative positron attachment

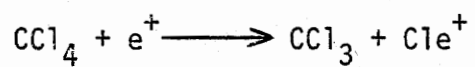


2. dissociative positron attachment



The capture type inhibition is a very effective process in many cases.

The possibility of attachment of slow positrons to molecules was suggested as early as the discovery of the positronium in order to explain an increase in the rate of positron annihilation in Freon at low pressure¹². Hughes and Wu^{23,24} reported studies on the effect of static electric field on the probability of positronium formation in gases. In noble gases and nitrogen an increase in the probability was observed in electric fields; however, in CO₂, methane, ethane and Freon such effect was not observed. When these gases were added to argon, even in very small amounts, they destroyed completely the effect of the field on Ps formation. Another interesting result was that in the case of SF₆, the electric effect inhibited positronium formation. In condensed phase, the inhibition effect has been observed for halogen derivatives, alcohols etc... Some of these results have been explained in terms of strong self-inhibition process especially in compounds containing two or more halogen atoms (bromoform, carbon tetrachloride) or nitro groups (dinitrobenzene)



That was the mechanism used to explain the strong inhibition of positronium formation in benzene containing a small amount of CCl_4 ²⁵ additive.

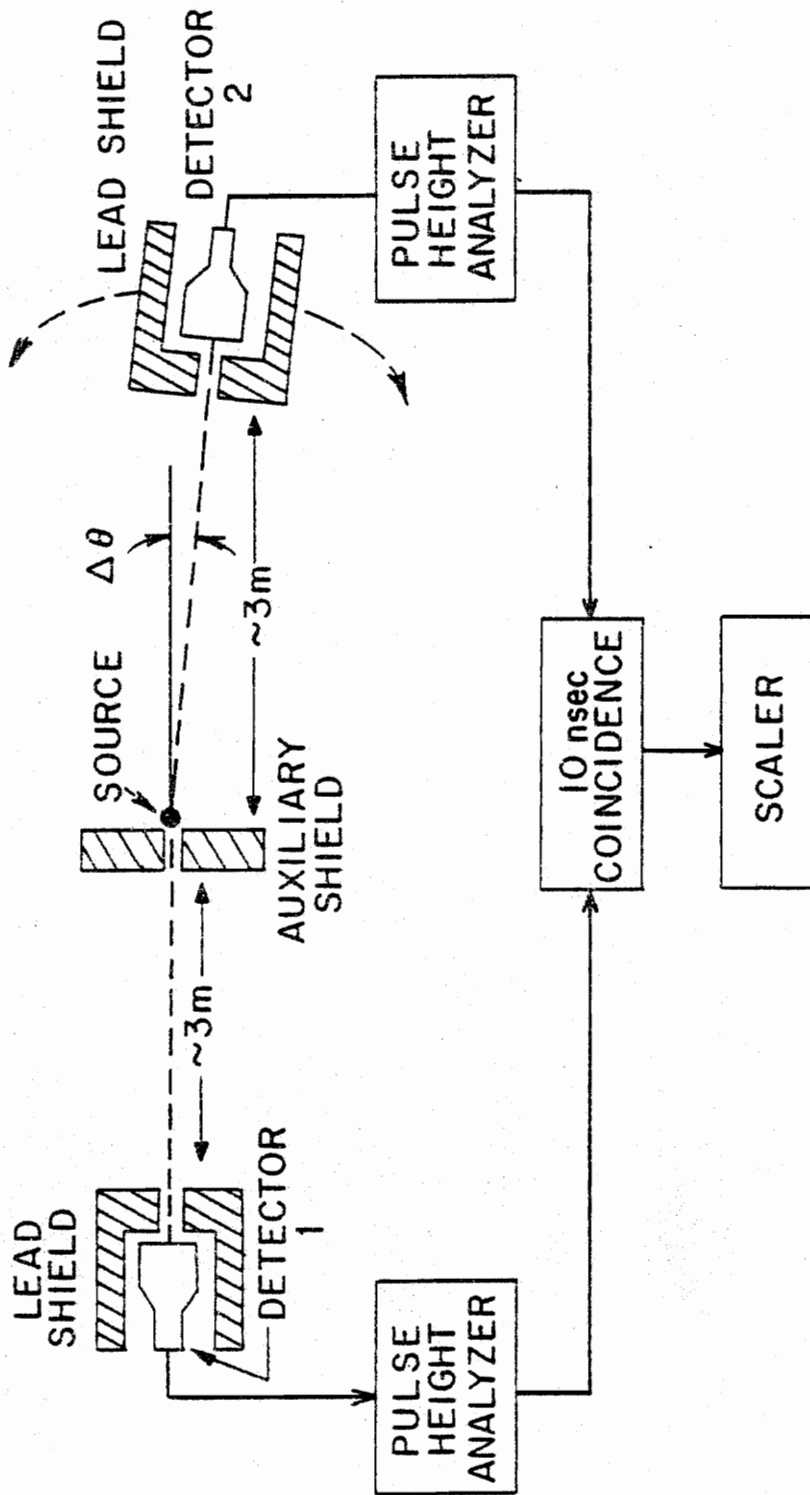
CHAPTER II: EXPERIMENTAL METHODS

A. Introduction:

When a positron is emitted in a condensed medium, it slows down to nearly thermal energy, interacts with an electron and both particles annihilate with emission of two gamma photons. The annihilation photons carry information about the electron-positron state at the moment of annihilation; therefore, experimental studies of the emitted photons may give information about the physical and chemical properties of the medium under investigation.

Three experimental methods^{14,26} are commonly used in positron annihilation research; namely, the angular correlation technique, the Doppler broadening, and the lifetime technique.

The angular correlation technique is based on the assumption that the total momentum of the annihilation electron-positron pair is distributed between the annihilation photons. Thus, if this momentum is zero, the two photons are emitted in opposite directions. If it is different from zero, there will be a deviation from 180° between the directions in which the photons are emitted. This angle is proportional to the momentum of the annihilation pair. The deviation, which is in the order of few milliradians in almost all cases, can be measured with the aid of the system shown in figure 10. The 0.51 MeV resulting from the annihilation process are recorded in this system as a function of $\Delta\theta$ (deviation from 180°). The form of the angular distribution yields information about the various annihilation mechanisms and the reactions of Ps and its formation. Processes resulting in free annihil-



ARRANGEMENT FOR MEASURING ANGULAR CORRELATIONS

Figure 10. Typical Experimental Arrangement for Determining the Angular Distribution ($\Delta\theta = \text{deviation from } 180^\circ$)

ation of positrons exhibit a broad component in the angular distribution due mainly to the momentum contribution of the electron (figure 11). The para-positronium loses most of its kinetic energy rapidly after its formation, and is at rest at the moment of annihilation; therefore the photons emitted deviate slightly from 180° and are responsible for the observed narrow component in the angular distribution. This component is indicative of the formation of the para-Ps and a change in the para-Ps formation yield will be revealed by an increase or decrease of the area under the narrow component. The angular correlation method is used essentially to follow the various reactions of Ps. As an example, increased ortho-para conversion results in a relative increase in the intensity of the narrow component.

In the Doppler broadening technique, the energy distribution of the annihilation photons is measured. The spreading of the annihilation peak caused by the motion of the electron-positron pair with respect to the detector can be observed. This technique can also be used to measure the momentum distribution of the annihilating pair, it is much simpler and faster than the angular correlation but has a very poor momentum resolution.

The third type is the lifetime technique. It has been used for the present studies; therefore, some of its principal aspects will be discussed in more details.

B. Positron Source:

The most commonly used source of positrons is sodium-22. This radioactive nuclide, half life 2.60 years, was obtained from Amersham

ANGULAR DISTRIBUTION CURVE

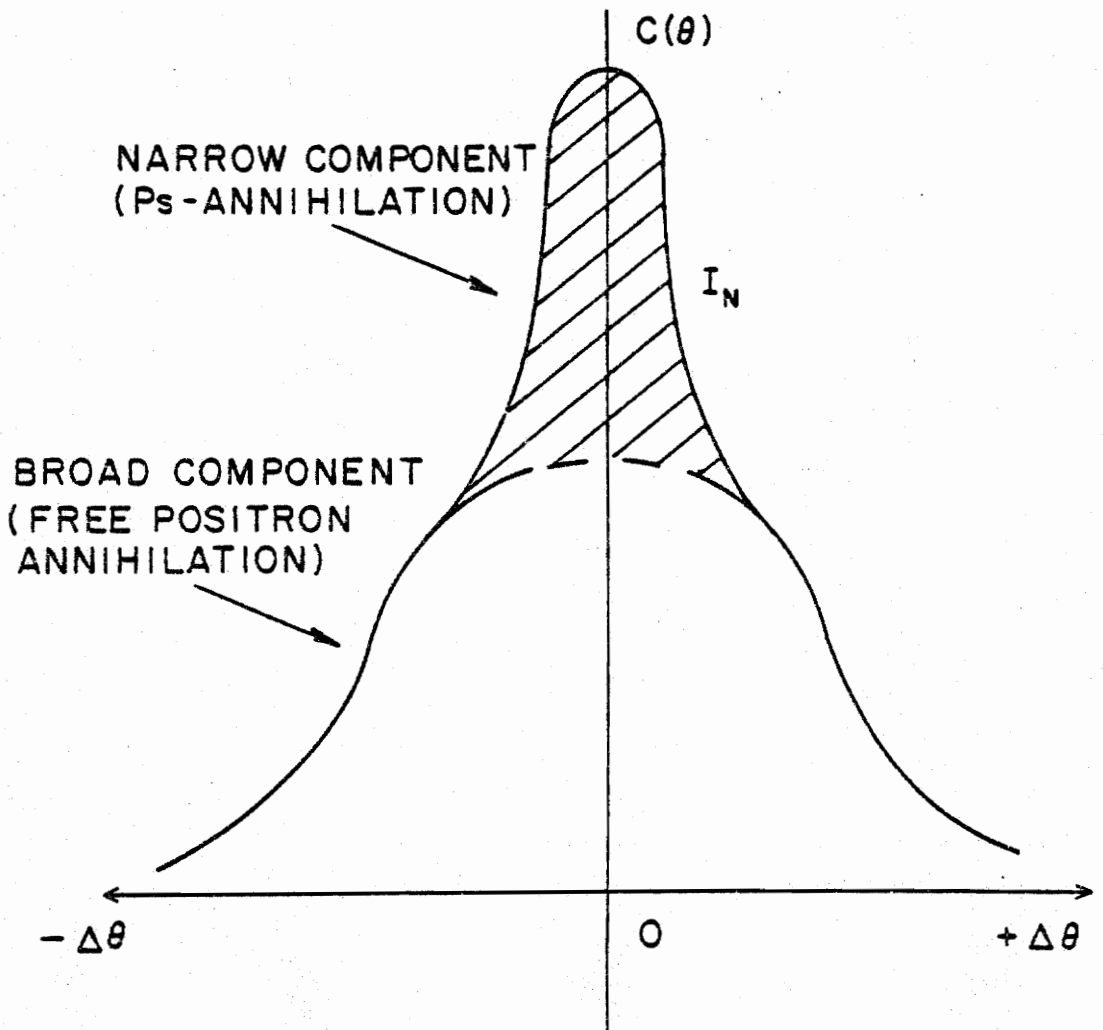


Figure 11. Angular Distribution in Two-Quantum Annihilation Frequency of 2γ Coincidences ($c(\theta)$) as a function of $\Delta\theta$. The Narrow Component I_N is shaded.

Co. as sodium chloride in carrier-free aqueous solution. ^{22}Na decays²⁷ with emission of a positron of 0.544 MeV maximum energy to give an excited Neon-22, which in turn decays to the ground state by the emission of a 1.28 MeV photon (figure 12). The excited Neon-22 has an average lifetime of 3 ps; therefore, for all practical purposes, it can be assumed that the positron and the 1.28 MeV gamma photon are emitted simultaneously. The use of Sodium-22 as the positron source offers some advantages such as its long half life, simultaneous emission of 1.28 MeV gamma photon and positron, and easy energy discrimination of the gamma-photon (1.28 MeV) and the annihilation photon (0.511 MeV).

A positron source consisting of $3 \sim 5 \mu\text{Ci}$ of sodium-22 incorporated into a thin glass or aluminum foil was used. The aluminum or glass should be as thin as possible so that emitted positrons interact mainly with the sample under investigation rather than the holder. The glass used was made of soda lime glass (density 2.47, softening point 695°C , from Corning Glass Co.) and had the dimensions $0.8 \text{ cm} \times 1.5 \text{ cm} \times 0.01 \text{ mm}$. This source was prepared by depositing $3 \sim 5 \mu\text{Ci}$ of $^{22}\text{NaHCO}_3$ solution in the center of the glass foil, which was subsequently sandwiched between two layers of graphite and annealed in an oven at 585°C for 24 h, a process by which ^{22}Na diffused into the glass. ^{22}Na activities remaining on or close to the surface were removed by placing the foil into water until the positron activity remained constant. It was found that about 90% of ^{22}Na was embedded in the glass. In order to determine the relative amount of positron annihilation occurring in the holder, the source was calibrated in nitrobenzene, a solvent which reacts very rapidly with thermal o-Ps. The amount of positrons annihilating in the

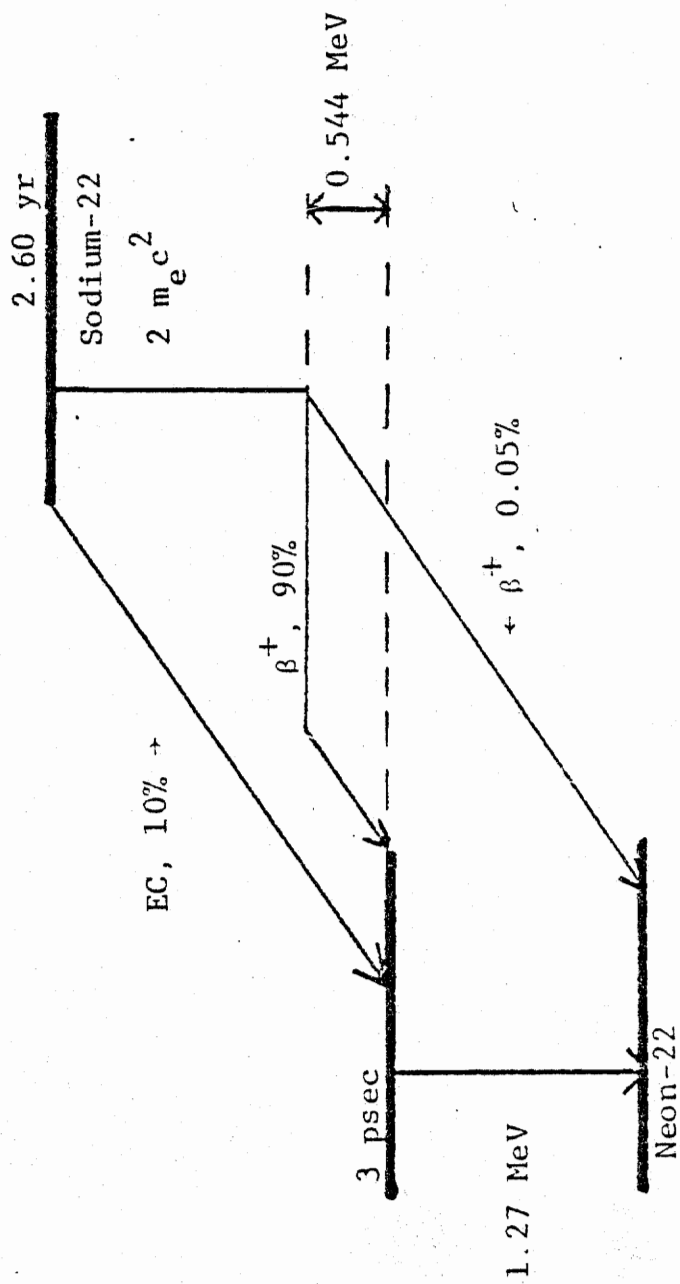


Figure 12. Decay Scheme for ^{22}Na

glass was found to be less than 2% for which corrections were made.

C. Fast-Slow Delayed Coincidence:

Positron lifetime measurements are carried out by conventional fast-slow coincidence technique (figure 13). The fraction of the emitted gamma photons (1.28 MeV and 0.511 MeV) are detected by two plastic scintillators (phosphors). The time difference between the signals from the two detectors is the positron lifetime. Each unit consists of a phosphor optically coupled to a photomultiplier tube. The phosphors used were 1" by 1" Naton 156 plastic scintillators. They have a fast decay constant in comparison to the positron lifetime and high light output. The photomultiplier tubes were RCA 8575 mounted on Ortec 265 photomultiplier bases. These tubes were used for their high gain, fast rise time, and their negligible emission of thermal electrons. The output signals from these two detectors are fed into two coupled electronic circuits. The circuits consist of a fast inner loop and a slow outer loop. Each circuit has two sides: a start side and a stop side. The inner circuit is used in order to determine the time interval between the birth of the positron and its subsequent annihilation with an electron into two gamma photons (0.511 MeV). For this purpose, the output signal from the anode of the detector is fed into an Ortec 473A fast discriminator. The units are operated at a biased voltage in order to reduce the noise level in the circuit by setting a lower threshold for accepting pulses from the photomultiplier tube. The output signal from the discriminator provides the start signal for the Time-to-Pulse-Height converter (Ortec 437A TPHC) which begins building a pulse until a

FAST - SLOW TIMING SYSTEM

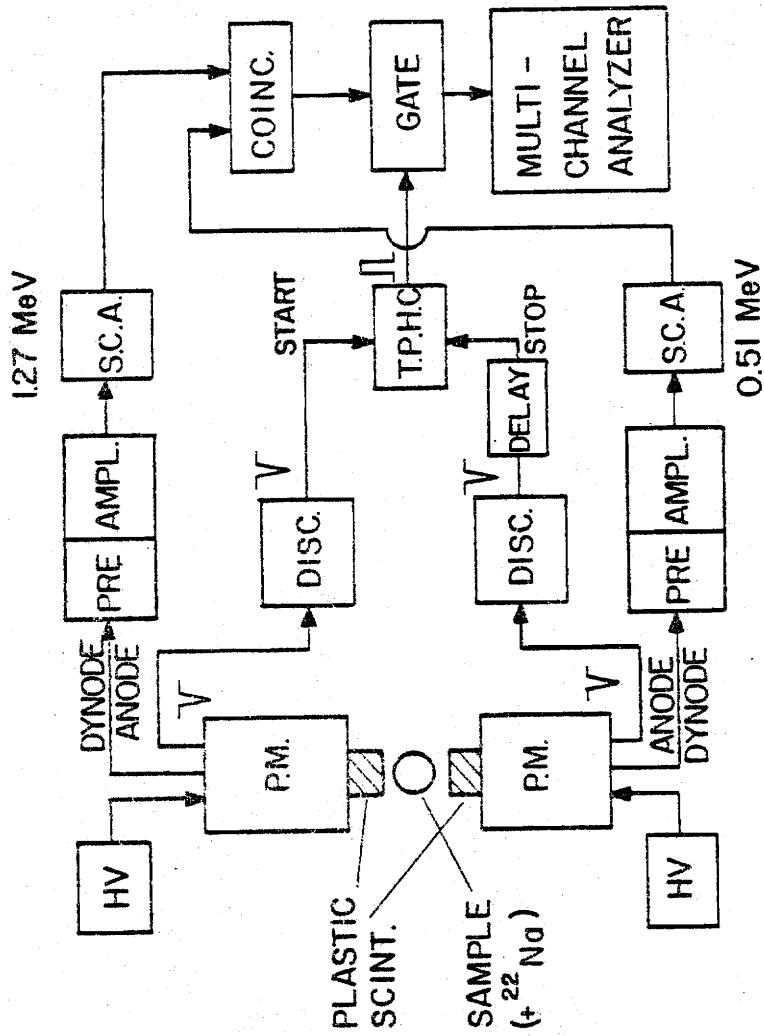


Figure 13. Simple Fast-Slow Timing System

stop signal is received resulting from the annihilation of the positron. 0.51 MeV photons are detected by the second detector and which is processed in a similar fashion. The amplitude of the TPHC output signal is proportional to the time difference between the arrival of the start and stop pulses. Before this pulse is fed into a multichannel analyzer, (MCA), which registers the signal amplitude (i.e. the positron lifetime) and stores the information, certain energy and coincidence conditions have to be satisfied. An Ortec 425 variable delay is inserted into the inner fast circuit to calibrate the channel width, time increment per channel, of the MCA.

The outer slow loop obtains the signal from the dynodes of the photomultiplier tubes. These signals are amplified and shaped by an Ortec 113 scintillator preamplifier and an Ortec 460 shaping amplifier. In both sides of the circuit, an Ortec 551 Timing Single Channel Analyzer (SCA), is inserted. On the start side, this unit is biased to accept only pulses corresponding to an energy of a 1.28 MeV photon. This corresponds to the energy of the gamma photon which is emitted simultaneously with the positron, i.e. corresponds to the birth of the positron. The SCA in the stop side of this circuit performs the same functions for 0.511 MeV pulses, which are generated by the annihilation process of the positron. The fast SCAs trigger a fast coincidence unit (Ortec 414A) which gates (Ortec 426) the TPHC. If the energy requirements are met and the timing pulses arrive within the time range selected, the fast coincidence unit provides a gate pulse that allows the MCA to accept the signal from the TPHC. The MCA used in this work is a Northern SC 600; it is operated in the pulse height analysis (PHA)

mode. This unit accepts pulses of different amplitude and sorts them out accordingly. The data representing the lifetime distribution of positrons are stored in the memory and can be read out of the memory with a teletype unit. Once the data are printed out, they are computer analyzed.

D. Positrons Lifetime Spectra:

The number, N , of coincidences observed can be plotted logarithmically as a function of time, t (figure 14). An experimental point $(\log N(t), t)$ on the curve represents the number of positrons that have lived a given time, t , and decayed by two gamma coincidence.

The lifetime spectrum can be analyzed mathematically as a sum of exponentials:

$$N = \sum A_j \exp(-\lambda_j t) + \text{Background} \quad (16)$$

Where the A_j are scaling factors related to the number of positrons annihilating at a rate λ_j (reciprocal of the positron lifetime τ_j).

The intensity I_j of each component corresponds to the number of the positrons decaying by each process and is determined by the area under each lifetime component. In most cases, two components can be isolated from the lifetime spectrum.

$$N = A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t) + \text{Background}$$

The short lifetime component with an associated lifetime τ_1 and intensity I_1 is attributed to the annihilation of the free positron and the annihilation of p - Ps and the products resulting from non thermalized o -Ps, whereas the long-lived component displaying a lifetime τ_2 and intensity I_2 is attributed to the annihilation of thermal ortho-Ps. A_1

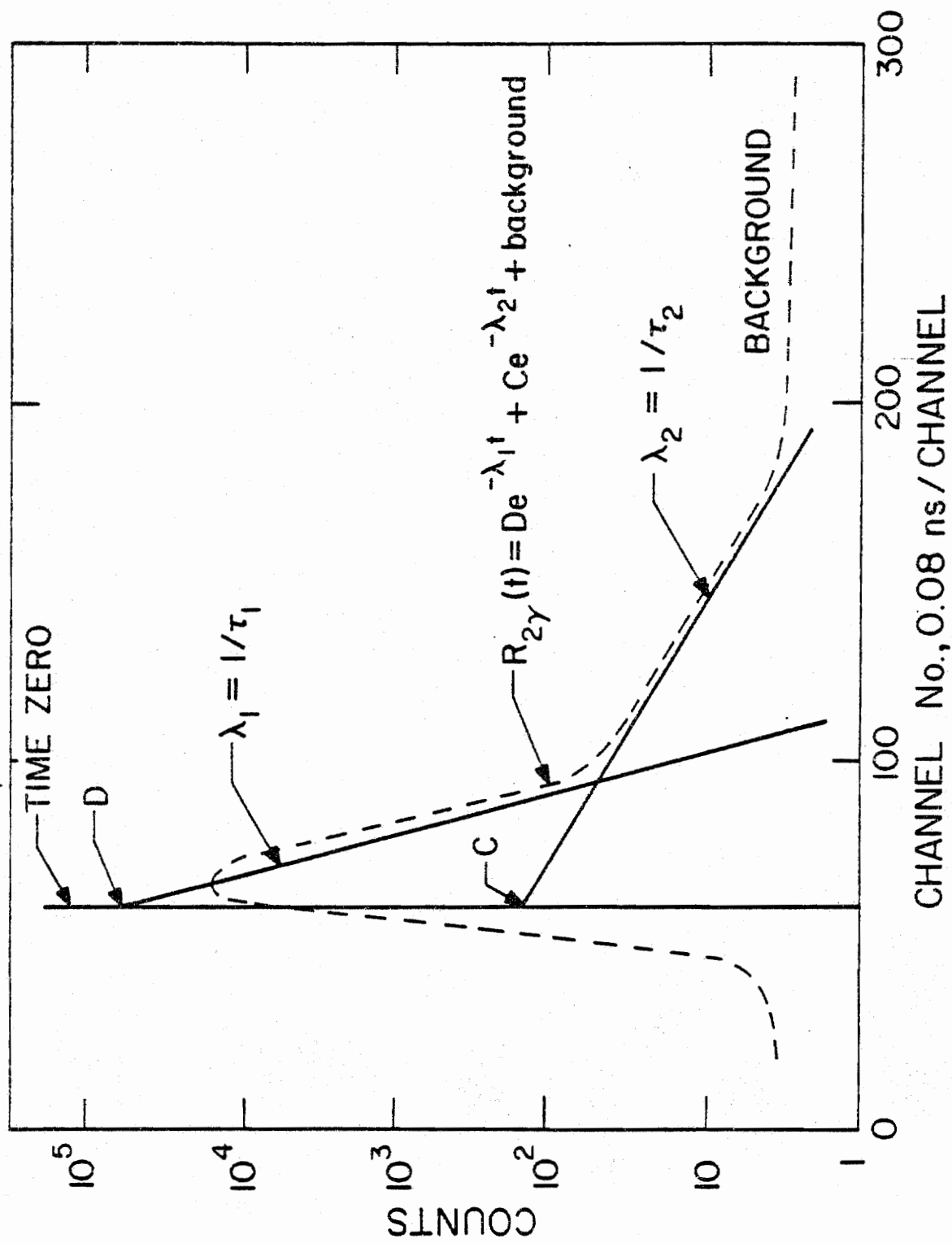


Figure 14. Typical Positron Lifetime Spectrum

and A_2 are scaling factors related respectively to the intensities I_1 and I_2 . Several computer programs such as POSITRONFIT²⁸, POSITRONFIT EXTENDED²⁹, PAL²² and others^{30,32} are available for the analysis of the lifetime spectrum into two components. These programs perform a linear least square analysis of the two components. The lifetime and intensity of the two components are calculated. In addition, a plot of the analyzed spectrum is obtained (figure 15).

The quality of the timing resolution is defined by the full width at half maximum (FWHM) of the prompt curve and the apparent half life associated with its slope. A prompt spectrum is one in which the photons are emitted simultaneously by a radioactive source. Experimentally, this can be done by using a Cobalt-60 source which emits a 1.31 MeV and 1.17 MeV photons simultaneously. The coincidence measurements of these two photons should therefore exhibit no delay, and should give a sharp line at $t = 0$. However in practice, one obtains a distribution as shown in figure 16 due to incomplete time resolution by the timing system. The time resolution as defined by the full width at half maximum of the prompt ⁶⁰Co peak was generally less than 400 psec. during the present studies. By introducing a known delay, i.e. 16 nsec, into the timing circuit, the prompt spectrum can be moved 16 nsec down the time axis. The number of channels between the maximum of the prompt spectrum with no delay and the maximum of the prompt spectrum with a 16 nsec delay can be used to calibrate the channel width and time increment per channel. For this work, it is equal to 0.131 nsec/channel.

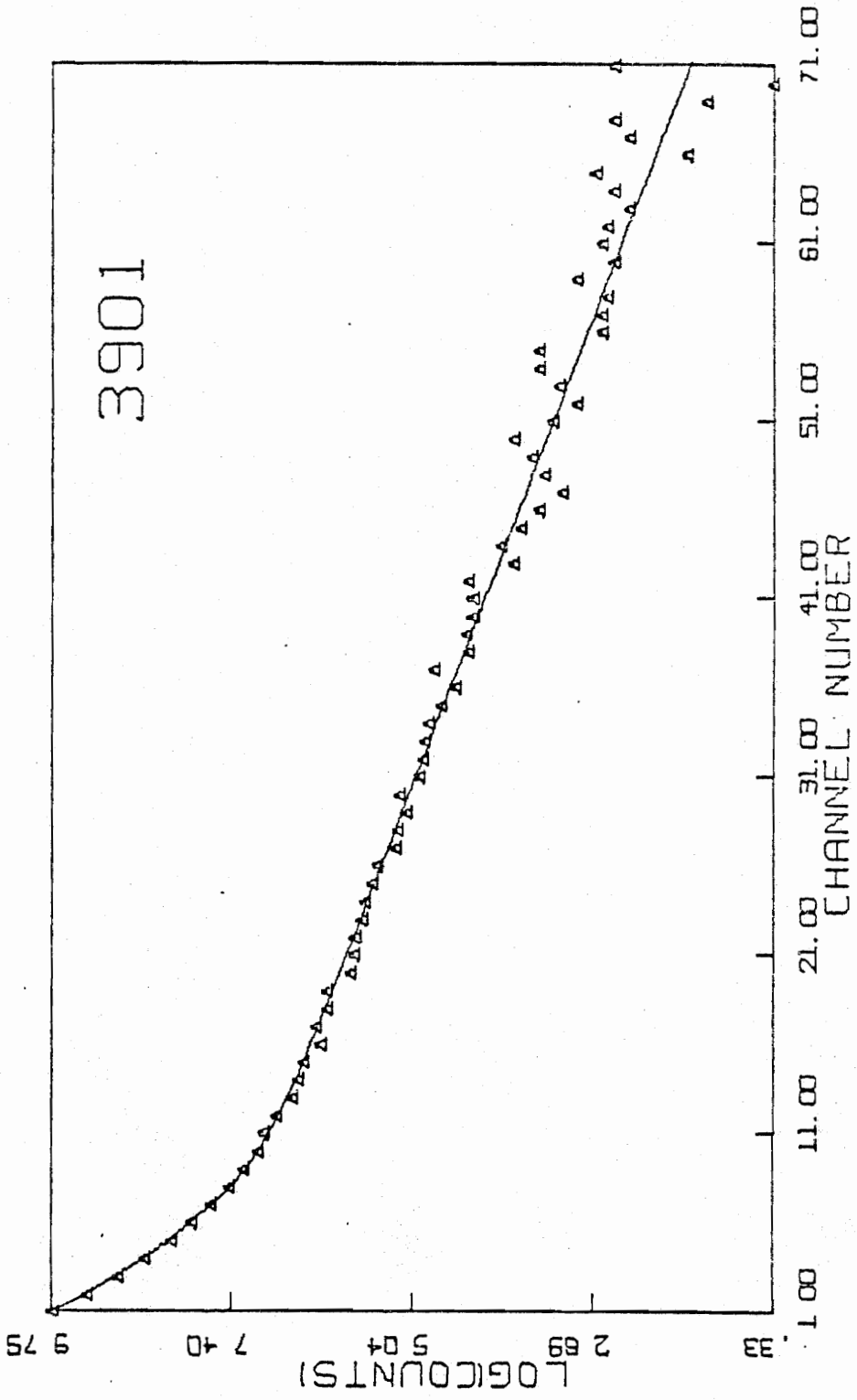


Figure 15. Typical Calcomp Plot of the Lifetime Data

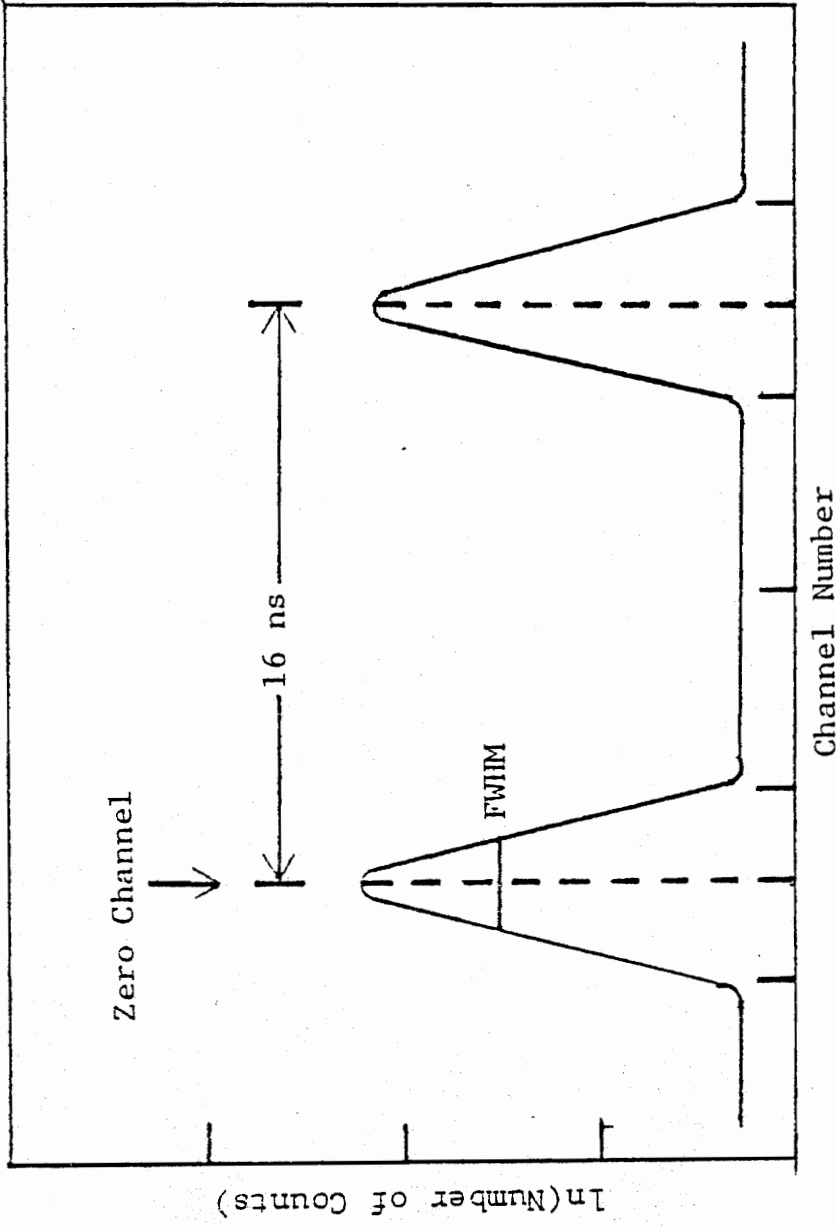


Figure 16. Prompt Spectrum of Colbolt-60

E. Sample Preparation and Degassing:

The material to be investigated can be in any physical form. The only requirement is that the overwhelming fraction of the positrons emitted by the source must stop and annihilate in the sample.

In the present work, the materials studied were liquid or solid, the latter as a film. Specially designed cylindrical vials were filled with about 2 ml of the appropriate solution; the radioactive sources were suspended in the center of the sample. Two different vials were used: one for the studies at room temperature (22°C), and the other for the studies at variable temperatures. The sample tube used for the first type of experiments is shown in figure 17(a). It was constructed of cylindrical pyrex glass tubing, approximately 200 mm long, 10 mm i.d. The source was isolated in the side tube during the degassing process in order to prevent it from being broken. The second type of design was used for measurements at various temperatures. The degassing bulb and sample tube used for these experiments are shown in figure 17(b). Here, also, for the same practical reasons, as previously, the sources were located in the upper section of the tube. It is well established that positronium is extremely sensitive to unpaired spin density and reacts via spin conversion with paramagnetic materials. Hence, removal of oxygen^{32,24} is necessary to obtain unambiguous results. This is accomplished by degassing the sample by freeze-thaw techniques under vacuum.

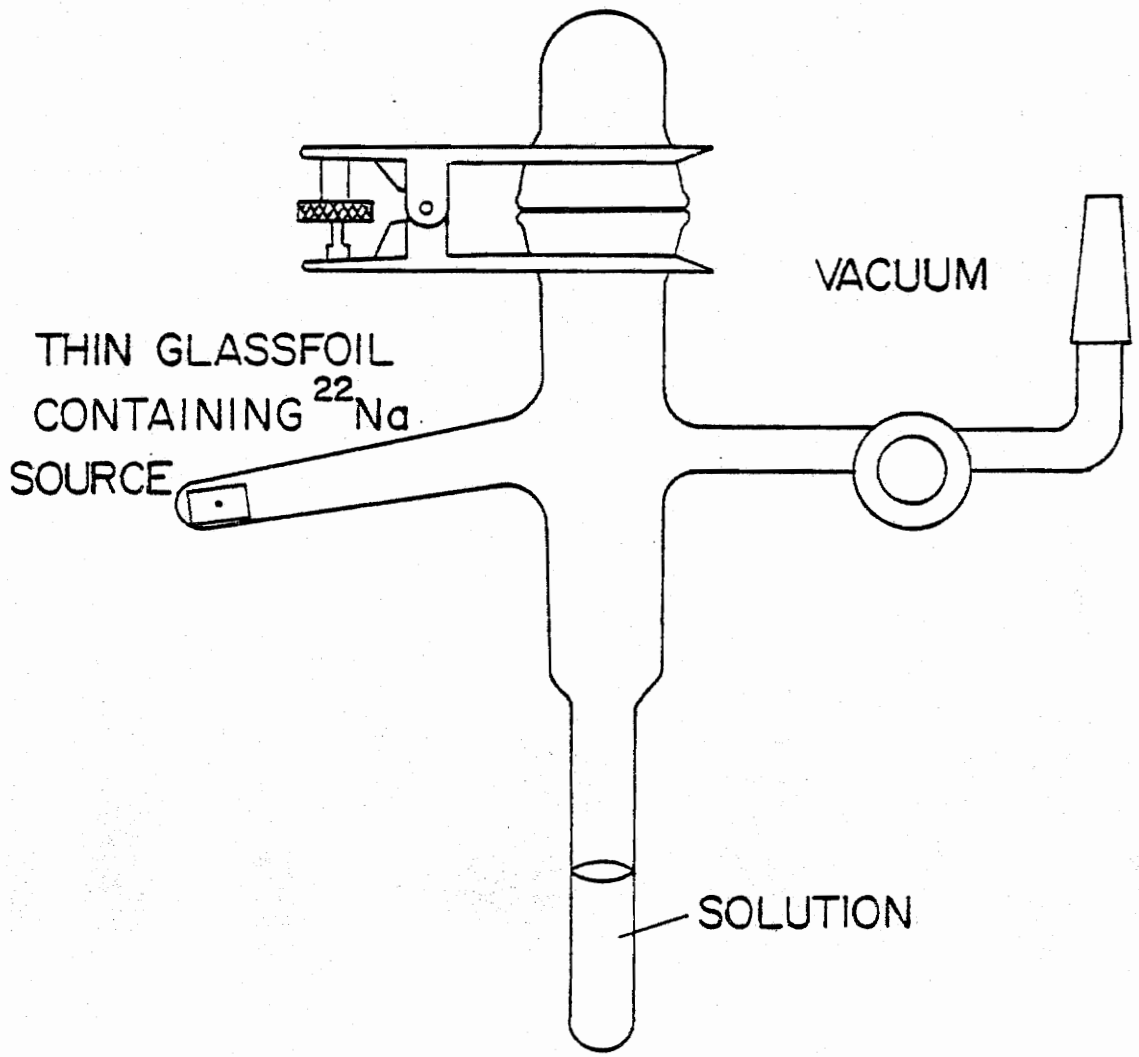


Figure 17. (a) Sample Vial Used at Room Temperature

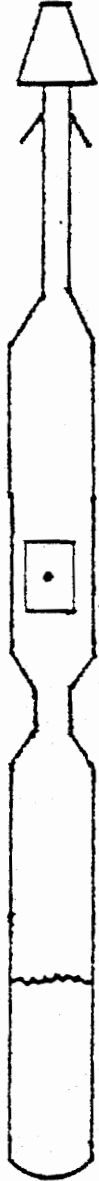


Figure 17. (b) Sample Vial Used at Variable Temperatures

CHAPTER III: POSITRONIUM FORMATION IN ORGANIC LIQUIDS

A. Introduction:

The exact mechanism for the formation of positronium is still the subject of considerable discussion. While for the formation of Ps atoms in gases the Ore gap model,¹⁵ which assumes that positrons slowing down from higher energies pass through an energy gap in which they are capable of abstracting electrons from the surrounding matter to form Ps (Chapter I), is the generally accepted model, other authors suggested that in liquids and solutions other mechanisms such as the combination of a positron and a secondary electron in the positron spur must be considered, which led to the postulation of the spur reaction¹⁸ and the modified spur reaction model²¹ (Chapter I).

Most of the studies on the Ps formation process were carried out via positron lifetime measurements (Chapter II). These studies have shown that the number of o-Ps atoms reaching thermal energies and reacting as such with the surrounding matter can be correlated with the intensity, I_2 , of the longlived component in the positron lifetime spectra.

They also revealed that certain compounds when added to a solution facilitate a strong reduction in I_2 . Several mechanisms have been proposed to account for this experimental observation.^{18, 21, 34-56}

In terms of the "Ore" model for Ps formation, this phenomenon could be explained in: (1) reactions of "hot" (nonthermal) Ps atoms^{35-39, 47} which will reduce the number of o-Ps reacting thermal energies or by (2) inhibition of o-Ps formation (in the Ore gap) either by "slowing down" or by positron capture.³⁶ Alternatively, consistent

with the spur reaction model, (3) inhibition of Ps formation may be caused by electron scavenging, which reduces the number of electrons available for combination with the positron.^{18, 40-44, 48-52.}

The "modified spur reaction model"²¹ combines the concept of Ps formation in the positron spur with subsequent fast interactions between the (hot) Ps atom and the substrates present in the spur, e.g. radicals generated by the positron or others which can form Ps compounds. According to this model, I_2 can be reduced either as the result of electron scavenging by solutes, which suppresses Ps formation, or in "hot" Ps reactions, or by both mechanisms.

The experimental results obtained so far appear to indicate that none of these models can explain satisfactorily all the experimental details without making several ad hoc assumptions. One of the criticisms of the "Ore" or "modified Ore" model is among others that it is not capable of explaining the so-called "antiinhibition effect"⁵² of substances such as C_6F_6 , which when added to solutions containing CCl_4 cause an increase of I_2 , without making some speculative assumptions about positron or positronium affinities, or the sharp decrease of I_2 when small amounts of CS_2 are added to certain hydrocarbons and the subsequent increase of I_2 at higher CS_2 concentrations.⁴⁹ On the other hand, the spur reaction model¹⁸, which tries to relate radiation chemical phenomena occurring in electron spurs to the Ps formation process, fails to provide an explanation for the fact e.g. that the I_2 values in solutions of halogenated halobenzenes in organic solvents level off at higher solute concentrations⁴⁸, a behavior which does not conform with a model which considers competition between positron-electron combination

process and the removal of electrons by the solute, acting as electron scavengers. However, in other aspects there are clear parallels between radiation chemical processes in electron spurs and the positronium formation process, e.g. as far as the dependence of I_2 on the nature and composition of the solvent is concerned.^{41, 49}

Thus, in order to formulate a model which can more accurately describe the detailed mechanism of the Ps formation, we have carried out several series of experiments, in which we further assessed the parameters responsible for changes in the observed I_2 values in various solutions of compounds, such as the halogenated aliphatic and aromatic hydrocarbons. For these compounds, the electron attachment cross sections have been previously measured as a function of electron energy (in the gas phase) and an attempt was made to correlate these parameters with I_2 , in order to further elucidate the exact Ps formation process.

B. Purity and Source of Reagents

The halogenated compounds such as CCl_4 , $CHCl_3$, CH_2Cl_2 , C_2HCl_2 , $1, 1, 1-C_2H_3Cl_3$, $O-C_6H_4CH_3Br$, $O-C_6H_4Cl_2$, C_6H_5Br , $O-C_6H_4ClCH_3$, C_6H_6 , C_6H_5Cl and other mono and dihalobenzene were of high available purity and redistilled and dried by means of molecular sieves.

C. Results and Discussion:

In the first series of experiments, positron lifetime spectra were obtained in various benzene solutions containing 0.1 Mole fraction of chlorinated or brominated hydrocarbons. Consistent with previous results⁵⁷, in each case the I_2 values are significantly reduced in comparison with the I_2^0 observed in neat benzene (table 1). A typical

TABLE I. I_2 (%) and ΔI_2 (%) Values Observed in Benzene Solutions of Various Compounds

Compd	peak energy, eV	peak cross section, cm^2	$I_2^{\text{sat.}}$, % (10 mol % in benzene)	I_2 , % (plateau)	ΔI_2 , %																																																														
CCl_4	0.038	2.62×10^{-14}	2.3	12.9	28.3																																																														
	0.78	5.2×10^{-16}				CHCl_3	0.038	3.66×10^{-16}	5.7	27.5	13.7	0.215	7.32×10^{-16}	CH_2Cl_2	0.038	1.48×10^{-18}	9.9	33.8	7.4	0.45	3.18×10^{-18}	C_2HCl_3	0.39	2.84×10^{-16}	7.2	30.6	10.6	$1,1,1\text{-C}_2\text{H}_3\text{Cl}_3$	0.038	1.51×10^{-15}	5.2	26.8	14.4	$o\text{-C}_6\text{H}_4\text{CH}_3\text{Br}$	0.95	6.0×10^{-17}	9.75	33.5	7.7	$o\text{-C}_6\text{H}_4\text{Cl}_2$	0.36	4.3×10^{-16}	8.5	26.9	14.9	$\text{C}_6\text{H}_5\text{Br}$	0.84	0.6×10^{-17}	8.2	32.4	8.8	$o\text{-C}_6\text{H}_4\text{ClCH}_3$	1.10	2.2×10^{-17}	13.6	36.2	5.0	C_6F_6	~ 0.0	1.23×10^{-14}	40.5	41.2		0.73	8.04×10^{-16}	$\text{C}_6\text{H}_5\text{Cl}$	0.86
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	0.215	7.32×10^{-16}				CH_2Cl_2	0.038	1.48×10^{-18}	9.9	33.8	7.4	0.45	3.18×10^{-18}	C_2HCl_3	0.39	2.84×10^{-16}	7.2	30.6	10.6	$1,1,1\text{-C}_2\text{H}_3\text{Cl}_3$	0.038	1.51×10^{-15}	5.2	26.8	14.4	$o\text{-C}_6\text{H}_4\text{CH}_3\text{Br}$	0.95	6.0×10^{-17}	9.75	33.5	7.7	$o\text{-C}_6\text{H}_4\text{Cl}_2$	0.36	4.3×10^{-16}	8.5	26.9	14.9	$\text{C}_6\text{H}_5\text{Br}$	0.84	0.6×10^{-17}	8.2	32.4	8.8	$o\text{-C}_6\text{H}_4\text{ClCH}_3$	1.10	2.2×10^{-17}	13.6	36.2	5.0	C_6F_6	~ 0.0	1.23×10^{-14}	40.5	41.2		0.73	8.04×10^{-16}	$\text{C}_6\text{H}_5\text{Cl}$	0.86	1.4×10^{-17}	13.7	35.5	5.7				
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	0.45	3.18×10^{-18}				C_2HCl_3	0.39	2.84×10^{-16}	7.2	30.6	10.6	$1,1,1\text{-C}_2\text{H}_3\text{Cl}_3$	0.038	1.51×10^{-15}	5.2	26.8	14.4	$o\text{-C}_6\text{H}_4\text{CH}_3\text{Br}$	0.95	6.0×10^{-17}	9.75	33.5	7.7	$o\text{-C}_6\text{H}_4\text{Cl}_2$	0.36	4.3×10^{-16}	8.5	26.9	14.9	$\text{C}_6\text{H}_5\text{Br}$	0.84	0.6×10^{-17}	8.2	32.4	8.8	$o\text{-C}_6\text{H}_4\text{ClCH}_3$	1.10	2.2×10^{-17}	13.6	36.2	5.0	C_6F_6	~ 0.0	1.23×10^{-14}	40.5	41.2		0.73	8.04×10^{-16}	$\text{C}_6\text{H}_5\text{Cl}$	0.86	1.4×10^{-17}	13.7	35.5	5.7												
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plot of I_2 vs. Mole fraction of an additive, in this case o-, p- and m-dibromobenzene, is shown in fig. 18.

If the electron-positron combination in the positron spur can be compared with the electron-ion recombination in the electron spur, as postulated by the spur reaction model, a simple competitive model can be derived to describe the removal of free electrons by the scavenger. The following correlation between the o-Ps formation probability P at a given solute concentration $[M]$ is obtained:⁵⁰

$$P = P^0 / (1 + K[M]) \quad (17)$$

$$\text{or } (P^0/P - 1) = K[M] \quad (18)$$

K is the scavenging or inhibition constant for the scavenging reaction between solute and electrons and P^0 the o-Ps formation probability in the neat solvent. Since P^0 and P can be correlated with I_2 and I_2^0 , the results shown in fig. 19, where $(I_2^0/I_2 - 1)$ is plotted as a function of solute concentration, m-dichlorobenzene or m-dibromobenzene in benzene solution, indicate that the simple correlation between positronium formation probability and inhibition constant as formulated in eq. 18 does not apply even at low solute concentrations in nonpolar solvents. Levay and Mogensen,⁵⁰ who investigated similar systems claimed that the empirical expression using a second adjustable parameter, α , in the exponent, provides a better fit:

$$P = P^0 / (1 + (K[M])^\alpha) \quad (19)$$

We find it very difficult to fit our results as shown in fig. 18 and 19 to this expression, or to a modified version of eq. 18, which was suggested by Eldrup et al.⁴² for aqueous solutions of certain

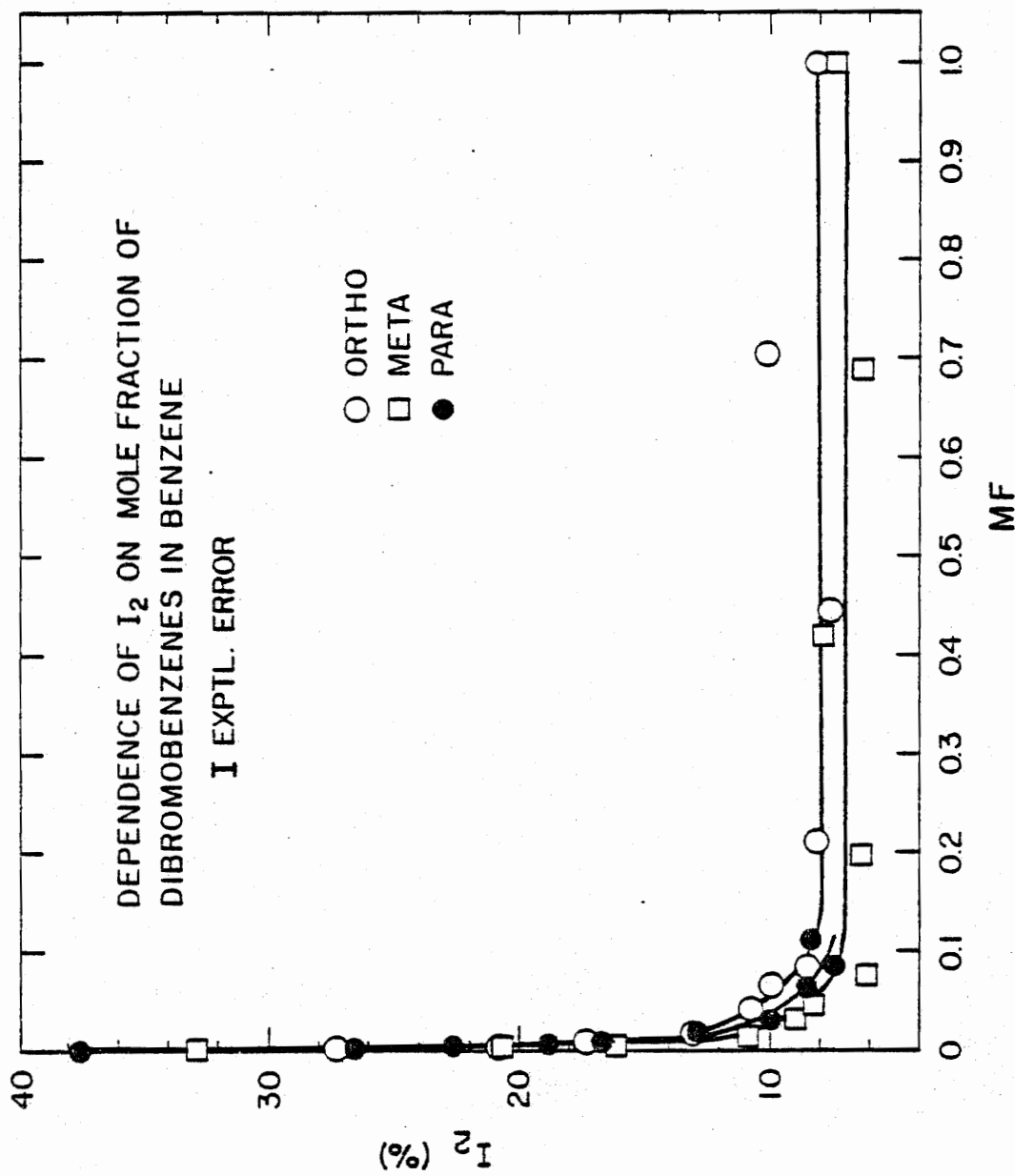


Figure 13. I_2 vs Mole Fraction o-, p- or m- dibromobenzene in Benzene (at room temperature)

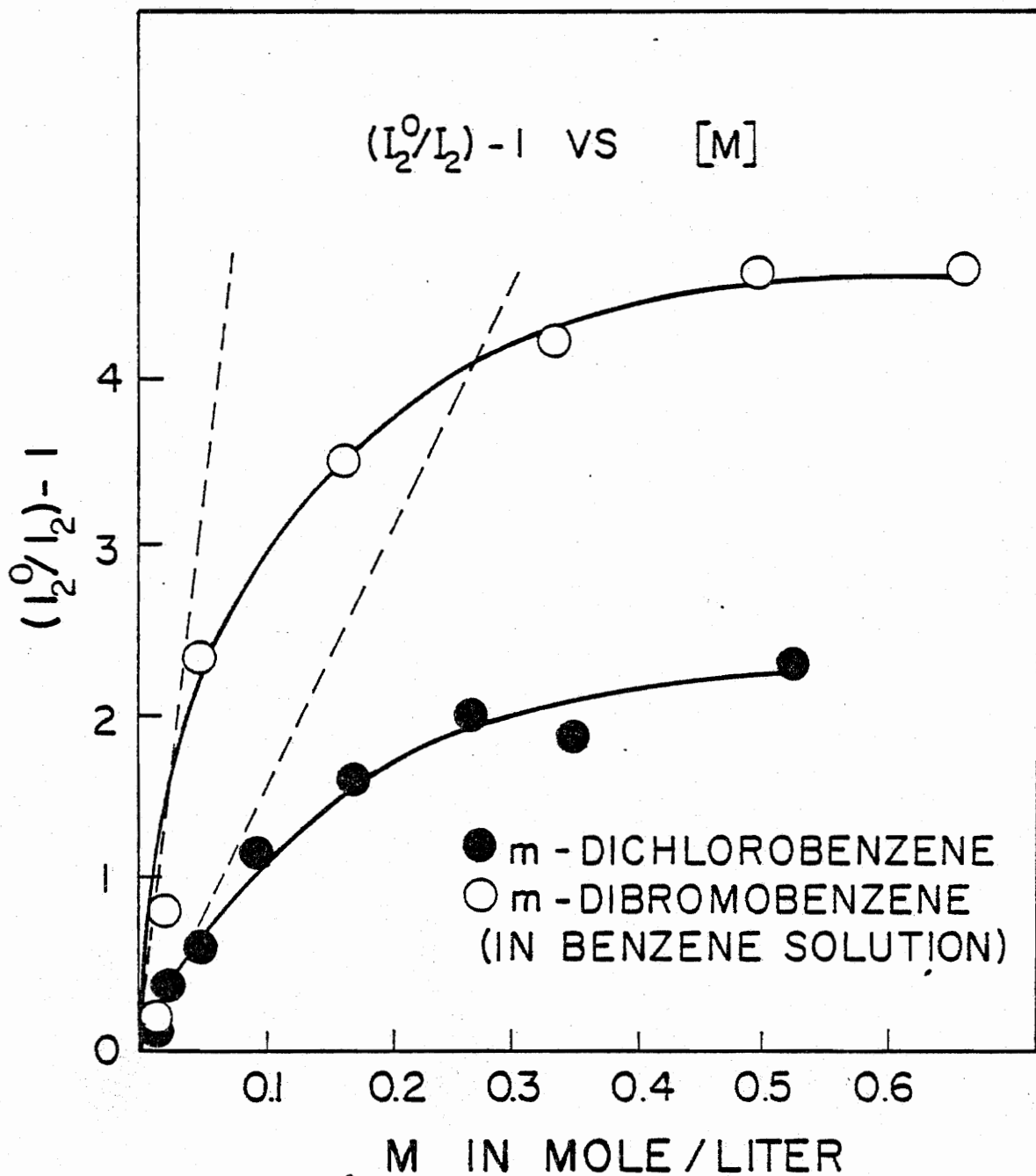


Figure 19. $(I_2^0/I_2 - 1)$ vs $[M]$ in Benzene Solutions of m-Dichlorobenzene and m-dibromobenzene

inorganic ions,

$$P = P^0(1-A)/(1+K[M]) + A \quad (20)$$

where A is a constant related to the saturation value of I_2 obtained at higher solute concentration.

Since there is no strict theoretical justification for either one of these expressions, we have not further pursued this line of interpretation and conclude that these results do not provide any evidence for a positronium formation mechanism which involves simple competition for electrons between positrons and solute species.

In the past, similar results, e.g. the variance in the I_2 observed for neat halogenated hydrocarbons, were explained qualitatively in terms of hot Ps reactions,⁸ (modified Ore model for Ps formation) and related to the C-halogen bond energies by using the correlation:

$$I_2 \sim \frac{D_{RX} - D_{PsX}}{I_{RX}} \quad (21)$$

where I_{RX} is the ionization potential of the halogenated hydrocarbon D_{RX} the C-halogen bond dissociation energy and D_{PsX} the Ps-halogen bond energy. Since, according to the Ore model, Ps atoms are formed in the Ore gap with energies from 6.8 eV to thermal, only the fraction of Ps atoms with kinetic energies above $D_{RX} - D_{PsX}$ can effectively react with the compound and undergo subsequent rapid annihilation in the reaction product. I_2 should therefore vary as a function of D_{RX} . While this trend has been qualitatively observed in a number of solutions and is also in qualitative agreement with the results of the present study, and would easily explain the saturation values, I_2 sat., which I_2

assumes at higher solute concentrations, as shown for $C_6H_4Br_2 - C_6H_6$ solutions in fig. 18, one would also have to consider the possibility that the electron attachment to these compounds followed by dissociation which would remove electrons from the spur may show a similar trend:



which can reduce the number of available electrons in this manner.

Thus in a second series of experiments, we tried to correlate the total reduction of the number of thermalized o-Ps atoms, which is proportional to $(I_2^0 - I_2^{sat.})$, caused by the presence of the solute with the properties of the solute molecules which control the dissociative electron attachment process.

In a previous study, Ache⁴⁸ et al. have found that the logarithm of the inhibition constant K increases linearly with the free energy change, $-\Delta G$, for the one electron transfer process $A_{aq}^{n+} + e^- \longrightarrow A_{aq}^{(n-1)+}$ for the corresponding scavenger ions in aqueous solutions and suggested that the energy maximum of the cross section curve for electron attachment coincides with the free energy change in this process.

As an analogy to this relationship, we tested whether a similar correlation would apply for organic compounds in a relative inert solvent such as benzene. Thus, as mentioned above, I_2 was measured in various benzene solutions containing 0.1 Mole fraction of a chlorinated or brominated hydrocarbon known to undergo dissociative electron attachment resulting in the formation of Cl^- or Br^- ions. The concentration of 0.1 Mole fraction of solute was chosen because at that point, in practically every case, the I_2 saturation value, $I_2^{sat.}$ was already reached. On the other hand, the solute concentration is

still reasonably low so that it is not expected to change significantly the spur properties, if indeed, the spur model applies. The results are listed in table 1. In order to correlate I_2^{sat} with the solute properties, one would need to know the electron attachment cross-section of these compounds as a function of energy in benzene solution. Since these values have never been measured, we had to rely on the corresponding cross-section found for these compounds in the gas phase.⁵⁷⁻⁶⁰ The limitations of such a comparison have been thoroughly discussed by Christophorou et al.⁵⁹ and by Allen et al.⁶¹ It is clear that this approach can be only a first approximation.

Thus, in order to correlate I_2^{sat} with the parameters responsible for the electron attachment to these compounds, I_2^{sat} was plotted as a function of the previously reported peak energies for (dissociative) electron attachment (fig. 20) and also shown in fig. 21 as a function of the peak cross sections.⁵⁷⁻⁶⁰ The results would suggest that both factors, i.e. peak energy as well as peak cross section, have a distinct effect on the capability of the additives to suppress thermal o-Ps formation.

A perhaps even better correlation exists if I_2^{sat} is plotted as a function of the activation energy E^* for the dissociative electron attachment to these compounds (fig. 22). As shown by Wentworth et al.⁶²⁻⁶³ for a series of aliphatic halogenated compounds, E^* is linearly related to the change in internal energy ΔE occurring during this process. $\Delta E = D_{\text{AB}} - EA_{\text{B}}$ where D_{AB} is the A-B bond dissociation energy and EA_{B} is the electron affinity of B.

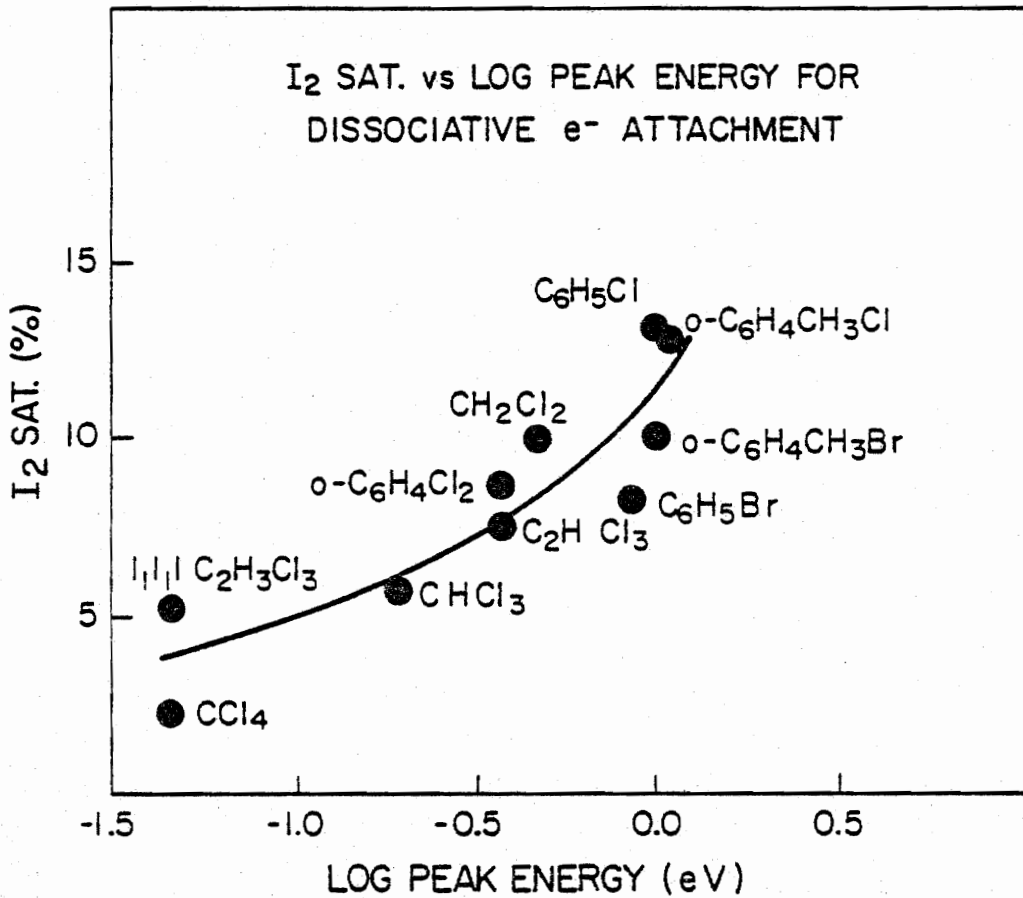


Figure 20. I₂^{sat.} vs Maximum Peak Energy (in eV) for e⁻ Attachment in Benzene Solutions Containing 10 Mole % of the Various Compounds (e⁻ attachment peak energies obtained from ref. 57-59 for the gas phase)

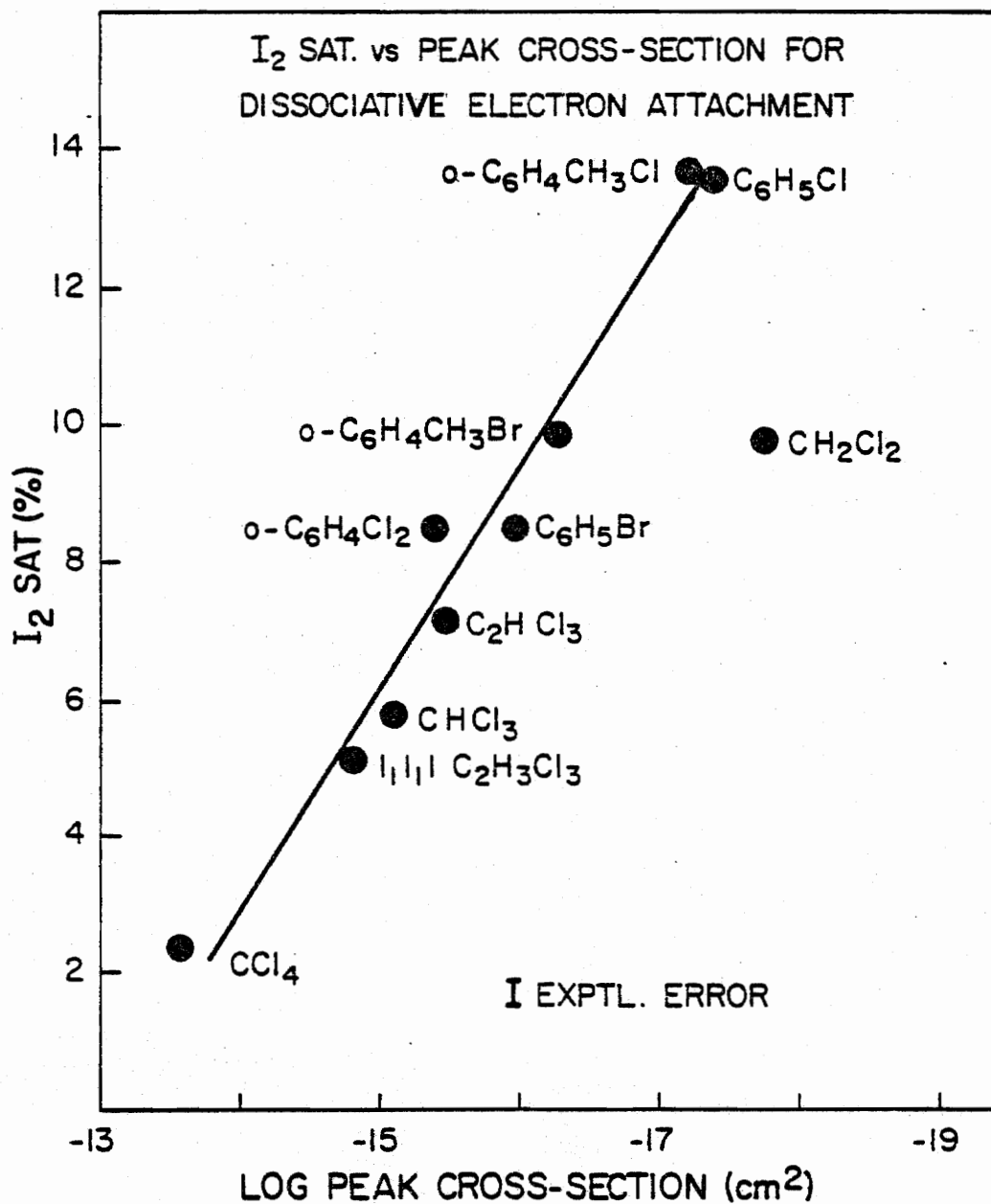


Figure 21. I₂^{sat.} vs Peak Cross Section for e⁻ Attachment in Benzene Solutions Containing 10 Mole % of the Various Compound (e⁻ attachment cross sections obtained from ref. 57-59 for the gas phase)

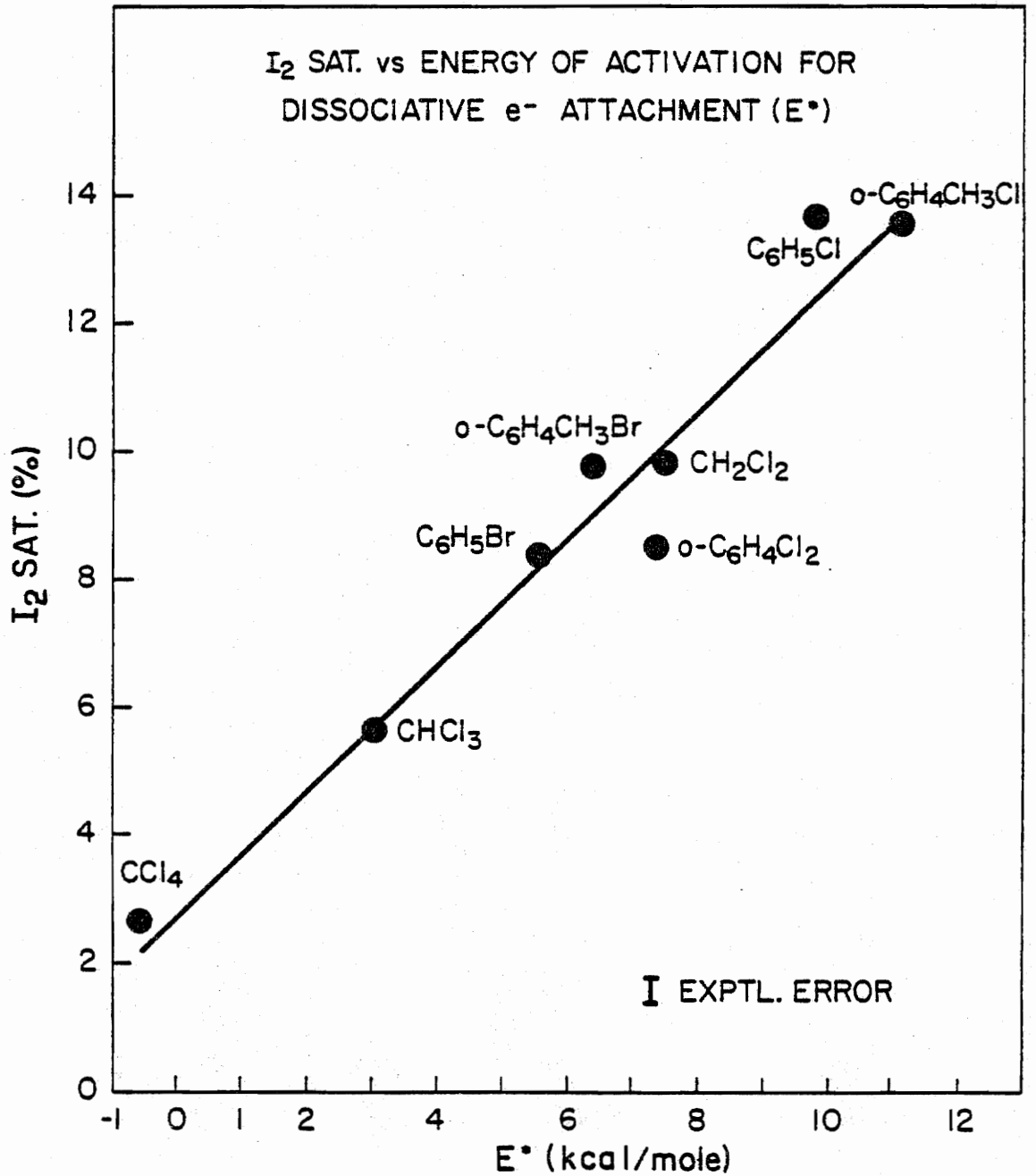


Figure 22. I₂^{sat.} vs E* (energy of activation for thermal electron attachment, from ref. 62-63)

Further evidence for the possible dependence of the number of thermal Ps atoms formed on the solute or solvent interactions with free electrons can be gotten from the results obtained upon addition of compounds such as hexafluorobenzene (which exhibit an extremely large cross-section for non-dissociative electron attachment).

In this series of experiments positron lifetime spectra were obtained in various $C_6H_6-C_6F_6$ mixtures which contained a constant amount, i.e. mole fraction of CCl_4 (10 Mole %) while the mole fraction of C_6H_6 and C_6F_6 was varied.

As it can be seen from fig. 23, where I_2 is plotted as a function of $[C_6F_6]/[C_6F_6] + [C_6H_6]$, I_2 increases from 2.3% in pure benzene (+10 Mole % CCl_4) to reach a plateau of 12.9% at about 0.1 MF of C_6F_6 . At higher C_6F_6 concentrations, I_2 slightly decreases before it further increases to approach eventually 41.2% in pure C_6F_6 (+10 Mole % CCl_4) solutions. Similar results are obtained in cyclohexane solution, although the plateau region is reached in this case only at higher C_6F_6 concentrations.

These experiments differ from those carried out previously by Anisimov et al.⁵² in the respect that, in these studies, the mole fraction of CCl_4 was kept constant while the other authors used a constant volume fraction of CCl_4 solution which leads to considerable changes of the number of CCl_4 molecules present in the various solutions. The slight decrease of I_2 in the concentration range of 0.4-0.5 MF C_6F_6 in $C_6H_6-C_6F_6-CCl_4$ solutions is real and probably a result of the sharp decrease of I_2 in neat $C_6F_6-C_6H_6$ mixtures as indicated in fig. 24.

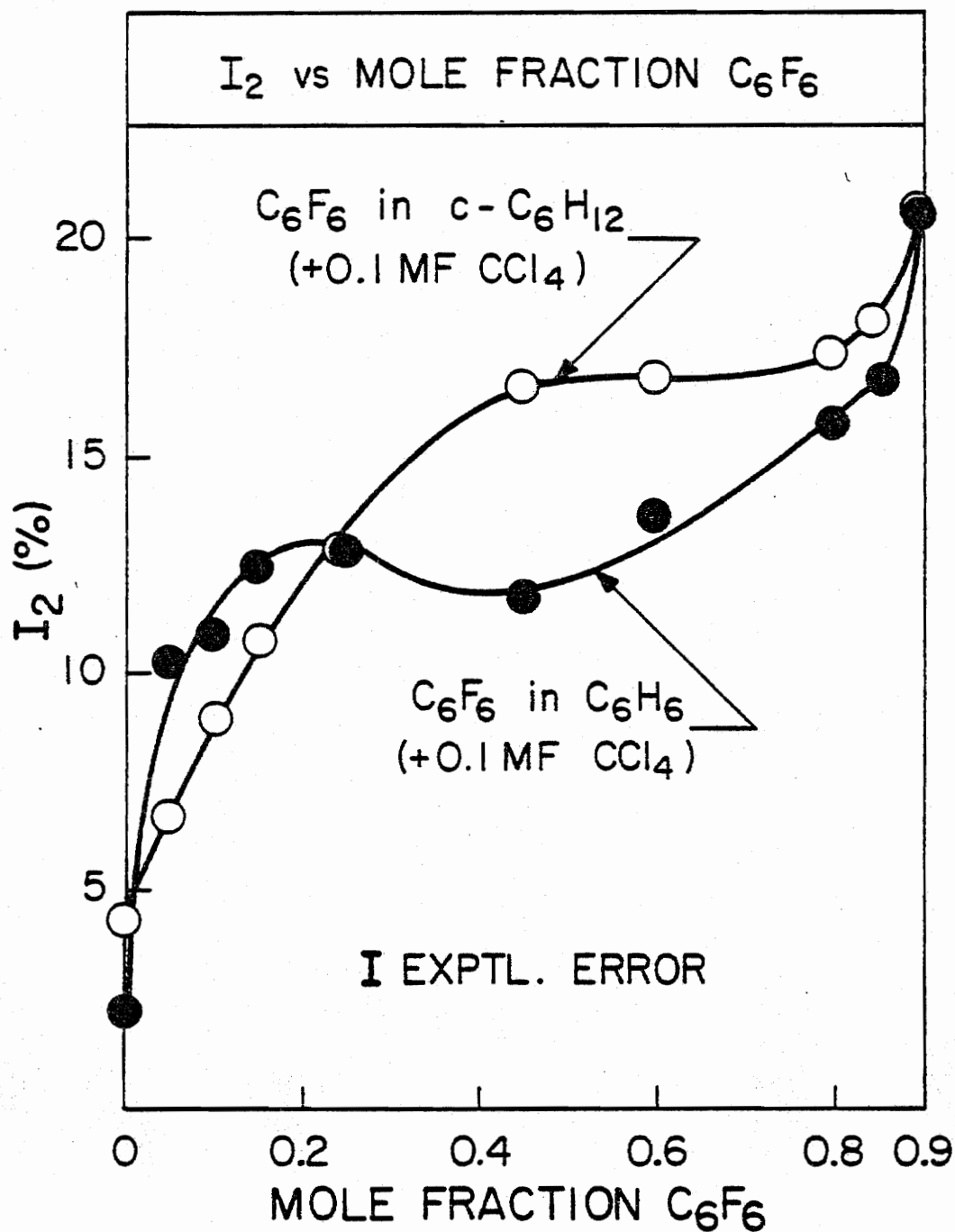


Figure 23. I₂ vs Mole Fraction of C₆F₆ in Solutions of Benzene and Cyclohexane Containing 0.1 Mole Fraction CCl₄

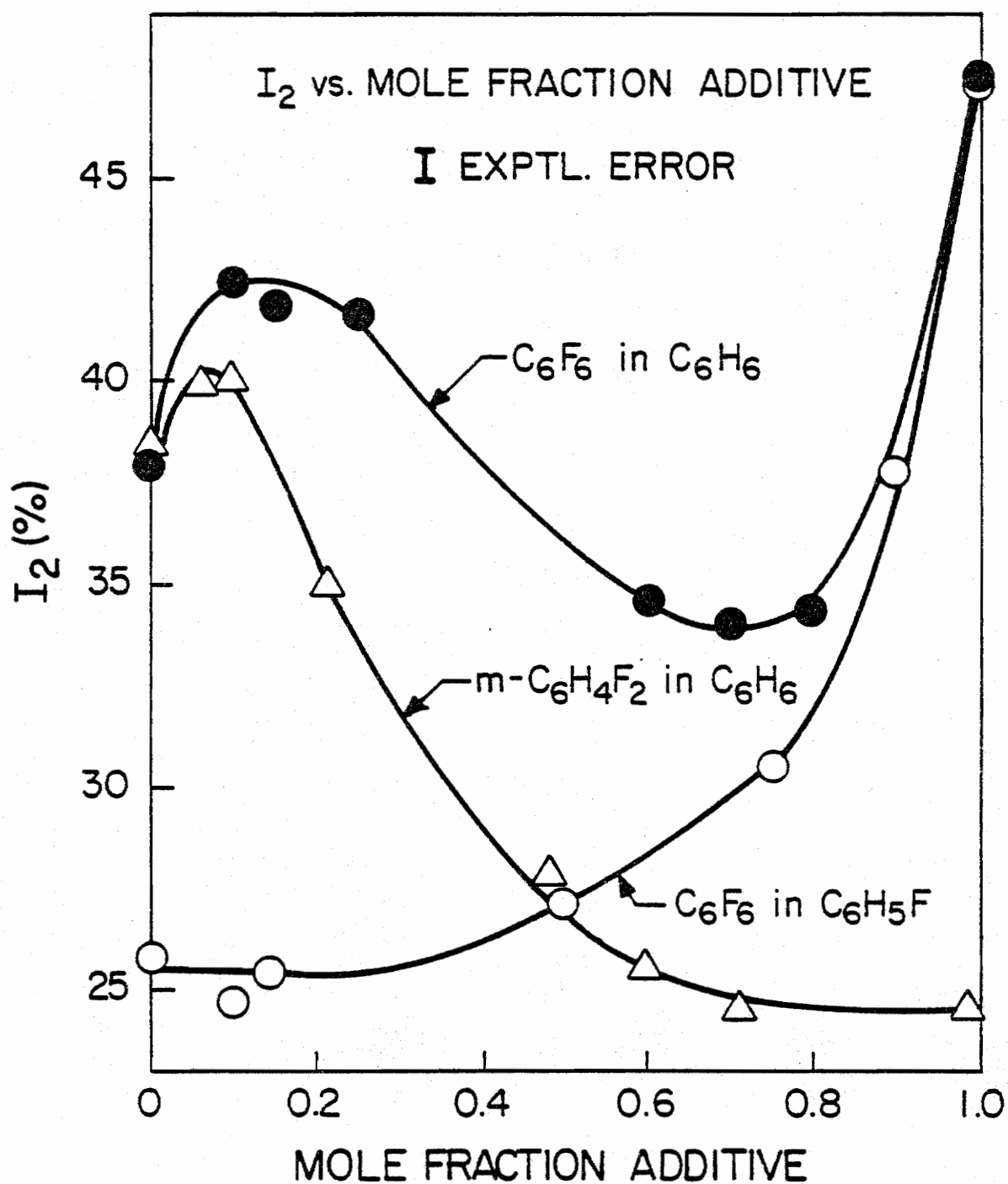


Figure 24. I_2 vs Mole Fraction of Additive in Solutions of C_6F_6 in C_6H_6 , $m-C_6H_4F_2$ in C_6H_6 and C_6F_6 in C_6H_5F

One can assume that electrons formed in the positron spur in $C_6H_6-CCl_4$ mixtures become preferentially attached to CCl_4 , which dissociates into CCl_3 and Cl^- . In the presence of increasing amounts of C_6F_6 , which has also a high cross-section for electron attachment, more and more electrons will become attached to C_6F_6 which competes for electrons with CCl_4 . In contrast to CCl_4 , however, the attachment to C_6F_6 is non-dissociative. Thus, the overall result of adding C_6F_6 or similar compounds to solutions is that fewer free electrons are available in the positron spurs to undergo dissociative attachment processes. This, again, emphasizes the role of free electrons in determining the number of thermal positronium atoms reaching thermal energies as indicated by the effect of these former compounds on the I_2 values.

These experiments were extended to study positron annihilation in benzene solutions of a series of compounds which are known to undergo dissociative electron attachment, such as: $CHCl_3$, CH_2Cl_2 , C_2HCl_3 , 1, 1, 1 $C_2H_3Cl_3$, $o-C_6H_4CH_3Br$, $o-C_6H_4Cl_2$, $o-C_6H_4CH_3Cl$, C_6H_5Br and C_6H_5Cl . As in the case of the $C_6F_6-C_6H_6-CCl_4$ system I_2 was determined as function of the mole fraction $[C_6F_6]/([C_6F_6] + [C_6H_6])$ in solutions containing 10 Mole % of the additive. Similar to the $C_6F_6-C_6H_6-CCl_4$ system, small amounts of C_6F_6 result in a drastic increase of I_2 leveling off to a plateau at about 0.1 MF of C_6F_6 present, followed by a second increase of I_2 with about 0.8 MF of C_6F_6 added. The I_2 's observed in the plateau region are listed in table 1. As a measure of the effectiveness of these solutes to compete with C_6F_6 for electrons we defined as ΔI_2 , the difference between the I_2 's of the

plateau observed in each of these mixtures and I_2 in $C_6H_6-C_6F_6$ solutions without any other additive present, measured over the same $C_6H_6-C_6F_6$ composition range. This procedure is schematically shown for CCl_4 and C_6H_5Br additives in fig. 25 and the ΔI_2 's are listed in table 1.

A large ΔI_2 would indicate that the additive effectively competes with the C_6F_6 for electrons and vice versa. A first qualitative evaluation of these data can be obtained by plotting ΔI_2 as function of the peak energies, peak cross section, or E^* , the activation energy for e^- attachment. (fig. 26, 27 and 28) The smooth correlation between ΔI_2 and these electron attachment parameters seems to confirm the expected trends. These results are in line with the observations that if a compound with a higher non-dissociative electron attachment peak energy and a definitely less expanded energy range in which it can attract electrons, combined with a smaller attachment cross-section such as $m-C_6H_4F_2$ is added to a solution containing CCl_4 , it cannot compete with CCl_4 for electrons and I_2 does not increase. On the other hand, a partial effect is seen in the case of C_6H_5Br or $C_6H_4Cl_2$ solutions, where the solutes have comparable cross-sections for electron attachment and a slight enhancement in I_2 can be observed as demonstrated in fig. 29.

Summarizing the results so far, one would have to draw the conclusion that the kinetic analysis of the I_2 data obtained with increasing amounts of chlorinated or brominated hydrocarbons present in neat benzene as solvent provides little evidence for a competition between solute species and positrons for free electrons as formulated in eq. 18, 19 or

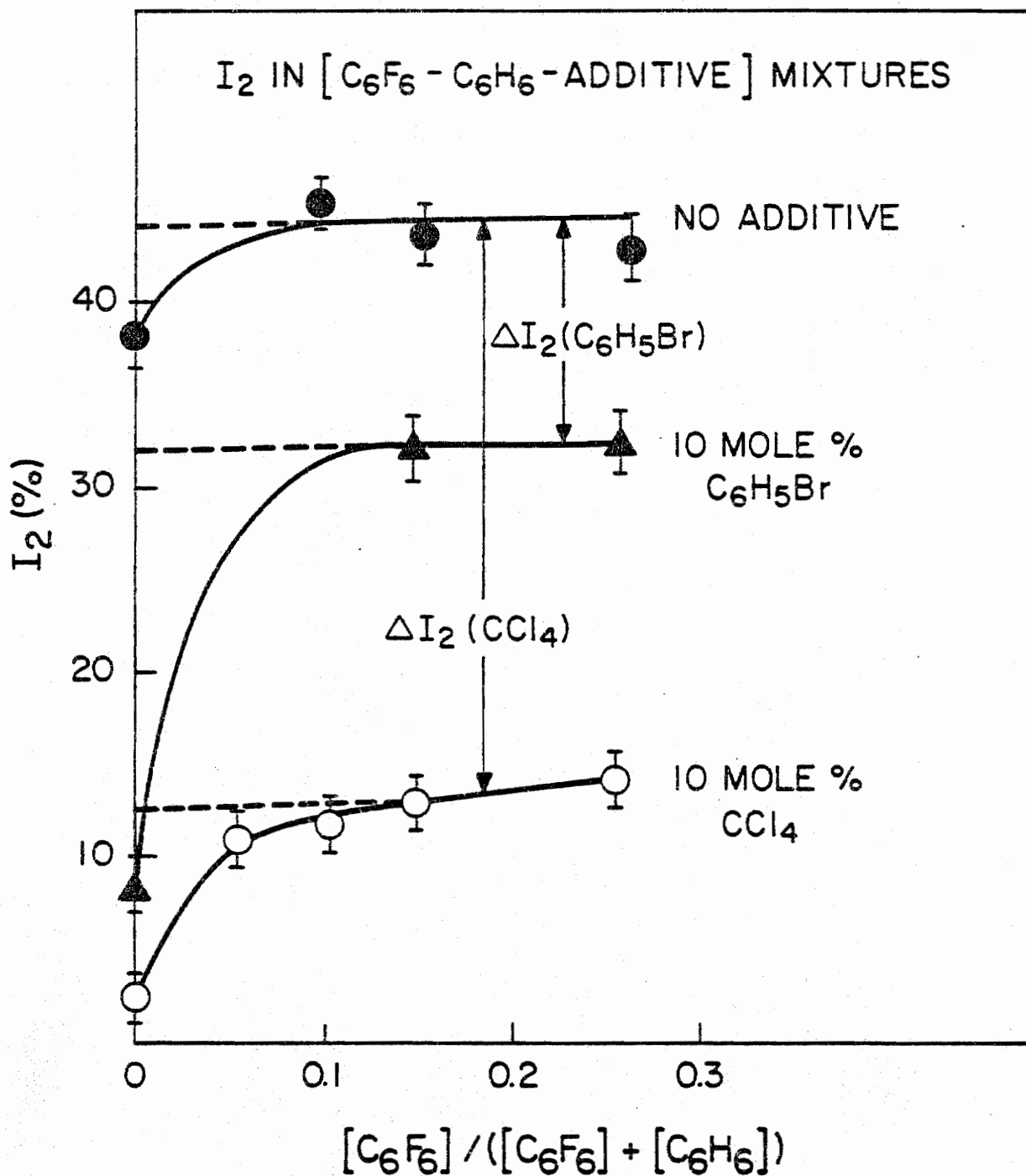


Figure 25. I_2 in $[C_6F_6 - C_6H_6 - \text{additive}]$ Mixtures as a Function of $[C_6F_6] / [C_6F_6 + C_6H_6]$. The Mixtures Contain Consistently 10 Mole % Additive

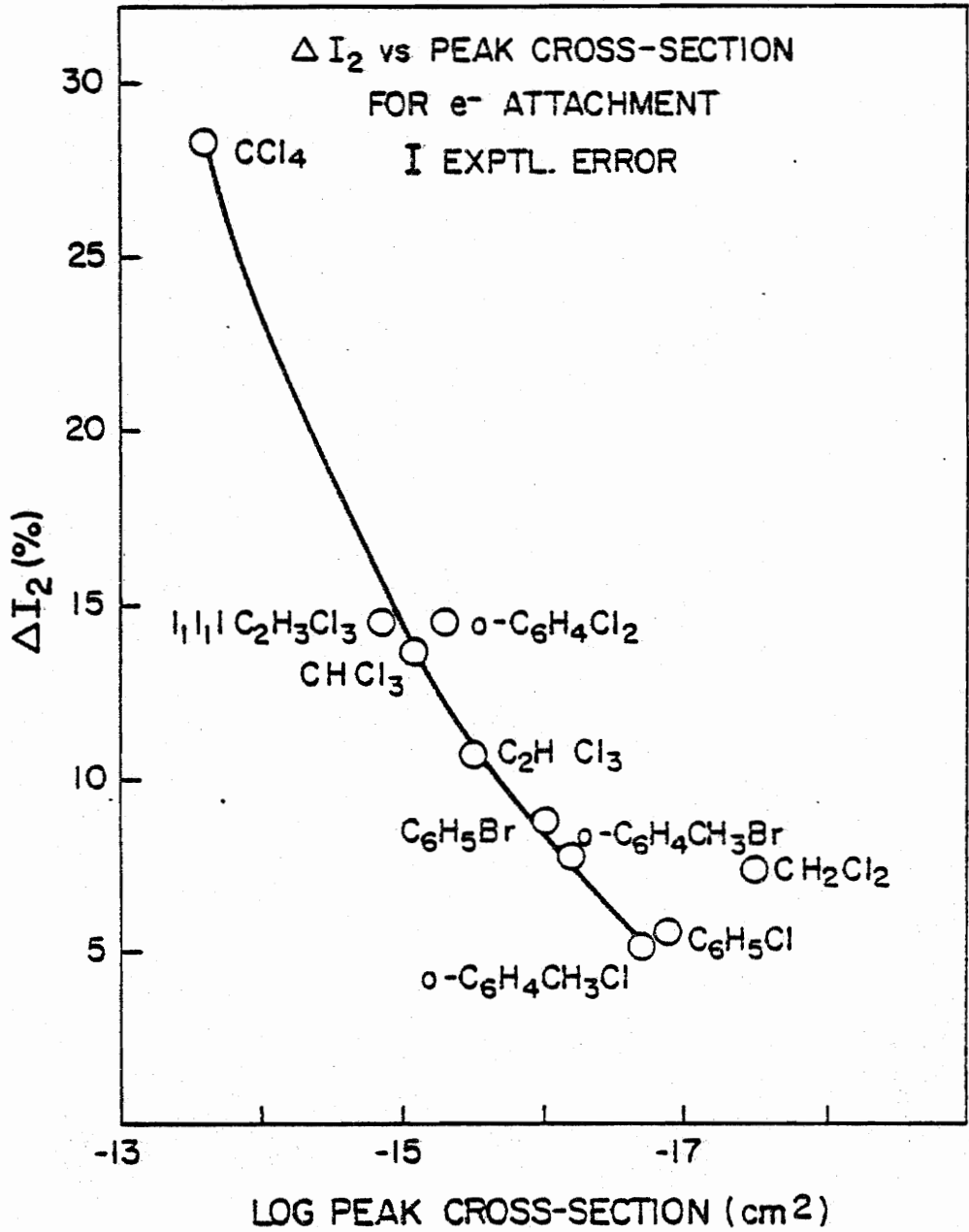


Figure 26. ΔI_2 vs Log Peak Cross Section for e^- Attachment in $C_6H_6-C_6F_6$ Solutions at Room Temperature Containing 10 Mole % of Additive (e^- attachment cross section from ref. 57-59)

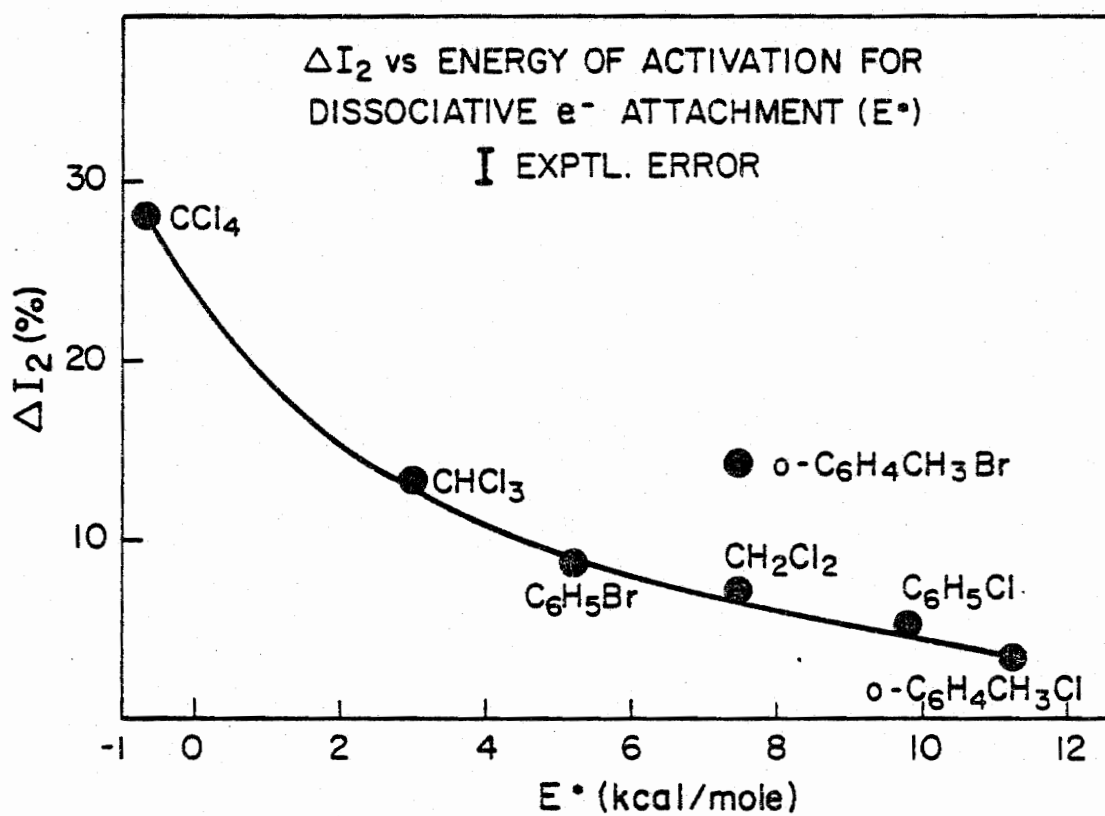


Figure 27. ΔI_2 vs Log Peak Energy for e^- Attachment in $\text{C}_6\text{H}_6\text{-C}_6\text{F}_6$ Solutions at Room Temperature Containing 10 Mole % Additive (peak energies taken from ref. 57-59)

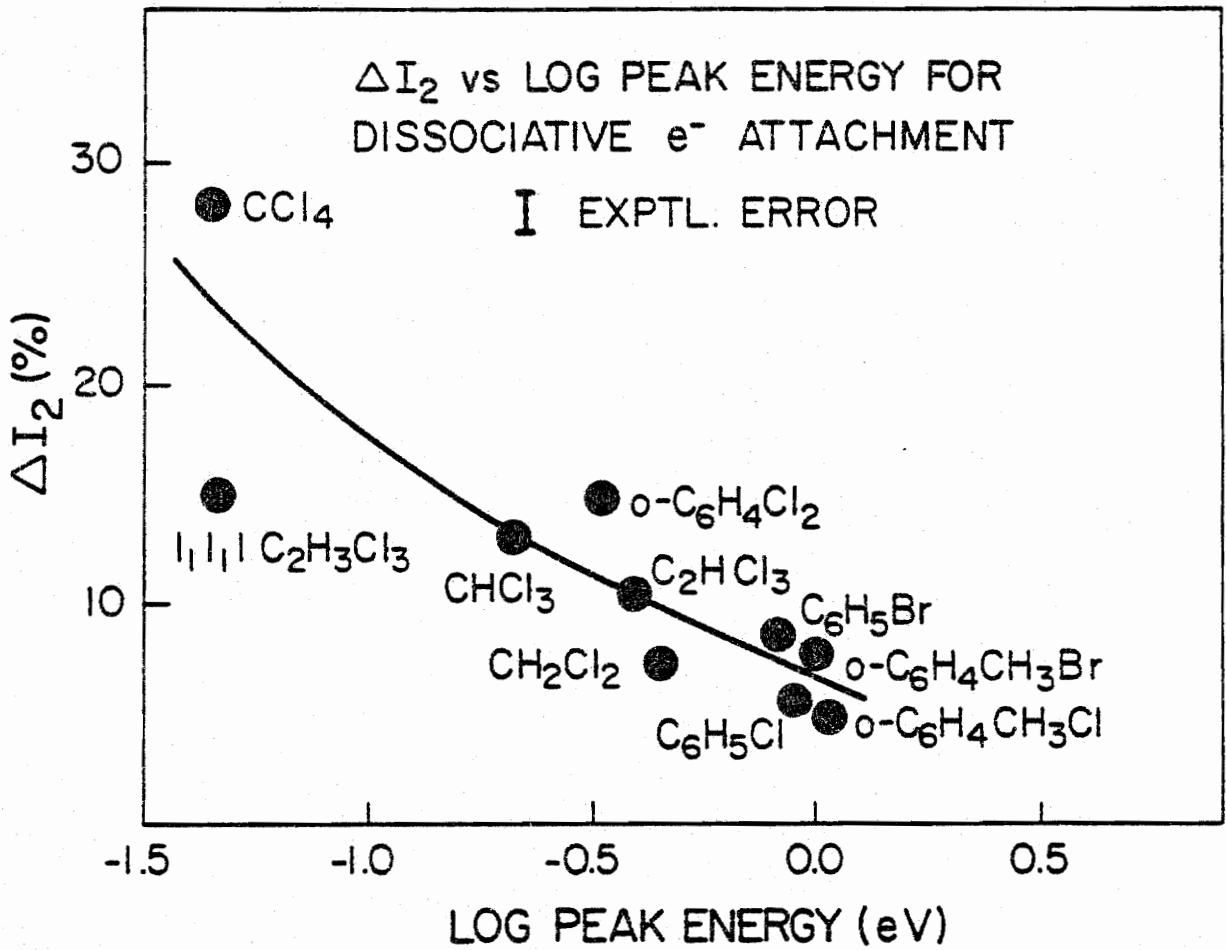


Figure 28. ΔI_2 vs E^* , the Activation Energy for Electron Attachment (E^* from ref. 62-63)

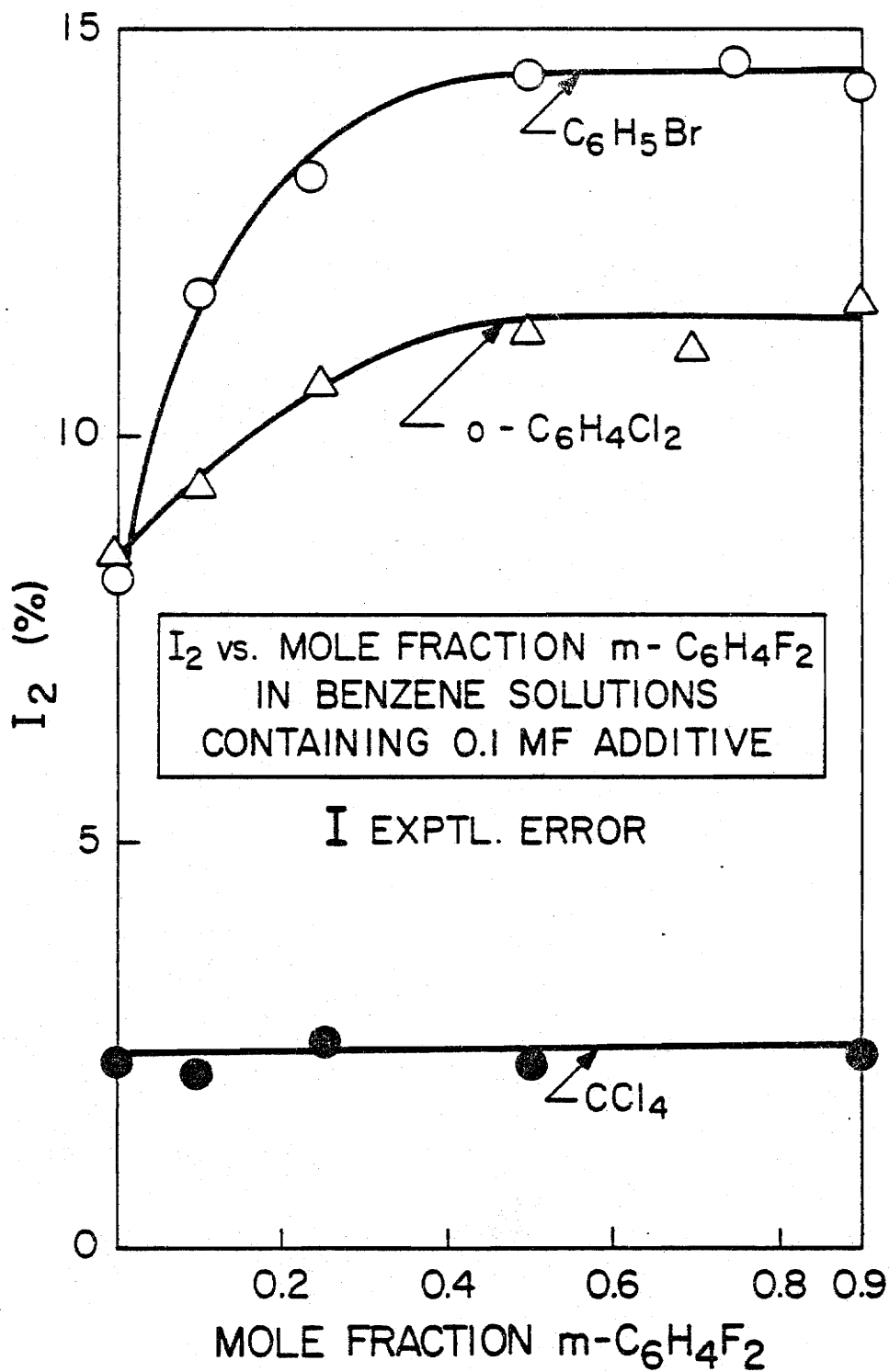


Figure 29. I₂ vs Mole Fraction of *m*-C₆H₄F₂ in Benzene Solutions Containing 0.1 Mole Fraction Additive

20 which casts some doubt on the applicability of the spur reaction model. On the other hand, the I_2^{sat} values observed at somewhat higher solute concentration, as well as the effect of CCl_4 , clearly suggest that the presence or absence of free electrons in the solutions has a profound effect on I_2 , i.e., on the number of Ps atoms reaching thermal energies.

It seems reasonable to consider the observed results in terms of two reaction schemes. In the first one, the assumption shall be made that Ps is formed by energetic positrons abstracting electrons from the surrounding. This would correspond to the classical Ore model,¹⁵ whose applicability has been supported in gas phase experiments. In any solvent, the Ps formed in this manner will, however, be surrounded by transient species, such as dry or solvated electrons and other reactive species formed in the positron spur by radiolysis. Rapid reactions of the Ps with these species may occur; so that, in a given solvent, only a certain number of these Ps atoms reach thermal energies. As an overall result I_2 , i.e., the number of Ps atoms reaching thermal energies in the neat solvent, will not only be governed by the number of Ps initially formed, which depend on the nature of the solvent, but also by the subsequent reactions of the "hot" Ps with radiolytic species, which prevent the Ps from reaching thermal energies. The effect of an added solute, such as CCl_4 , on the number of thermal Ps atoms could in this case be explained by either assuming that "hot" Ps react with CCl_4 itself, followed very rapidly by almost immediate positron annihilation from the reaction products, or that Ps atoms react with one of the

transient species; again, leading to rapid annihilation.

The fact that the addition of C_6F_6 increases the number of Ps atoms makes it very doubtful that the "hot" Ps reactions with CCl_4 are the only processes occurring. As discussed above, C_6F_6 will scavenge electrons and thus reduce the number of electrons which could directly interact with Ps or the number of products formed in the reactions between electrons and the solute, CCl_4 etc., with which the Ps may subsequently react. The good correlation between $I_2^{sat.}$ and the dissociative electron attachment parameters; especially, the activation energies (as shown in fig. 22) determined from thermal electron attachment, would suggest that the reactive products formed in this radiolysis are organic radicals and halogen ions. Since halogen ions have been shown to be fairly unreactive, it stands to reason that the reactions between the freshly formed Ps and these radicals are responsible for the rapid positron annihilation.

If one wants to adopt this mechanism one would also have to consider the fact that I_2 shows a saturation behavior. To explain this observation, one can postulate that the number of electrons in the spur and their kinetic energy distribution is a constant for all systems; it will be also small compared with the number of solute concentrations where I_2 levels off.

Benzene will not significantly interfere with the electron attachment to the solute or (C_6F_6) since the onset energy for dissociative electron attachment to benzene in the gas phase is comparatively large⁵⁷⁻⁶⁰ and the thermal attachment rate for nondissociate attach-

ment very small, compared with fluorinated compound, see e.g. table 6.8 p. 501 in ref. 57.

Under these conditions, it seems reasonable to assume that all electrons which are energetically capable of carrying out this process, i.e., those which have kinetic energies in excess of the required activation energy for electron attachment, will become attached to the solute of C_6F_6 molecules.

This would explain the observed $I_2^{sat.}$ values and their dependence on the electron attachment parameters, which in turn are related to the corresponding bond dissociation energies.

A distinction between the direct "hot" Ps reactions with the substrate and the reactions of Ps with the reactive species formed in the spur via electron attachment which both should show the same dependence on the bond dissociation energies of the solute^{21, 35-39} molecules involved, can be derived from the experiments in which C_6F_6 has been added.

Because of its low activation energy for non-dissociative electron attachment, C_6F_6 should (at a concentration of 0.1-0.2 MF) have effectively scavenged the available free electrons and protected the solute molecules from radiolysis via dissociative electron attachment.

However, under these conditions where no reactive species should have been formed in the spur, the results showed that I_2 does not increase to the level observed in the absence of the solute. We suggest that this fraction of Ps, which is ΔI_2 , is lost due to direct interaction of Ps as a hot species with the solute, in accordance with the "modified Ore model" (vide supra)^{21, 35-39}.

Thus, as discussed above, a similar dependence should exist between the energies of activation for dissociative e^- attachment and ΔI_2 , if this latter fraction corresponds to hot Ps reactions with solute molecules. This correlation has indeed been observed, fig. 27. This model would be also in agreement with a number of experimental results obtained in aqueous solutions of simple inorganic ions.^{21, 35-39} It would be, however, beyond the scope of this work to review all the experimental observations made in this area within the framework of this thesis.

The starting point of the second reaction scheme is that Ps is formed by a combination of a free positron with an electron.¹⁸ (Spur reaction model)

Its various aspects^{21, 40-44, 48, 52} have been discussed in several papers and shall not be repeated. This model can provide an explanation for most of the experimental observations made in this study.

The effect of C_6F_6 additives can again be understood as non-dissociative electron-attachment of electrons to form $C_6F_6^-$ which have a relatively long lifetime (12 s at ~ 0.0 eV and 1 s at 0.7 eV), from which positrons can subsequently abstract an electron under Ps formation as discussed by Anisimov⁵² et al. in their "antiinhibition effect". Such an abstraction from the considerably more electronegative Cl^- , ion which has an electron affinity of about 3.1 eV, is energetically less favorable than from the $C_6F_6^-$ ion, whose electron affinity is about 1.8 eV.⁵⁹ The fact that C_6F_6 cannot completely

restore the I_2 values to those numbers observed in neat $C_6H_6-C_6F_6$ mixtures may be seen as an inefficient electron abstraction process by the positron from $C_6F_6^-$, although this would not explain the observed correlation between ΔI_2 and the C-X bond dissociation energies.

By making some ad hoc assumptions, e.g., that only dry, i.e., kinetically excited, electrons are involved in the positronium formation, an explanation may also be found for the observed leveling off of I_2 at increasing solute concentrations.

In summary, it appears that both mechanisms could reasonably well explain the experimental data. The main purpose of this investigation was to show that a viable alternative to the spur reaction model exists which does not involve positron-electron combination but Ps formation with energetic positrons as postulated in the Ore model. We feel that it encompasses well recognized features of the Ps formation in the gas phase, which we feel cannot be excluded in the condensed phase. On the other side, it incorporates the clear parallels and similarities between electron spur properties and radiation-chemical phenomena in general. It is closely related to Tao's modified spur reaction model²¹, with the exception that it does not assume Ps formation via free positron-electron combination in the spur. We hope that the obvious importance of positronium studies as a tool to obtain information not only about electron reactions, but also about hot radical studies in general, will encourage more work in this area and eventually lead to the exact evaluation of the positronium formation mechanism in the condensed phase.

CHAPTER IV: POSITRON ANNIHILATION IN MICELLAR SYSTEMS

A. Introduction:

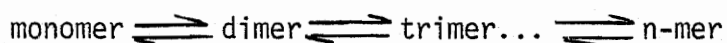
Surfactants are amphiphilic compounds which form micelles in solution. The fundamental characteristic of micelle forming monomers is their amphiphilicity or amphipathicity, i.e., the presence in the same molecule of polar and non polar moieties. The classification of surfactants as non-ionic, anionic, cationic or Zwitterionic depends on the nature of the head group. The ionic surfactants are always associated with counter ions and their properties are often influenced by the nature of the counter ion. The hydrophobic part can be of different length, can contain unsaturated portions or aromatic moieties and can consist of two or more chains. When surfactant molecules are dissolved in water, they can achieve segregation of their hydrophobic part from the solvent by self-aggregation. The aggregate products are known as "Normal Micelles". When the hydrophobic part of the surfactant is a hydrocarbon chain, the micelle will consist of a hydrocarbon core, with the polar group at the surface. On the other hand, when surfactant molecules are dissolved in apolar solvents, the aggregate products are known as "Reversed or Inverted Micelles". The "Inverted Micelles" are characterized by aggregates of surfactant molecules with their polar groups centered in the interior of the aggregate while their hydrophobic moieties are at the surface and are surrounded by the bulk apolar solvent.

Micelles formed by amphiphile molecules are generally very small. Their formation results from the existence of two opposing forces, an

attractive force favoring aggregation and a repulsive force that prevents growth of the aggregate to large size. The attractive force arises from the hydrophobic effect acting upon the hydrocarbon chain of the surfactant, while the repulsive force is due to the head group. An important feature is that a minimum number of surfactant molecules have to become associated with each other. Therefore the micelle formation is necessarily a cooperative process, requiring simultaneous participation by many surfactant molecules (or ions)⁶⁴.

There is ample evidence that in "Normal Micelles" the aggregation can be characterized by a monomer \rightleftharpoons n-mer type association. However in the case of "Inverted Micelles", two models had been developed in order to describe the mechanism responsible for the micellization process namely (1) the multiple equilibrium model⁶⁵ and (2) the pseudo-phase model^{66, 67}.

The first model assumes stepwise formation of the aggregates in an indefinite association process:



The second model is the same as the one developed in the case of "Normal Micelles" and is characterized by an equilibrium between the formed micelles and the molecules or ions from which they are formed. There is a relatively small range of concentrations separating the limit below which no micelles are detected and the limit above which all additional surfactant forms micelles. This narrow range of surfactant concentration at which the micelles first become detectable is defined as the critical micelle concentration (cmc). It is an important physical chemical property in both "Normal Micelles" and "Inverted Micelles".

These two models have been recently discussed by Muller⁶⁷ for the ionic surfactants. This author suggested that most surfactant-solvents fall into one of the two classes showing different aggregation behavior. The type I aggregation has the following characteristics: 1. The average aggregation number, \bar{n} , is rather small, most often in the range $3 \leq \bar{n} \leq 7.2$. There is no well-defined critical micelle concentration (CMC). 3. The average aggregation number, \bar{n} , increases without reaching a limit constant value. The type II aggregation may be described as follows: 1. Aggregation numbers are relatively large, often in the range $12 \leq \bar{n} \leq 30$. 2. Aggregation commence at a relatively well defined CMC. 3. At high surfactant concentrations, \bar{n} reaches a constant limited value which depends on the nature of the surfactant and solvent.

The multiple equilibrium model⁶⁵ would predict that changes in the physical parameters of the micellar solutions occur gradually with increasing surfactant concentration, while on the basis of the pseudo-phase model^{66, 67} a drastic change in these properties would be expected at a given surfactant concentration.

While there is ample evidence that in aqueous micellar system the aggregation can be described by a monomer n -mer type association, there still exists a question whether the aggregation can be characterized by the pseudo-phase model, in the case of reversed micellar systems, or whether the multiple equilibrium model applies.

A relatively large body of experimental evidence is available about aqueous micellar solutions. However, only little information on the physical and chemical properties of reversed micelles is available.

Because of the increasing importance of reversed micelles in industrial applications, energy storage and conservation, tertiary oil recovery, dry cleaning as well as catalyst in chemical and biological reactions, it is essential to obtain additional information.

The sensitivity of the positronium formation process toward structural changes has been previously recognized in experiments with liquid crystals^{69, 72}. Therefore, the positron annihilation technique appeared to be extremely suitable for the study of micellar systems and several series of experiments were carried out in reverse micellar systems utilizing the positron annihilation technique.

B. Purity and Source of Reagents

Aerosol OT (AOT = Sodium-2-ethylhexylsulfosuccinate) as obtained from Fisher Scientific Co. with a stated purity of 100%, was recrystallized and dried in accordance with the procedure described in ref. 73. Butyl -(BAP), hexyl -(HAP), octyl -(OAP), decyl -(DeAP) and dodecyl -(DAP) ammonium propionates were prepared by neutralization of their respective amines (obtained from Aldrich Co.) with propionic acid (Fisher Sci. Co.) in n - hexane^{74, 75}. Dodecylammonium butanoate (BAP) was prepared by neutralization of dodecylamine with butyric acid (Fisher Sci. Co.) in n-hexane. BAP, HAP and OAP were purified by distillation at reduced pressure. Repeated recrystillation of DeAP and DAP from n-Hexane resulted in products with a melting point in agreement with the values published in the literature⁷⁴. The commercially available amines had been purified by distillation under reduced pressure.

Dodecylammonium benzoate (DABZ) was prepared by the neutralization of dodecylamine with benzoic acid (Fisher Sci. Co.) at about 70°C. The crystalline salt was washed with reagent grade acetonitrile in order to remove any free benzoic acid⁷⁵.

Dodecylammonium nitrobenzolate (DABZNO₂) was prepared, as its analog DABZ, by neutralization of dodecylamine with p-nitrobenzoic acid.

Alkylammonium surfactants, $[R^- N^+H_4, R^- N^+(CH_3)_4 \text{ and } R^- N^+(C_2H_5)_4]$, were prepared by replacing the counter ion (Na⁺) in di-2-ethylhexyl-sulfosuccinate by N⁺H₄, N⁺(CH₃)₄ and N⁺(C₂H₅)₄ respectively. Stoichiometric amounts of Aerosol OT (10mM) and tetraalkylammonium chloride (10 mM) were dissolved in a mixture of ethanol and toluene (100 cc of ethanol and 250 cc of toluene). This solution was heated under reflux for 6 hours. After cooling, the excess alkylammonium chloride and the resulting salt (NaCl) were filtered off and the solvents evaporated.

The remaining compound was dissolved in a small amount of toluene and the insoluble NaCl filtered off. This procedure was repeated three times in order to remove any NaCl present in the solution⁷⁶. All surfactants were very hygroscopic; appropriate care had to be taken to avoid any hydration.

Solvents such as n-hexane, benzene and cyclohexane, were glass distilled spectroscopic grades from Burdick and Jackson Lab., isooctane was obtained from Aldrich Co., with the highest purity available. These solvents were further dehydrated by distillation over metallic sodium. The redistilled solvents were stored in desiccators to avoid any further contamination with water.

C. Study of Cooperative Effect Exhibited in Reversed Micellar Solutions Via Positron Annihilation Technique:

Positron annihilation parameters such as the lifetime (τ_2) and particularly the intensity (I_2), which represents the number of thermal o-Ps, were found to be sensitive to microphase changes. A typical example is shown in figure 30 where the I_2 values are plotted as a function of temperature for p-methoxycinnamic acid. The mesomorphic phase transitions are clearly indicated by abrupt changes of I_2 . For comparison a differential thermogram of this substance is included⁶⁹.

Recent investigations in our laboratory⁷⁷⁻⁸², have revealed similar changes in the intensity I_2 at certain surfactant concentration in a variety of reversed micellar solutions (figure 31). These discontinuities in the I_2 vs surfactant concentration plots, clearly indicate the appearance of a cooperative effect, characteristic of aggregate formation, in the reversed micellar solutions within a very narrow surfactant concentration range, leading to a reduction in the formation of thermal o-Ps. This cooperative effect has been recently independently confirmed by Eicke et al.⁸³ whose measurements in dodecylammonium propionate and sodium-di-2-ethylhexylsulfocinate systems, show clear discontinuities of the dielectric increment at surfactant concentration which coincide with those at which I_2 abruptly drops.

It is very difficult to reconcile these results with the gradual changes predicted by the multiple equilibrium model and an explanation in terms of the pseudo-phase model seems to be more likely.

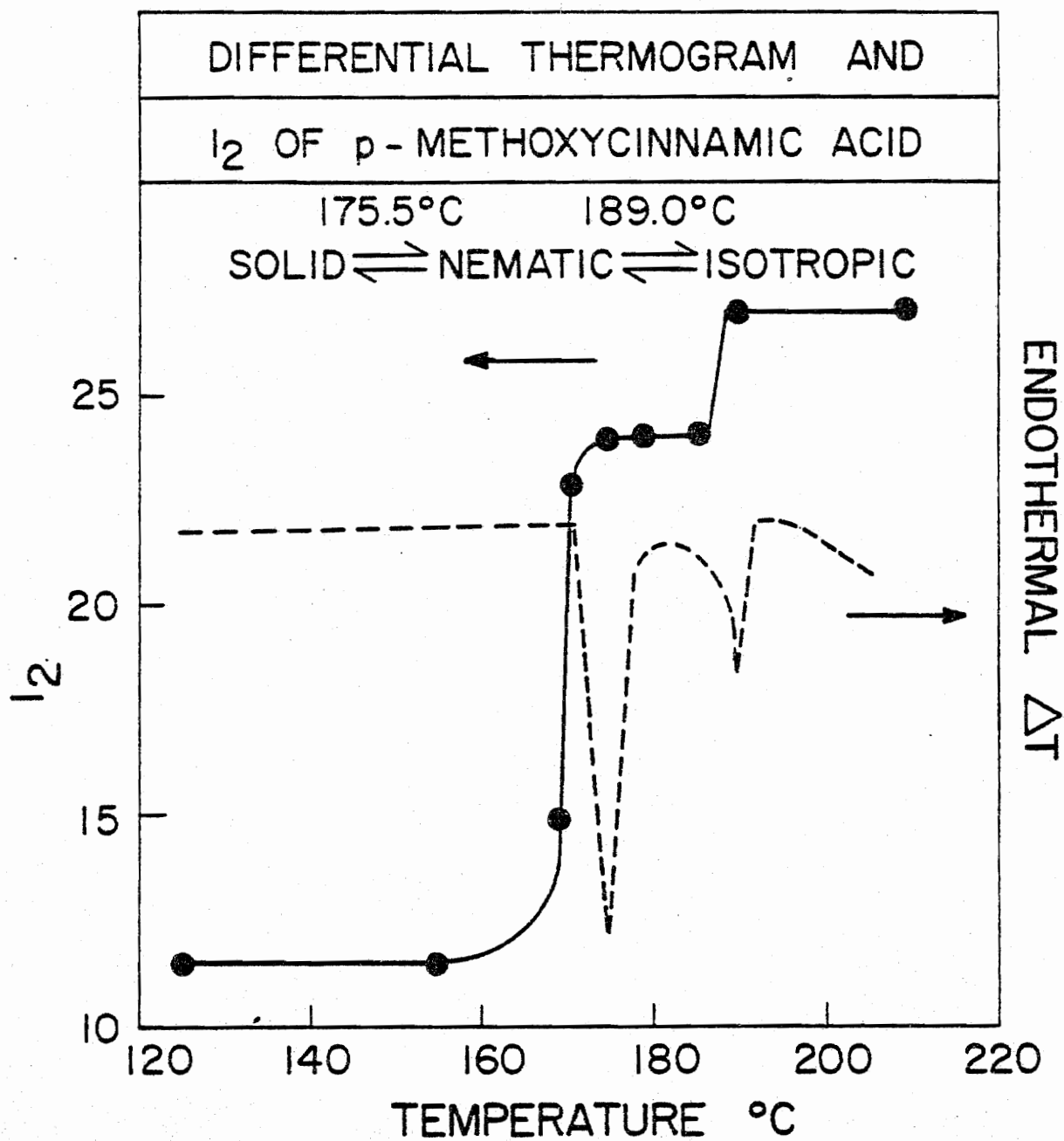


Figure 30. I₂ vs Temperature Plot and Differential Thermogram of p-Methoxy Cinnamic Acid

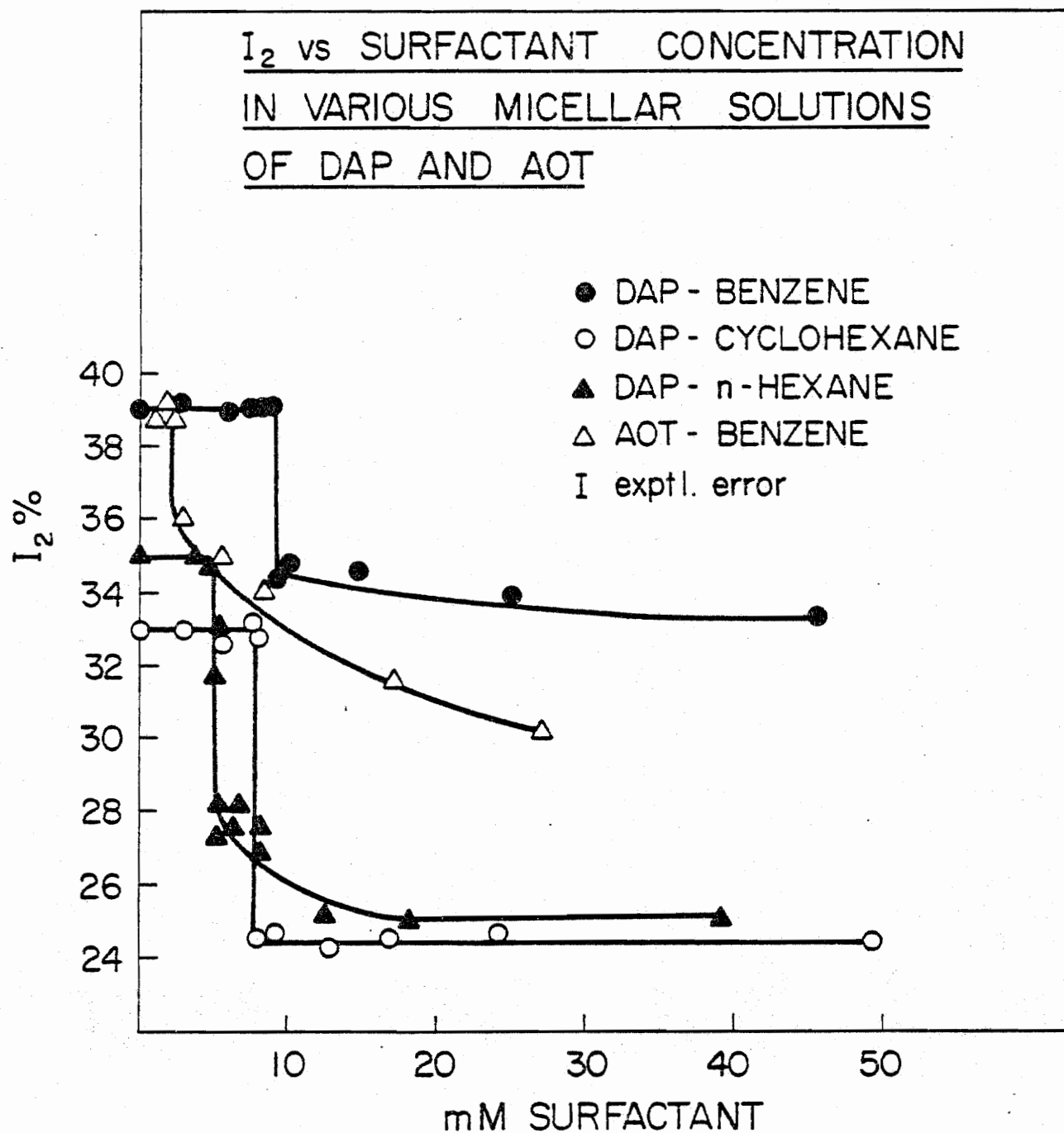


Figure 31. I_2 vs Surfactant Concentrations in Micellar Solutions of AOT and DAP in Various Solvents

D. Effect of Temperature and Counter Ion on the Micelle Formation

I. Introduction

In order to obtain further information on the details of the micelle formation mechanism, the study of micellar solution was extended to include an assessment of the effects of the temperature on the surfactant concentration at which a cooperative effect can be observed. Furthermore, experiments were carried out to investigate the effect of the nature of the counter ion on the aggregation behavior by substituting the sodium-ion by tetraalkylammonium ions in sodium-di-2-ethylhexylsulfosuccinate dissolved in apolar solvents.

2. Results and Discussion

In the first series of experiments, the temperature dependence of the surfactant concentration at which a cooperative effect resulting in a sudden reduction in I_2 could be observed was studied in AOT-isooctane systems at different temperatures (Fig. 32). The onset of the cooperative effect is practically temperature independent over a temperature range from 20-80°C, which would suggest that the heat of formation of the species responsible for this effect (vide infra) is zero. On the other hand, in the DAP-benzene system (fig. 33), the surfactant concentration at which I_2 suddenly changes is shifted to higher values going from 20° to 40°C, remaining approximately the same from 40°C up to 80°.

Regardless, however, whether the concentration at which the cooperative effect appears is changed as a function of temperature or not, the remarkable finding in this study is that in these systems,

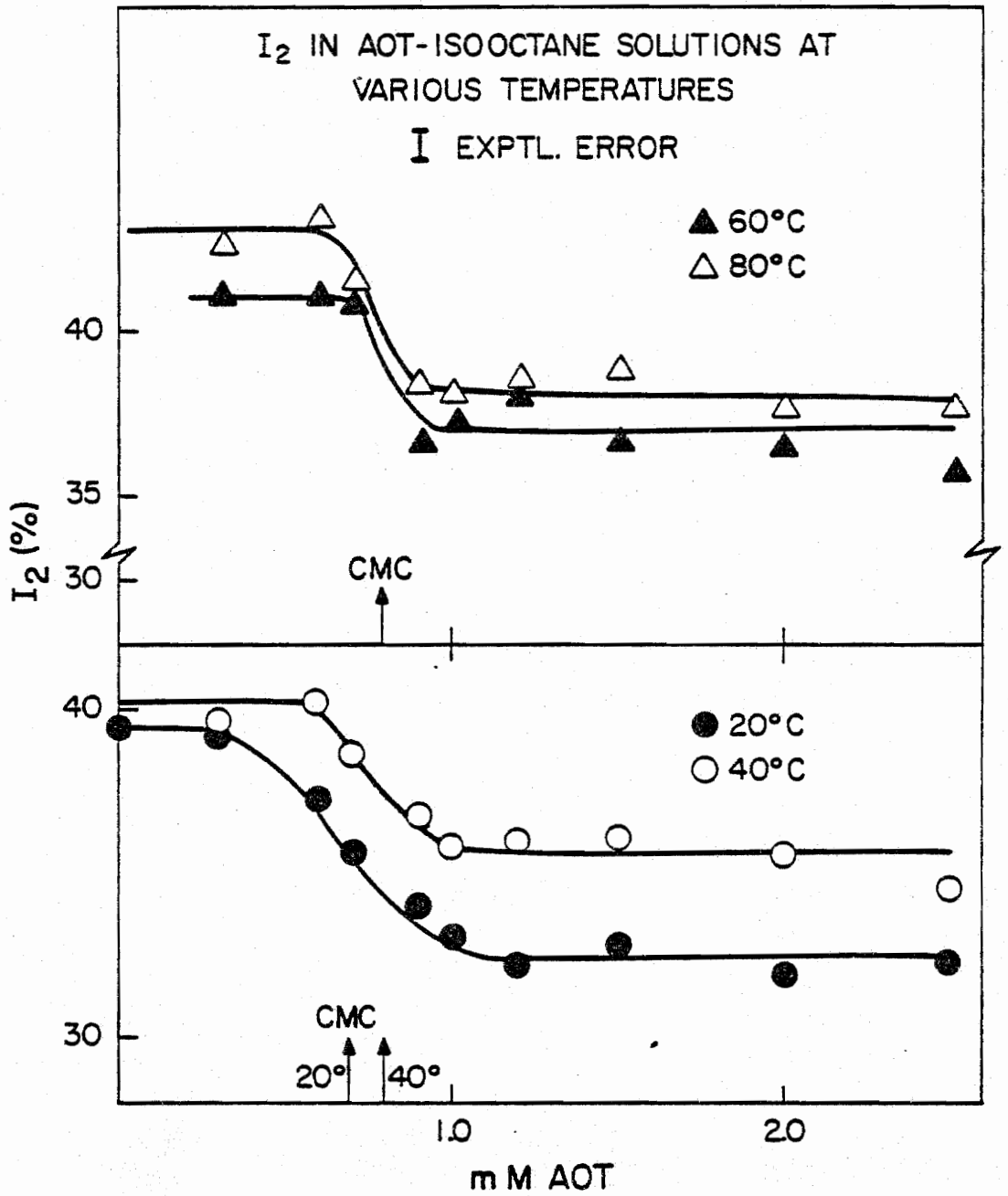


Figure 32. I₂ vs AOT Surfactant Concentration in AOT-Isooctane Solutions at Various Temperatures

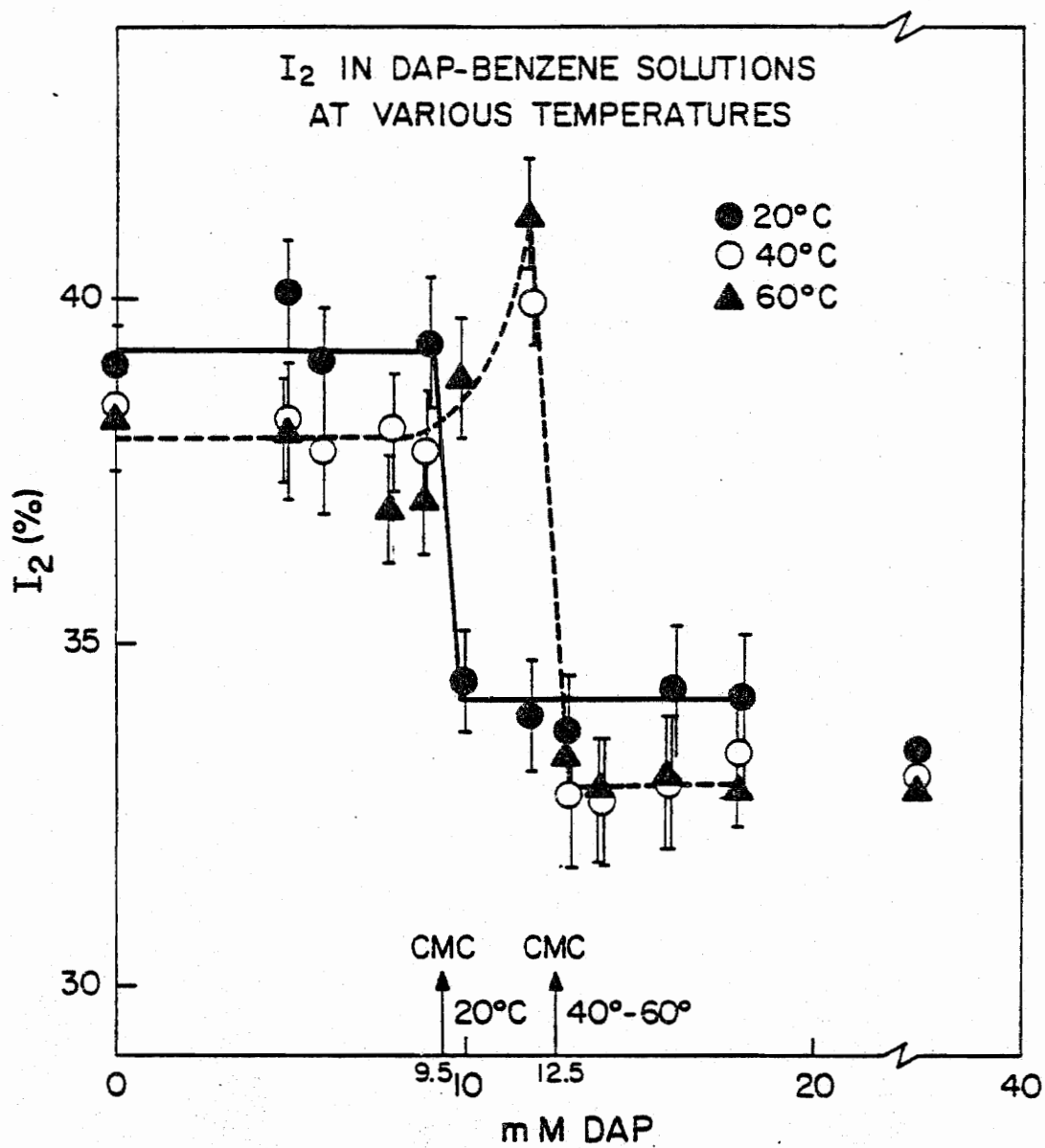


Figure 33. I₂ vs DAP Surfactant Concentration in DAP - Benzene Solutions at Various Temperatures

even at higher temperatures, a narrow surfactant concentration range exists at which a cooperative effect can be observed and thus, by definition, micelles are being formed.

It should be noted that the thermal o-positronium annihilation rates λ_2 associated with the intensity I_2 of the long lived component in the positron lifetime spectra are only slightly affected by the micelle formation in the system included in this study.

In a second series of experiments, we investigated the influence of the nature of the counter ion on the aggregation mechanisms. For this purpose, we replaced the alkali counter ion (Na^+) in AOT by N^+H_4 , $\text{N}^+(\text{CH}_3)_4$ and $\text{N}^+(\text{C}_2\text{H}_5)_4$ and studied the resulting surfactants in benzene solution by positron annihilation techniques.

In figure 34, the I_2 values observed in the various systems are plotted as a function of surfactant concentration. For comparison, the data obtained for AOT (Na^+) are also included. The results show a completely different behavior in the case of the alkylammonium counter ions as compared with that previously observed with Na^+ as the counter ion.

While in the latter systems, the typical abrupt drop of I_2 over a small concentration range is observed, the solutions containing the alkylammonium salts of di-2-ethylhexylsulfosuccinate display a gradual change in I_2 over a wide concentration range. Taken at face value, these results would suggest that in the AOT(Na^+) system, the pseudo-phase model is operative; whereas, in the (alkylammonium $^+$) salt solutions, the aggregation is controlled by the multistep equilibrium model and one can postulate that as soon as aggregates (dimer, trimer or tetramer) are

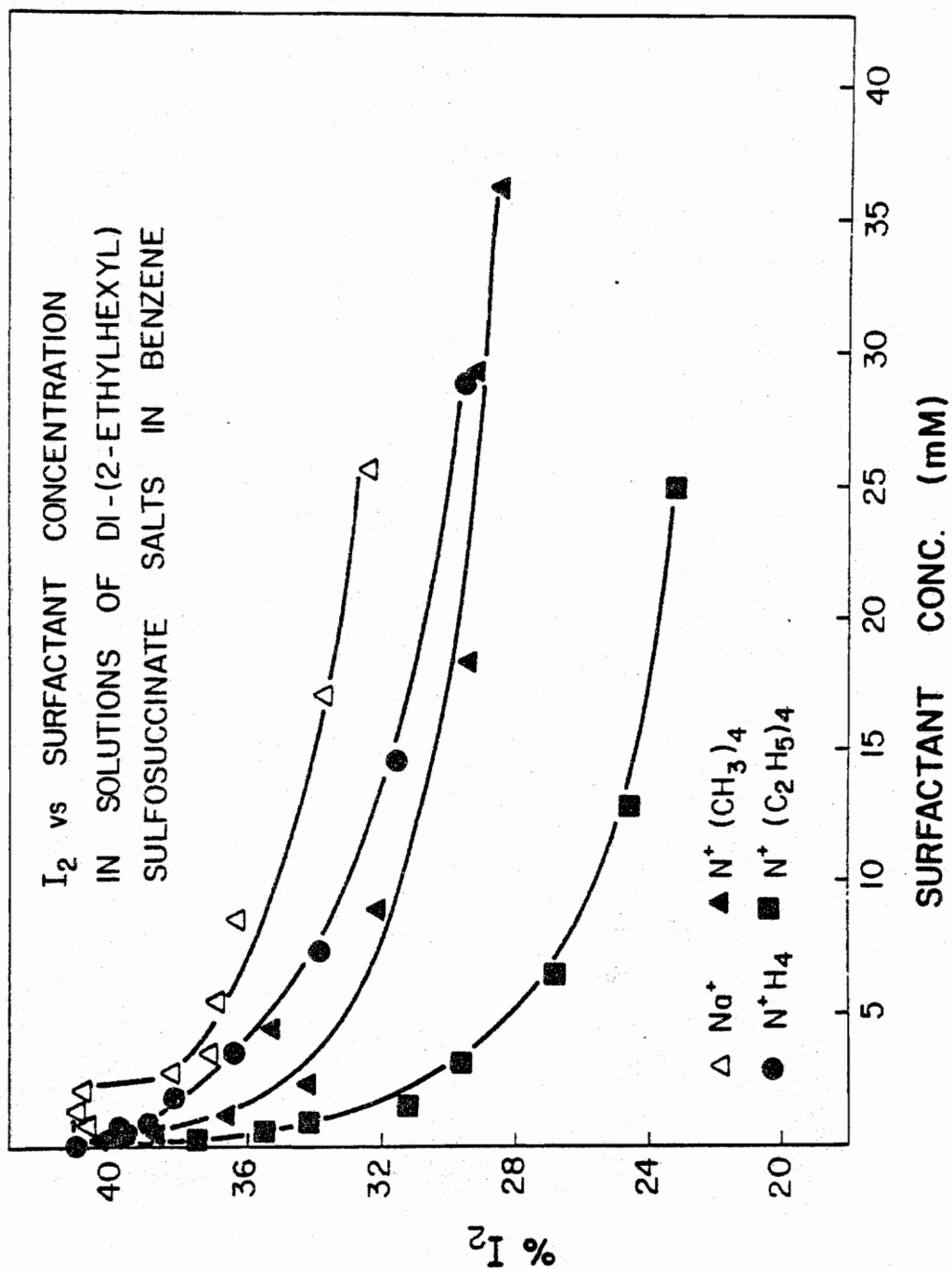


Figure 34. I₂ vs Surfactant Concentration in Micellar Solutions of AOT and the N⁺H₄, N⁺(CH₃)₄ and N⁺(C₂H₅)₄ Salts of Di-2-Ethylhexylsulfosuccinate in Benzene (at room temperature)

formed, they can interfere with the formation of thermal o-Ps atoms.

Similar differences between these two categories of surfactant molecules have recently been found by Eicke et al.⁸³ who have determined the average aggregation numbers of di-2-ethylhexylsulfosuccinate with different counter ions in benzene. They found that if Na^+ is present as counter ion, the average aggregation number remains constant, whereas in the case of the other alkylammonium counter ions, the average aggregation number increases with surfactant concentration.

These results are again consistent with the assumptions made on the basis of the positron annihilation data; namely, that micelle formation occurs via pseudo phase transition with AOT(Na^+) and by indefinite self aggregation in the alkylammonium-di-2-ethylhexylsulfosuccinate systems.

The question remains, however, why do these systems exhibit such a different aggregation behavior? It appears, that although research on reverse micellar systems has been carried out for many years, the factors responsible for stabilizing the aggregates or micelles have not yet been clearly identified.

An attempt to provide a unified interpretation of the self association of ionic surfactants in solvents of low dielectric constant has recently been made by Muller⁶⁸. On the basis of thermodynamical calculations, this author concluded that in systems where the solvent has a relatively high dielectric constant, or the sum of the radii of the ionic headgroups is large, association is best represented by a stepwise sequential formation mechanism, whereas in the opposite case the formation should follow the pseudophase model. According to these calculations, AOT in benzene or isooctane should fall into the latter

category, which is indeed borne out in the experimental measurements. The replacement of Na^+ by NH_4^+ , $\text{N}^+(\text{CH}_3)_4$ and $\text{N}^+(\text{C}_2\text{H}_5)_4$ will, however, lead to an increased radius of the ionic headgroup favoring aggregate formation via the multistep mechanism which is consistent with the results observed in this study. It was found, however, that the distance of the closest approach by another ion is identical both for the sodium and tetramethyl ammonium ions⁸⁴, a fact which does not seem to support the existence of a strong sterical effect which could explain the different aggregation behavior.

Another factor, which has certainly not been sufficiently considered in the previously proposed models, is the role which impurities (especially water or alcohols) may play in the micelle formation process. Evidence that small amounts of a third component present in these solutions can significantly affect the aggregation behavior was observed in apolar solutions of DAP by positron annihilation studies⁸⁰.

In the present study, one would have to assume that the solvent, benzene or isooctane, although carefully dried, will contain small amounts of water. Thus it appears possible that water molecules are instrumental in the aggregation process of AOT as recently postulated by Eicke et al.⁸³.

A water molecule becomes attached to the Na^+ counter ion, which connects, simultaneously, via two hydrogen bridges two other sulfonate groups forming a trimer. Such trimers were frequently detected and considered by Eicke et al.⁸⁵⁻⁸⁶ within the framework of the pseudo-phase model as nuclei in the micellization process.

Further evidence for such hydrogen bridging was obtained by Zundel et al.⁸⁷ in the I.R. study of thin sodium polystyrene sulfonate membranes. If the Na^+ counter ion is replaced by the tetra alkylammonium ions, which according to Zundel et al.⁸⁷ should interact only weakly with water molecules and therefore are not capable of forming an ordered hydrogen bond network promoting trimer formation, a different aggregation behavior would be expected. This is indeed borne out in figure 34 where the latter systems show a gradual change of I_2 , in contrast to AOT, as a function of surfactant concentration consistent with the multiple step equilibrium model. It should be noted that in AOT, the initial aggregation leading to the suggested trimers could be followed by a continuous concentration dependent aggregation.

While this hypothesis could rationalize the findings made in the di-2-ethylhexyl sulfosuccinate systems and also the observation that AOT micelles are more stable than DAP micelles over the temperature range from 20° to 80°C , there is no independent evidence available which would support the assumption that the abrupt appearance of the cooperative effect and thus the spontaneous aggregate formation in the DAP systems is facilitated by a similar hydrogen bonded network.

It appears that the nature of the mechanism by which surfactant molecules undergo self association in apolar solvent depends in a rather subtle way on the properties of the surfactant molecules, the solvent and possible impurities or additives.

E. Micelle Formation in Reversed Micellar Systems of Alkylammonium

Carboxylates:

I. Introduction

An attempt to find a unified interpretation of the self-association of ionic surfactant in solvent of low dielectric constant has been recently reported by Muller⁶⁸. This author postulated the existence of two fundamental modes of aggregation; he suggested that, in a given solvent, the main parameter which determines the mode is the sum of the headgroup radii. His model calculations predict that when the solvent has a relatively high dielectric, ϵ , or the sum of the ionic headgroup radii, d , is large, association is best represented by stepwise sequential formation of open-chain oligomers with approximately equal equilibrium constants for the binding of additional monomers. When ϵ and d are small, compact clusters are preferred. Steric factors then limit the growth of the aggregates at $n = n_{\max}$. However when $n_{\max} \geq 16$, most of the aggregated surfactant should be present in the form of clusters with $n \simeq n_{\max}$. The association process then becomes nearly analogous to micellization in aqueous solutions. The existence of systems with intermediate values of ϵ and d has been postulated as a possibility. This should give rise to a mixed behavior in the association process where the preferred forms of the oligomers coexist with the less-favored ones.

In order to test these predictions, we carried out several series of experiments in solutions of alkylammonium propionates in which the alkyl group in the alkylammonium ion was varied from butyl to hexyl-, octyl-, decyl-, and dodecyl-.

We also investigated the effect of the nature and size of the hydrocarbon chain of the carboxyl ion, i.e. replacing - propionate by - butanoate, -benzoate and -p-nitrobenzoate on the aggregation mechanism. Another parameter studied was the nature of the solvent.

2. Results and Discussion

In the first series of experiments, the length of the hydrocarbon chain in the alkylammonium ion of the alkylammonium propionates was successively increased from 4 to 6, 8, 10, and 12 carbon atoms going from BAP to HAP, OAP, DeAP and DAP.

While λ_2 , the annihilation rate of the o-Ps atoms in the cyclohexane solution of these various systems, does not change significantly over the surfactant concentration range studied, I_2 which is related to the (thermal) o-Ps formation probability shows abrupt changes at certain surfactant concentrations similar to those previously reported for DAP in cyclohexane and benzene. As the results in fig. 35 indicate, for comparison see also fig. 36, where the DAP data are shown, the surfactant concentration at which the drastic changes occur fall into a relatively small range of about 7-9mM, with the exception of OAP for which a smaller concentration of about 3mM was observed. This appears to be somewhat in variance with the results of earlier experiments by Fendler et al.^{75, 88} who observed discontinuities when he plotted the chemical shifts of the different protons obtained by ^1H NMR spectroscopy in benzene solutions of these systems. The breaks in the curves occur in his investigation generally at higher concentrations than those observed in our experiments, especially in shorter chain hydrocarbons, whereas good agreement between his and our measurements exists in the case of DAP.

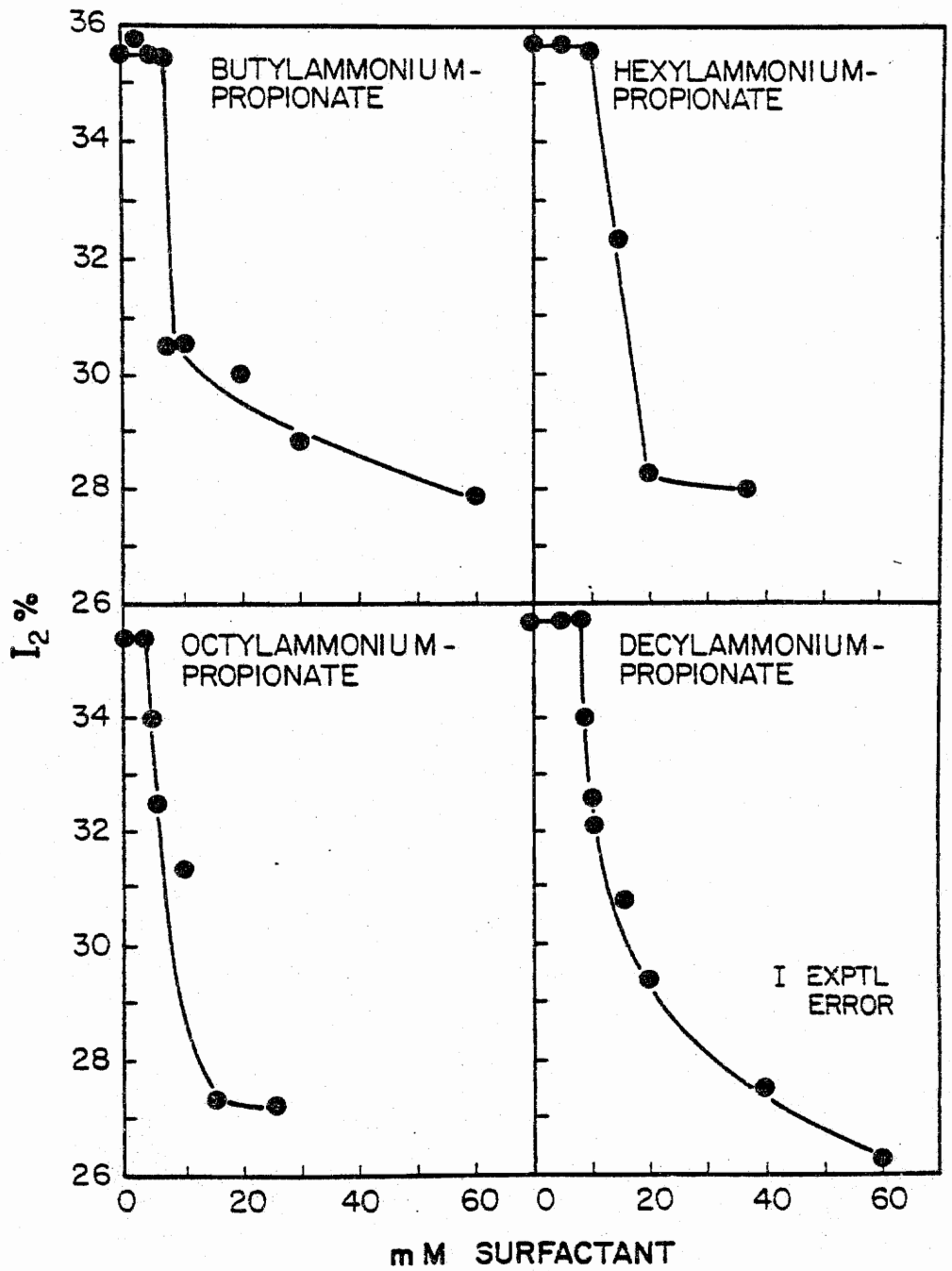


Figure 35. I_2 vs Surfactant Concentration in Various Alkylammonium Carboxylates in Cyclohexane at Room Temperature

In this context, it seems important to point out that in the shorter chain systems (BAP, HAP, OAP and DeAP) in our experiments, after an initially sharp drop, the I_2 values, (fig. 35 and 36), display a much less pronounced decline followed by a leveling off at surfactant concentrations between 20-60 mM, depending on the system, whereas in the case of DAP, the sharp decline in I_2 is characterized by an equally sudden leveling off at 9-10 mM. It might be that the ^1H NMR measurements are indicative of the situation which corresponds to the one at which our positron annihilation parameter, I_2 , has leveled off. This in turn may reflect the different sensitivity of the two techniques to two or more different types of species present.

While the present results further confirm the sudden appearance of a cooperative effect in these systems at a given surfactant concentration, the results also indicate that the length of the hydrocarbon chain in the alkylammonium ion has relatively little effect on (1) the type of aggregation mechanism and (2) on the surfactant concentration at which the cooperative effect appears.

In the second series of experiments, the length and the structure of the hydrocarbon chain in the carboxylate ion of the surfactant molecule was varied from -propionate to -butanoate and -benzoate.

While, as shown in fig. 36, the results observed for DAB in cyclohexane solution vary only slightly from those obtained for DAP, the corresponding I_2 values for DABz display a definitely different trend. The apparent surfactant concentration at which a drop in I_2 occurs is shifted to a very low concentration, well below 1.0 mM, and it remains doubtful whether a discontinuity in the I_2 vs surfactant concentration

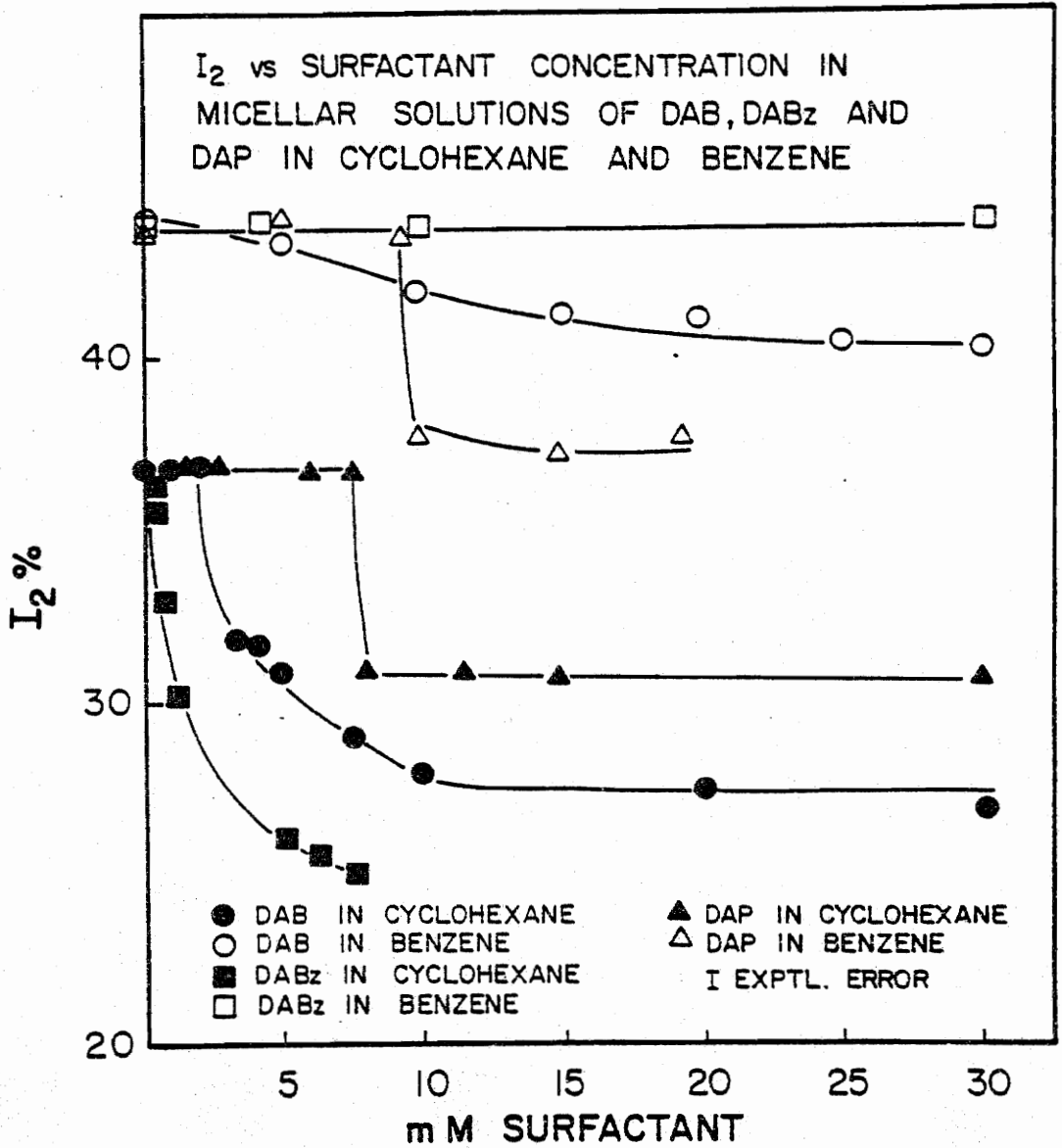


Figure 36. I_2 vs Surfactant Concentration in DAP, DAB and DABZ in Cyclohexane and Benzene Solutions at Room Temperature

plots can be clearly defined at all.

The effect of the nature of the solvent on the appearance of a cooperative effect in these solutions, as indicated by a sudden change in the thermal o-Ps formation probability (I_2) was studied by replacing the cyclohexane as solvent by benzene in the above systems. The results, which are shown in fig. 36 where I_2 is plotted as a function of surfactant concentration, exhibit a rather dramatic effect. While DAP in benzene shows the familiar behavior, namely a sharp drop at about 8.7 mM, no such discontinuity could be observed either in DAB nor in DABz - benzene solutions. The DAB system shows a slight monotonous decline of the I_2 values with increasing surfactant concentrations from 0 to 30 mM, and the I_2 values observed in DABz -benzene solutions remain constant essentially over the whole concentration range studied, i.e., up to 50 mM.

In order to further evaluate the aspect of the influence of the nature of the solvent on the appearance of a cooperative effect, a third series of experiments was performed in which I_2 was measured in cyclohexane-benzene mixtures of various composition without any surfactant and with 10 mM DABz surfactant present. The latter concentration was chosen since the previous data in cyclohexane-DABz solutions revealed that at this concentration I_2 levels off. (fig. 35).

The results of these latter experiments are shown in fig. 37 where I_2 is plotted as a fraction of the mole fraction of benzene. In the neat benzene-cyclohexane, the I_2 's vary only slightly over the whole range, leading to a maximum at approx. 0.25 MF benzene which indicates the non ideal behavior of the mixture, the maximum probably

I_2 vs MF BENZENE IN CYCLOHEXANE - BENZENE
MIXTURES CONTAINING 10 mM DAB₂

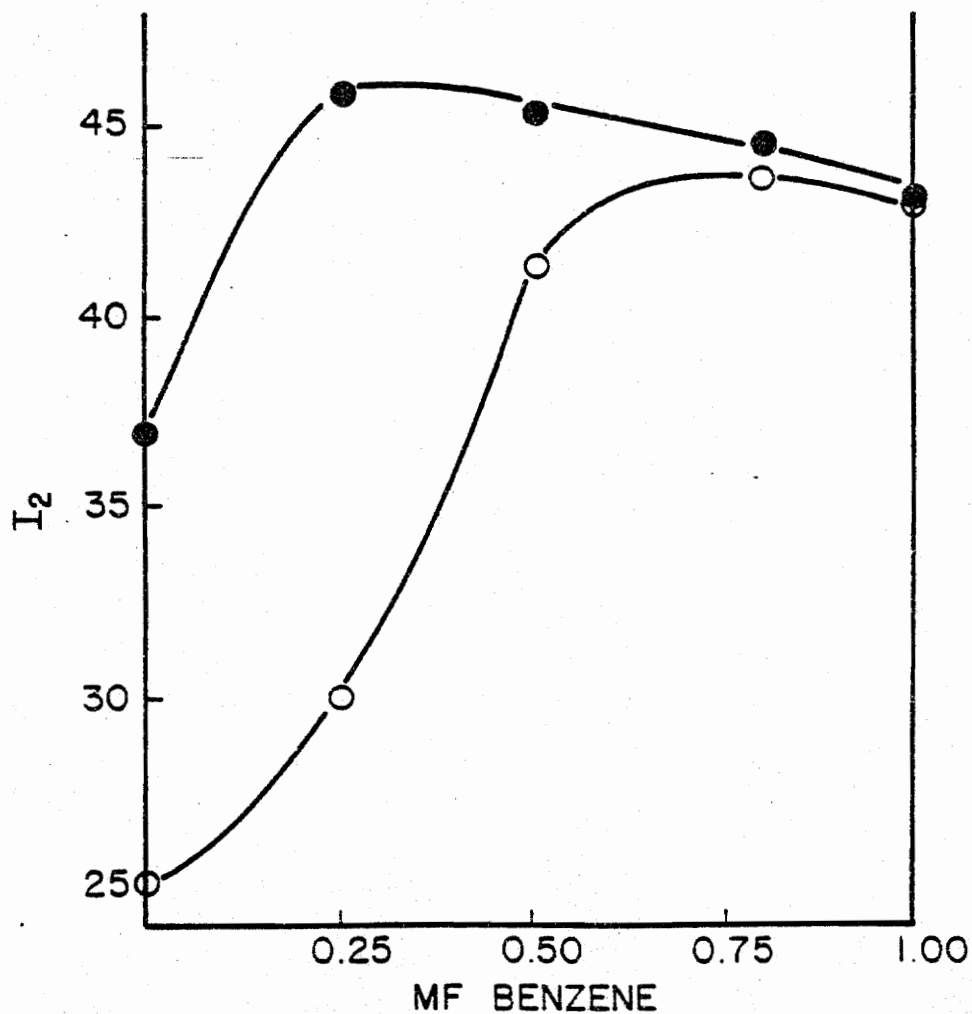


Figure 37. I_2 vs Mole Fraction Benzene in Cyclohexane-Benzene Mixture Without (●) or with 10 mM DABZ (○) Present (at room temperature)

caused by some benzene-cyclohexane clusters etc. formed at this composition. The I_2 values observed with 10 mM DABz on the other hand increase rapidly with the MF benzene and become (at 0.5 MF benzene) almost indistinguishable from those measured in a neat benzene-DABz solution.

These latter data certainly demonstrate the dominating influence of the benzene and clearly indicate that the changes of I_2 are not an additive effect of the two solvents⁹⁰.

The introduction of a nitro group in the para position of the benzene ring in DABz leads again to a completely different behavior. If DABzNO₂ is dissolved in benzene, (because of the limited solubility of DABzNO₂ the measurements were carried out at 54°C) the thermal o-Ps formation probability drops significantly with the surfactant concentration as shown in fig. 38, without displaying any discontinuities. Since, in this system, the surfactant reacted strongly with o-Ps as indicated by a significant change in λ_2 , the number of thermal o-Ps formed ($3/4 P$) had to be calculated from I_2 , the intensity of the long lived component in the positron lifetime spectra by using the correlation between I_2 , λ_2 and $3/4 P$ as previously discussed:

$$I_2 = 3/4 P (1 + K_1[M]) / (\lambda_F - \lambda_p - K_1[M])$$

where K_1 is the observed rate constant of o-Ps with the surfactant. $[M]$ is the surfactant concentration, λ_p is the positron annihilation rate in the neat solvent, and λ_F corresponds to the annihilation rate of the free positrons in these solutions. It was approximated as $2.5 \times 10^9 \text{ s}^{-1}$.

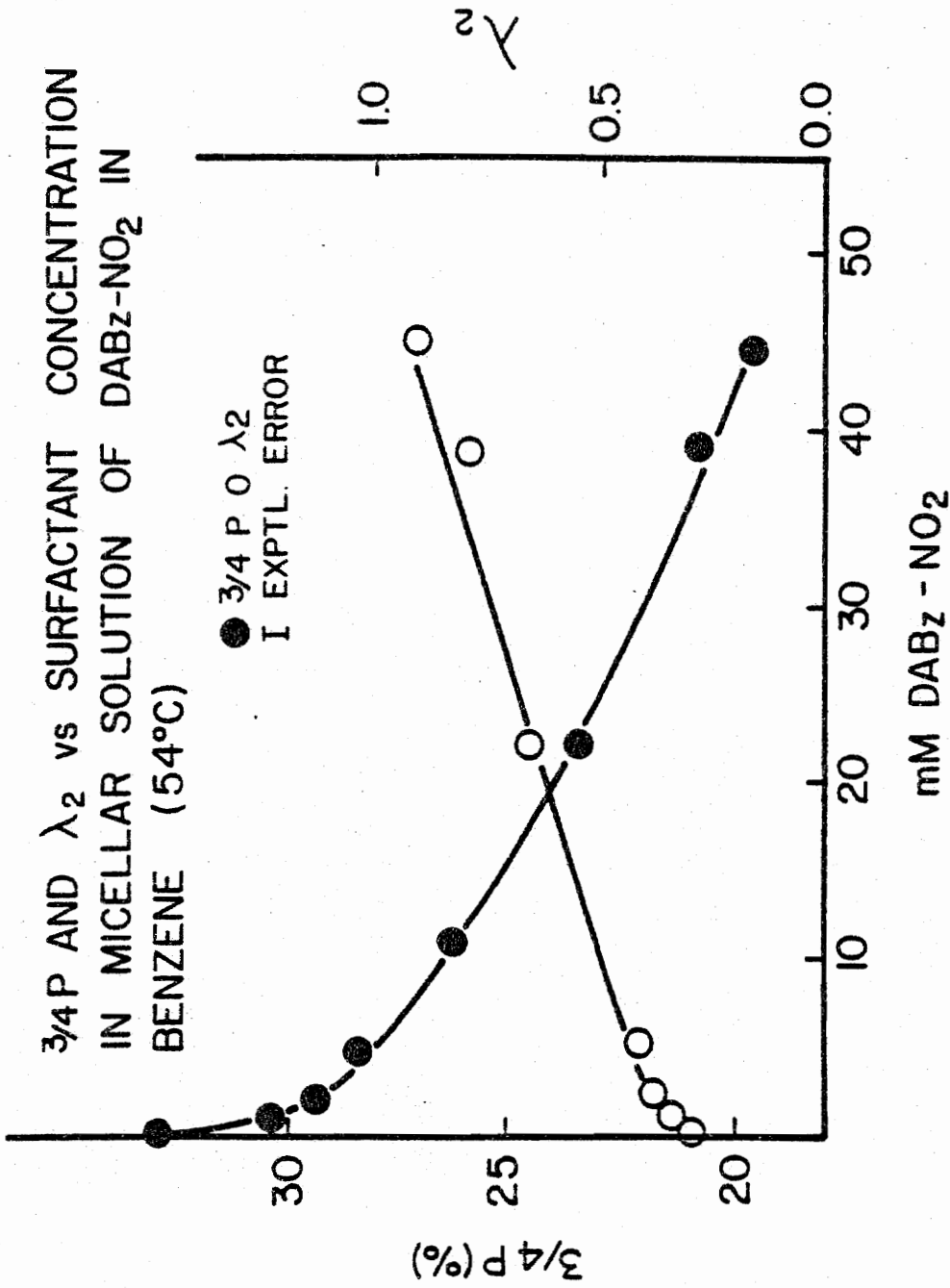


Figure 38. 3/4 P (●) and λ_2 (○) vs DABzNO₂ Concentration in Benzene Solutions at 54°C

Such a correction was not necessary in the other systems, where thermal o-*Ps* interacted only very weakly with the surfactant and no significant change in λ_2 could be observed as a function of surfactant concentration. Consequently, I_2 remained proportional to the number of thermal o-*Ps* atoms formed independent of surfactant concentration.

Muller⁷⁴ has postulated that most surfactant-solvent systems fall into one of two classes showing different aggregation behavior and he considers DAP in benzene or cyclohexane as a prototype for what he calls type I aggregation, which has the following characteristics: (1) small average aggregation number (\bar{n}) (3-7), (2) no well defined critical micelle concentration (CMC), (3) \bar{n} progressively increases with increasing surfactant concentration without reaching a limiting constant value, (4) the dependence of the micellar molecular weight on the surfactant concentration is accounted for by using a step-wise sequential multiple-equilibrium model.

The second class of surfactants, according to Muller⁶⁸, is characterized by (1) a large aggregation number (12-30), (2) aggregation appears to commence at a moderately well defined CMC, (3) at fairly high surfactant concentrations, \bar{n} reaches a constant limiting value which depends on the nature of the surfactant and solvent, (4) aggregation is better described by a single equilibrium or monomer \rightleftharpoons n-mer model. A typical example for this second category would be the alkali dialkylsulfosuccinates in solvents of low dielectric constants.

A comparison of the present results obtained with the alkylammonium carboxylates such as BAP, HAP, OAP, DeAP, DAP and DAB in cyclohexane solutions which all show the appearance of a cooperative effect as a

well defined surfactant concentration, with the previously reported results with AOT benzene or cyclohexane solutions, however, reveal no qualitatively different behavior^{78, 80}. Furthermore, measurements of the dielectric increment in AOT/benzene and DAP/benzene solutions carried out by Eicke et al.⁹¹ as a function of surfactant concentration show abrupt changes in this parameter in both systems at surfactant concentration range at which I_2 in the positron annihilation studies also sharply declines.

Thus, it appears that the process which is recognized by both of these techniques occurs with surfactants falling into either one of Muller's classifications.

Furthermore, it seems reasonable to assume that this sudden change in these two physical parameters is related to the formation of a new species via a pseudo-phase transition. This new species may be a trimer or another cyclic aggregates as previously postulated by several authors⁸⁵⁻⁸⁶.

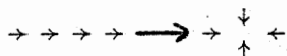
This does not exclude, however, that this pseudo-phase transition leading to the appearance of the cooperative effect is followed by a continuous concentration dependent aggregation. Judging from the shape of the I_2 vs surfactant concentration plots as shown in fig. 35 and 36, the latter process seems to be more pronounced in the shorter chain surfactants BAP, HAP, OAP and DeAP than in DAP, which would emphasize the steric effect involved in the aggregation step. This becomes even more evident, if the anionic part of the surfactant molecule contains an aromatic ring system, as in DABz (in cyclohexane) in which case this initial pseudo phase transition cannot be observed

at all. On the other hand the simple extension of the hydrocarbon chain of the anion by one C atom seems to have little influence on the aggregation behavior (fig. 37).

Of special interest is the effect of the nature of the solvent on the positronium formation probability with DAP, DAB or DABz in cyclohexane as compared to benzene solutions of these components.

While in the cyclohexane solutions of all three systems the thermal o-Ps formation is clearly affected by the presence of different amounts of surfactant, in benzene solutions this is true only for the DAP system and to a much lesser degree for the DAB surfactant while no change at all in I_2 can be observed in the case of DABz over the total micelle concentration range (fig. 37) studied.

These differences are somewhat puzzling and will demand further investigation. Tentatively, one might want to consider that this different behavior is inherent to the system, and perhaps a result of strong intermolecular interaction between the solvent benzene molecules with the aromatic ring in the benzoate portion of the surfactant molecules which prevents sudden rearrangements or pseudo-phase transitions, as e.g. postulated by Eicke⁶⁶. This author has suggested that in the DAP solutions at low surfactant concentrations the surfactant molecules could be lined up in an open chain like structure and undergo at a certain concentration a pseudo phase transition to a multipolar structure:



which would explain the drastic drops in the I_2 values at a certain surfactant concentration. As pointed out above this sudden transition

might be hindered by strong intermolecular interaction between the benzoate ion and the solvent, benzene. This would be consistent with the previously made observation that certain additives, such as nitrobenzenes or tetracyanoethylene which form molecular complexes with DAP, eliminate the drastic changes of I_2 giving rise to a more gradual drop of I_2 ⁸⁰.

While this may present a possible explanation of the differences between the DAP and DABz system, an open question still remains regarding the drastic variation of I_2 in DAB/cyclohexane while hardly any change in I_2 can be seen over the same surfactant concentration range in DAB/benzene systems.

Qualitatively, this solvent effect may be also expected on the basis of Muller's model⁶⁸, which would predict a preference of open chain oligomers which might not be detectable by the positron annihilation technique if the product ϵd is large (ϵ : cyclohexane 2.0 D vs benzene 2.3 D). Although as shown by our experiments, steric factors will play a significant role.

Interesting is the observation that the DABzNO₂ surfactants show a distinctly different behavior in benzene as compared to DAB or DABz in the same solvent. In line with the above assumption, one would have to postulate that the presence of the polar nitro group favors the formation of cyclic aggregates; which, in turn, can be recognized by the positron annihilation method.

The general picture which emerges from this study is that the aggregation behavior of these surfactants is governed in a rather subtle way by the nature of surfactant and solvent. An attempt to

develop a general model for the aggregation process will be further complicated by the fact that small amounts of water or other impurities which cannot be completely excluded in the experiments may have a profound effect on the association mechanism⁹¹⁻⁹³.

F. Positron and Positronium Interactions With Micelle Aggregates:

It is a known fact that the absorption spectra and the nature of the solvated electron in polar solvents and in binary liquid solutions of polar solvents are determined mainly by bulk solution properties⁹⁴⁻⁹⁵. However, recent studies of the pulse radiolysis of alcohol-alkane and alcohol-amine solutions showed that electron solvation in solutions of polar molecules in apolar solvents occur entirely in polar molecule aggregates. Brown⁹⁶ et al. observed that the absorption spectrum of the solvated electron is essentially the same in solutions containing 5% moles of ethanol in n-hexane as in pure ethanol. These observations have been confirmed by other groups⁹⁷ in different systems. From these studies, it was concluded that alcohol molecules exist mainly in alkanes solutions as associated aggregates which scavenge and solvate free electrons. Jansen¹⁴ et al. adopted this interpretation to explain their results obtained in positron studies in solutions of dioxane and some amines in heptane by positron or electron trapping in clusters of the amines in these solutions. According to these authors, the mobilities of positrons and electrons are decreased in these traps which inhibits the positron electron combination and therefore the positronium formation as postulated by the positron spur model.

Similar explanations can be suggested in terms of the other models for positronium formation. As a result I_2 , which represents the number

of thermal ortho-positronium, decreases.

By definition, micelles are formed through the aggregation of surfactant (amphiphilic) molecules. In polar solvents, the structure of these micelles is such that the polar headgroup are in contact of bulk water, while the hydrophobic hydrocarbons moieties comprise the interior. In apolar solvent, the aggregate structure is the converse, with the polar groups surrounding the interior cavity and the hydrocarbon chains extending into and penetrated by the bulk apolar solvent.

From the results obtained by positron annihilation technique, in aqueous micelles, for which there is ample evidence that the pseudo-phase model is operating, the I_2 values decreases as soon as micelles are formed. One can postulate that positrons are trapped in the core or at the surface and, therefore, its ability to abstract an electron from the water or surfactant molecules now present as aggregates is decreased resulting in a drastic reduction in the number of thermal ortho-positronium.

In the case of reversed micelles, the I_2 values decrease in two different ways. The first type of behavior is similar to the one observed for the aqueous micelles and therefore the same interpretation is adopted. The second type involves a gradual decrease of I_2 . This type of behavior is observed only in surfactant solutions for which it was reported that the aggregation number increases with increasing surfactant concentration and then levels off at high concentration. It can be postulated that I_2 decreases as soon as surfactant molecules form small aggregates such as dimer, trimer, etc... As a result, the

positron is trapped in these aggregates and increasing the aggregation number leads to an increase in the degree of trapping of the positron, i.e. decrease its availability to form a positronium. It also seems that this process is stepwise and results in a gradual decrease in I_2 .

CHAPTER V: TEMPERATURE DEPENDENT CHANGE OF POSITRON
ANNIHILATION IN SONICATED DIOCTADECYLDIMETHYLAMMONIUM
CHLORIDE

A. Introduction

The presence of similarities in properties between liposomes and biological cells has stimulated the use of the liposomal system as an experimental model for biomembranes. General rules on selective permeability with respect to molecular size and polarity could be deduced from studies on the swelling and shrinkage behavior of liposomes in various solutes⁹⁸. These rules are very similar to those found for biomembranes. Furthermore, temperature effects on several of these permeability processes appeared to be identical when compared in pure lipid bilayers and biomembranes⁹⁹. It is a well known fact that studies of biological membranes are complicated by the chemical heterogeneity of their constituents. Therefore, it is expected that the liposome systems offer possibilities for studying the molecular interactions and various functions of isolated and selected membrane constituents. These studies will provide a better understanding of the properties of biomembranes as a function of chemical and physical parameters. Studies on liposomal systems have been diversified and their possible use as carriers of molecules in therapeutic applications has become, by itself, an important research topic. This new aspect of liposomes has recently been reviewed¹⁰⁰ and many other papers dealing with individual aspects, have been published and include considerations of liposomes as carrier of enzymes, drugs (specially antitumor drugs),

chelating agents, radionuclides. . .to name a few of them.

Surfactant vesicles, formed upon the sonic dispersal of dialkyldimethylammonium salts¹⁰¹⁻¹⁰⁶ and dihexadecyl phosphate¹⁰⁴ proved, however, to be the simplest functioning membrane models. They can be prepared in the pH 1-13 range, remain stable for months, entrap and retain substrates in substantial amounts^{104, 107}. Fendler et al. have characterized dioctadecyldimethyl-ammonium chloride (DODAC) surfactant vesicles. Sonic dispersal of DODAC initially formed multicompartiment and subsequently single compartment bilayer vesicles as it is shown in figure 39.

A common feature of all membranes and liposomes is the existence of a temperature-dependent transition, the so-called thermotropic transition, which may be described as a highly cooperative order-disorder transition. This transition is a very important property of membranes and liposomes¹⁰⁸⁻¹¹¹. The positron annihilation has been used for investigating the phase transition and osmotic behavior of DODAC vesicles. These results provide additional information on fluidities and allow further assessments of cationic surfactant vesicles as membrane mimetic agents.

B. Purity and Source of Reagents

The preparation, purification and characterization of dioctadecyldemethylammonium chloride (DODAC) was done in accordance with the procedure described in ref. 112. Cholesterol was obtained from Aldrich Co. The typical vesical preparation involved the dispersal of 12.0 mg solid DODAC in 2.0 ml water at 56°C by means of the microprobe of a Branson Sonifier Cell Disruptor, (power setting 45 watts) for 30 min.,

STRUCTURAL MODELS ASSOCIATED WITH THERMAL
TRANSITIONS IN SYNTHETIC PHOSPHOLIPIDS

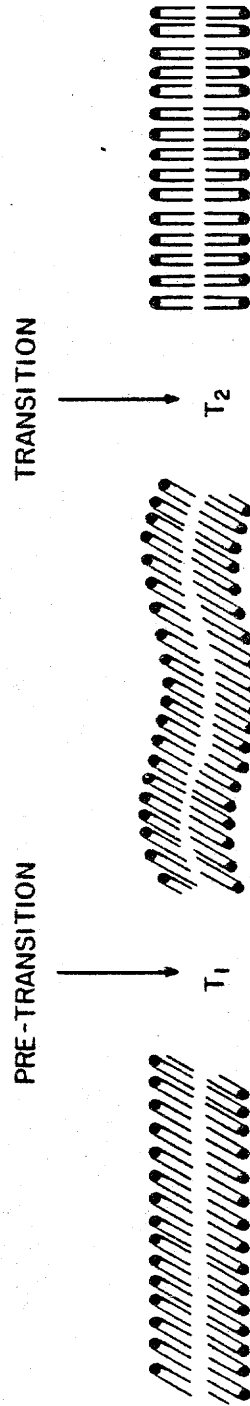


Figure 39. Scheme of Synthetic Phospholipids Bilayers

unless specified otherwise in the results. Cholesterol containing vesicles were prepared by cosonicated cholesterol with DODAC. Sonication times were 15 and up to 45 minutes in the absence and in the presence of cholesterol respectively. The water used was deionized distilled water.

C. Results and Discussion:

Positron annihilation parameters, λ_2 and I_2 , were determined as a function of sonication time. 0.30 g of DODAC in 50.0 ml of triple distilled water was sonicated at 56°C for different times. Bulk viscosities, λ_2 and I_2 values were determined on aliquots withdrawn at appropriate times. Although I_2 remained constant, λ_2 values decreased markedly with increasing sonication time in the 1 to 10 minute period. Further sonication did not alter, however, the positronium reactivities. This behavior paralleled nicely the corresponding bulk viscosities of the DODAC-water dispersions (figure 40).

In a second series of experiments λ_2 and I_2 values were determined for DODAC vesicles, formed by 30 minute sonication of 12.0 mg of DODAC in 2.0 ml H_2O , as a function of increasing temperature. No significant changes in I_2 could be observed. However, λ_2 -values increased with increasing temperature in the 15-31°C region and exhibited a well defined plateau in the 31-36°C region. This plateau was followed by a steep increase of λ_2 -values, which leveled off above 37°C (figure 41).

Positron annihilation rate in cholesterol containing DODAC vesicles as a function of increasing temperature are also shown in figure 41. In the presence of cholesterol, the λ_2 versus temperature curve is seen to shift to a lower temperature.

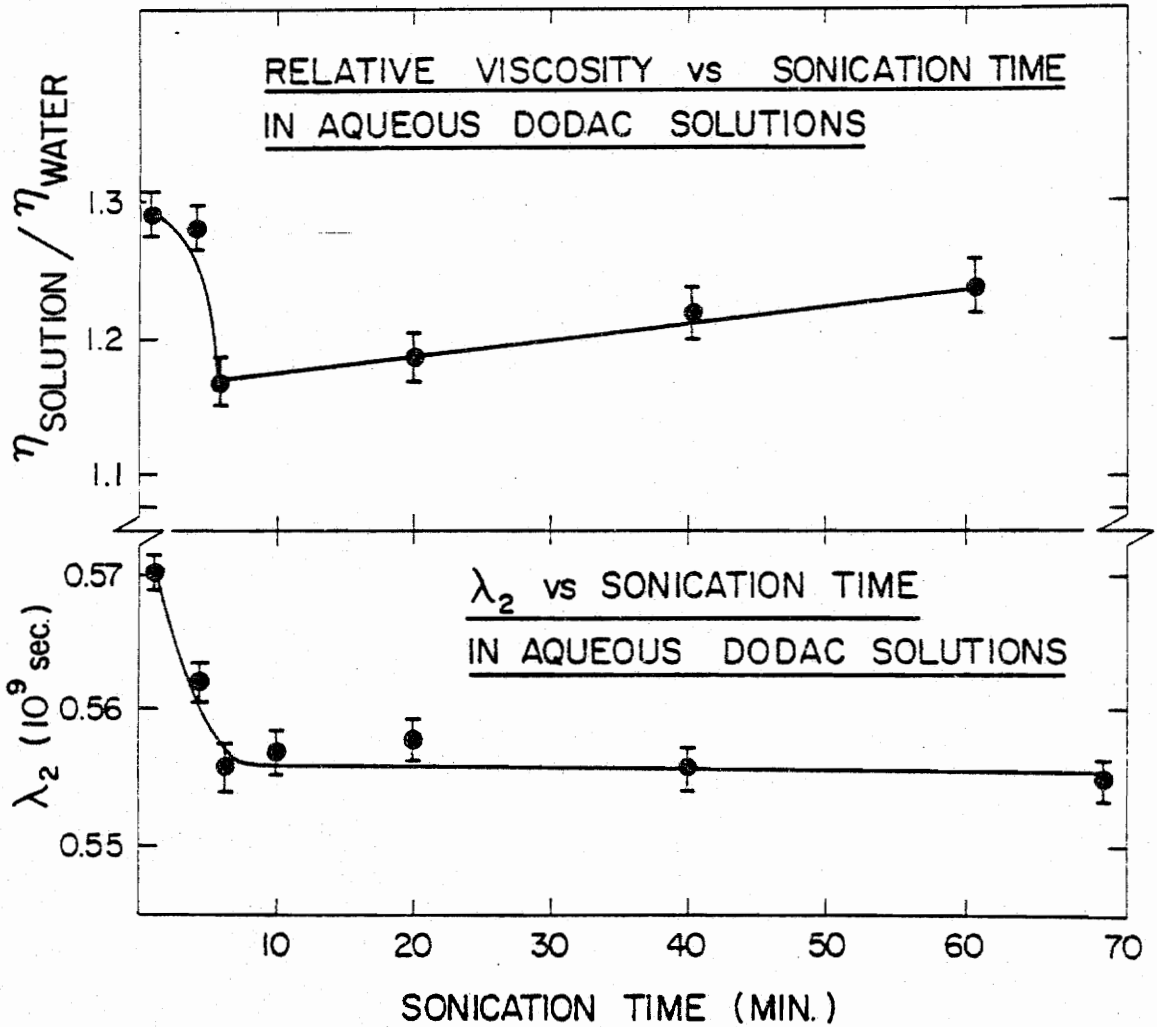


Figure 40. (a) Plots of Viscosities and (b) Positronium Annihilation Rate Against Sonication Time for DODAC Vesicles

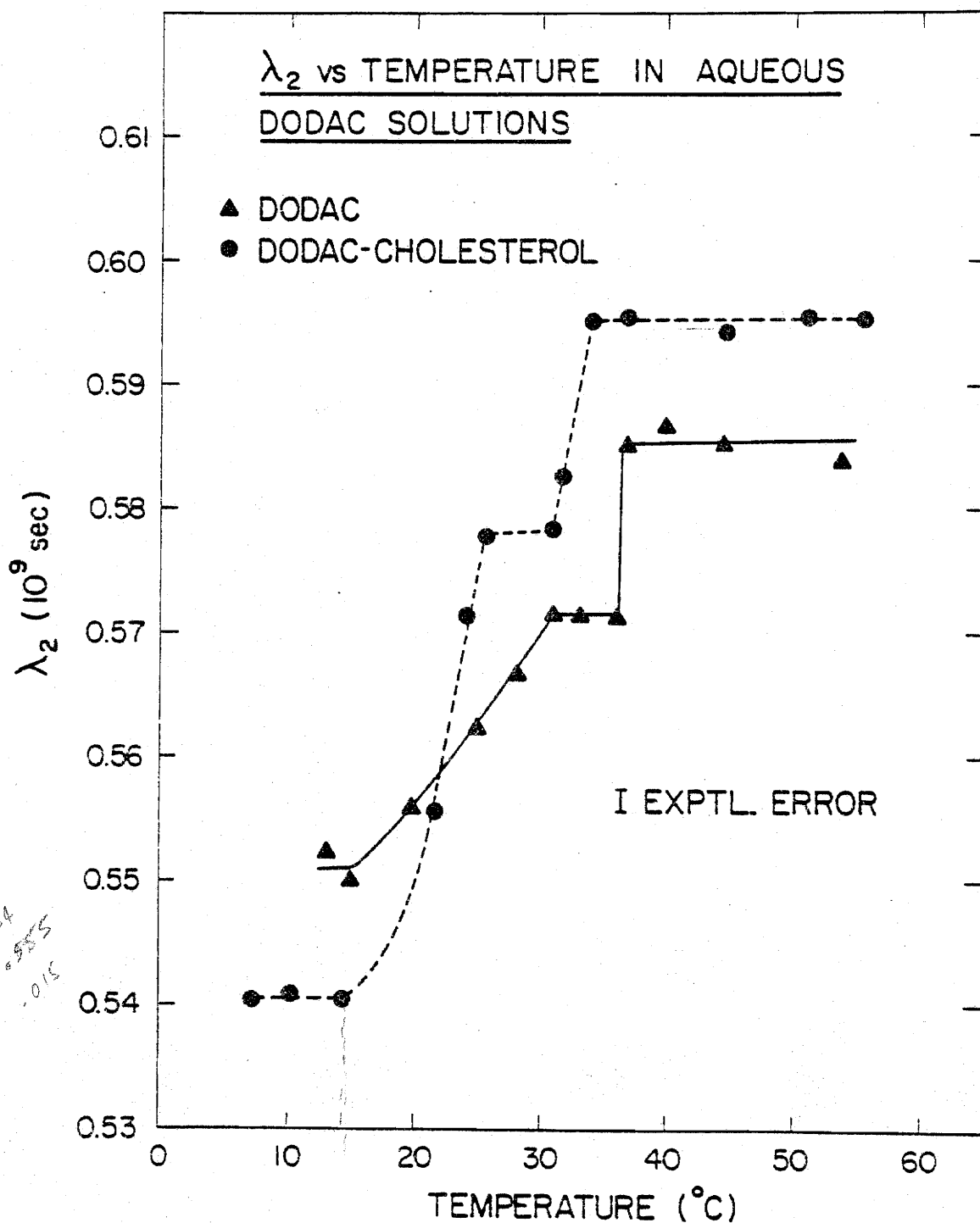


Figure 41. Plots of Positronium Annihilation Rate Against Temperature for DODAC Vesicles in the Absence (Δ) and in the Presence of 17.2%, (\bullet) Cholesterol

Temperature dependence of positronium lifetimes in DODAC vesicles became more apparent when plotting $\Delta\lambda_2/\Delta T$ against temperature. As shown in Figure 42, clear peaks for $\Delta\lambda_2/\Delta T$ emerge at 24° and 37°C for the aqueous solution containing DODAC vesicles and at 23° and 33°C for the DODAC vesicles, which were formed by co-sonicating DODAC and cholesterol. It should be pointed out that, in both systems, λ_2 seems to level off below 15°C (Figure 41).

If the positron lifetime measurements are carried out by decreasing the temperature (cooling cycle) as shown in Figures 43 and 44, in both systems λ_2 exhibit a sharp drop at considerably higher temperatures than in those experiments where the temperature was increased (heating cycle), e.g. about 42°C compared with 37°C in aqueous DODAC vesicle solutions, and 37°C compared with 33°C in aqueous DODAC - cholesterol vesicle solutions. In both cases, the plateaus in the 31-36°C and 26-32°C region, respectively, observed with increasing temperatures were considerably less well-defined and also shifted to higher temperatures.

Several methods (turbidity, viscosity and fluorescence polarization measurements) have been used, separately, to measure the phase transitions of DODAC vesicles¹¹³. Positron annihilation emerged as the most sensitive method. Perturbations are minimal since no reagent is added and the size of the vesicles remain unaltered. Furthermore, positron annihilation measures a microscopic property efficiently on the subnanosecond timescale whereas all macroscopic motions and morphological changes are frozen. Positronium annihilation rates in pure water and in pure octadecane have been determined to be $0.57 \times 10^9 \text{ sec}^{-1}$ and $0.32 \times 10^9 \text{ sec}^{-1}$, respectively⁶⁴. The determined annihilation rates in DODAC represent

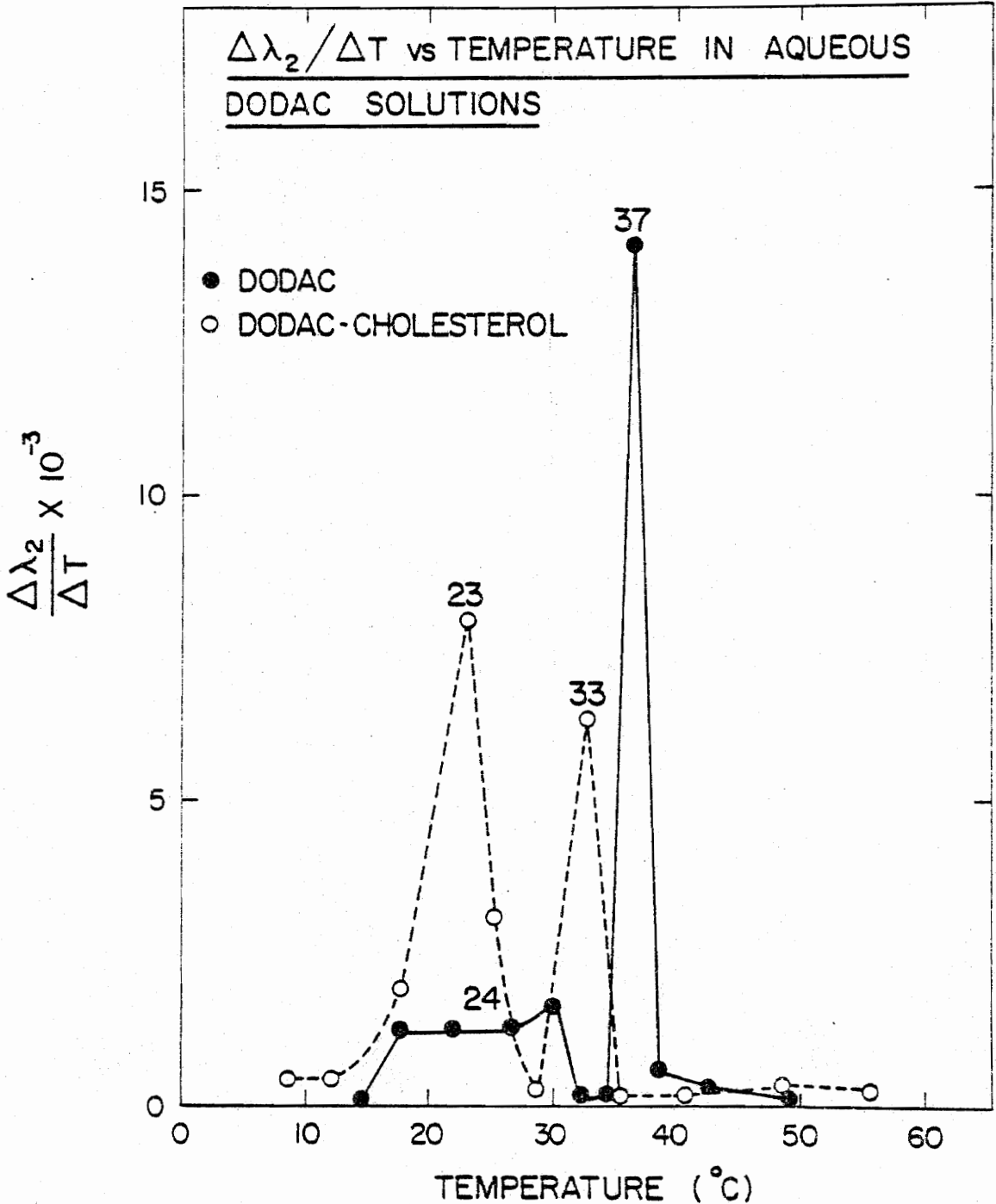


Figure 42. Differential Plots of Positronium Annihilation Rate as a Function of Temperature for DODAC Vesicles in the Absence (broken line) and in the Presence (solid line) of 17.2% Cholesterol

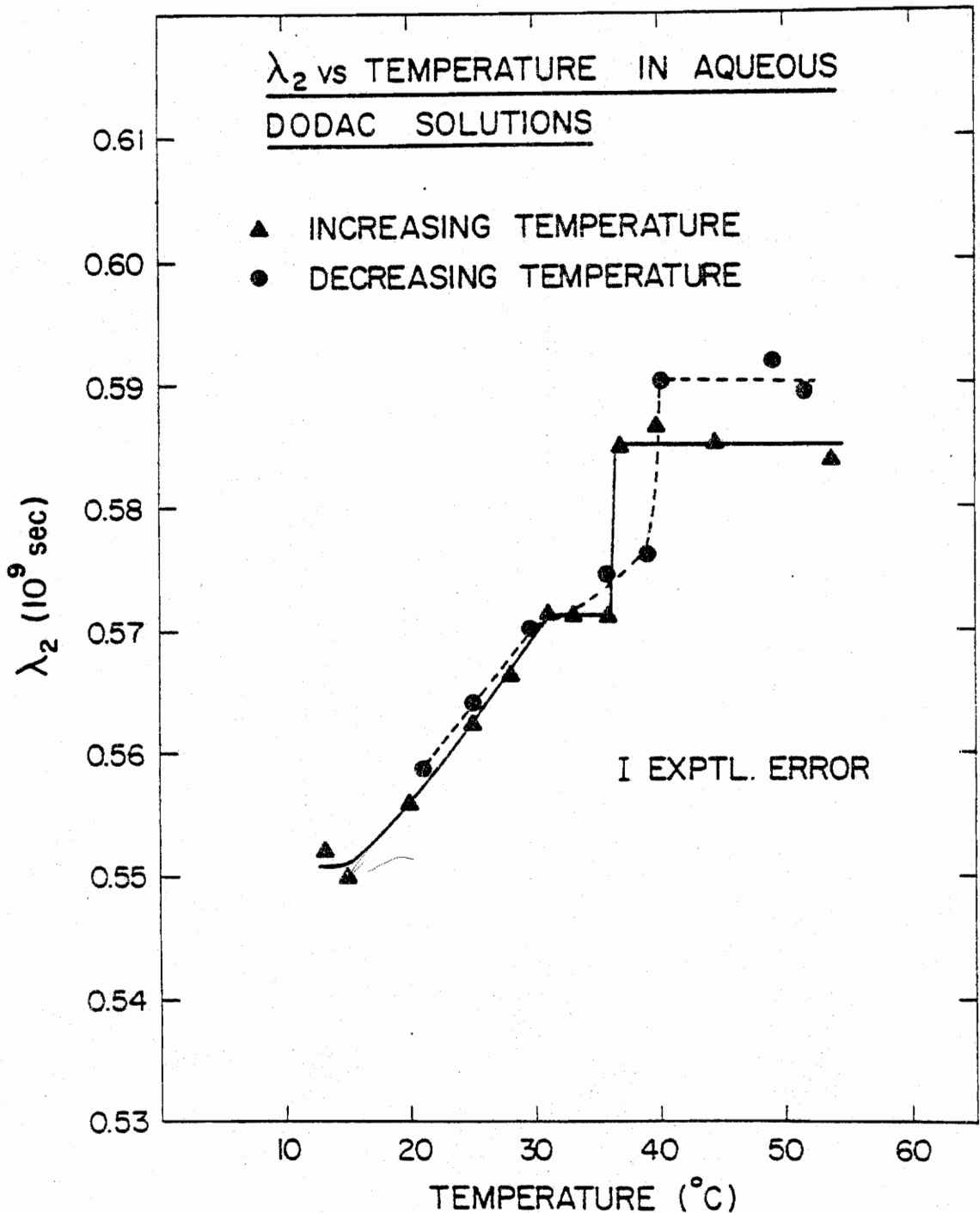


Figure 43. Plots of Positronium Annihilation Rate Against Temperature for DODAC Vesicles. In the Heating Cycle, the Temperature of the Sample was Gradually Increased (▲), Whereas in the Cooling Cycle, the Temperature was Gradually Decreased (●)

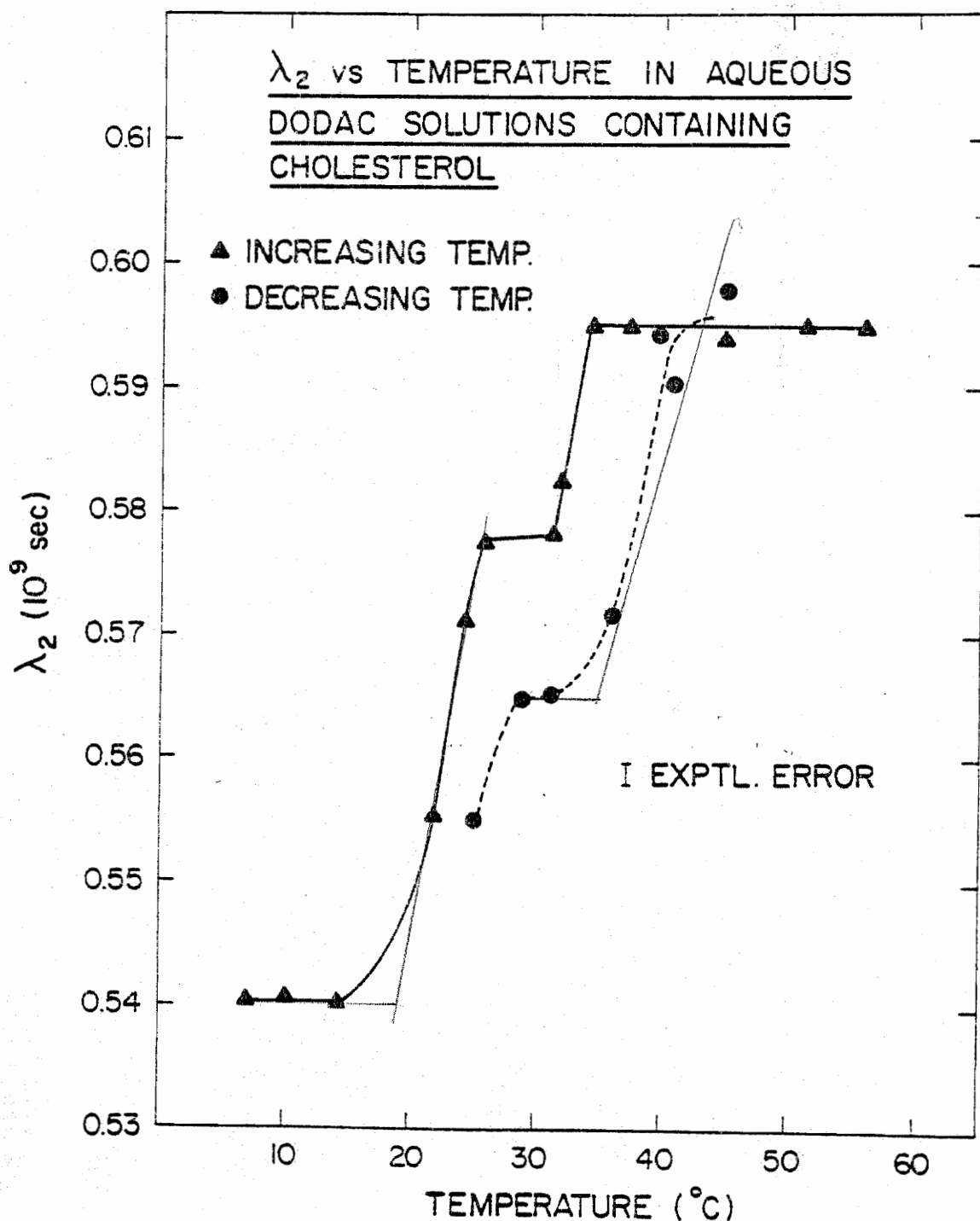


Figure 44. Plots of Positronium Annihilation Rate Against Temperature for DODAC Vesicles Containing 17.2% Cholesterol. In the Heating Cycle, the Temperature of the Sample was Gradually Increased (▲), Whereas in the Cooling Cycle the Temperature was Gradually Decreased (●)

the weighted average of the rates for annihilation in water and in a hydrophobic environment. This method probes, therefore, hydrophobicity changes. The decrease of positronium annihilation rate with increasing sonication times of DODAC dispersion (figure 39) supports this interpretation. Once the vesicles are formed, increasing the temperature results in higher annihilation rate. This is a consequence of increased fluidities and water penetration between the bilayers and hence of increased probabilities of positron annihilation in an apparently aqueous environment.

The phase transition temperature of single compartment bilayer DODAC vesicles, 37°C, is essentially identical to that observed for dipalmitoyl-D, L- α -phosphatidylcholine liposomes (36.4°C)¹¹⁴. Significantly, pretransition changes are clearly seen in DODAC vesicles (Figure 42). The appearance of pretransition temperature has been attributed to specific interactions between the choline moieties of the phospholipid and the water hydrating them¹¹¹. The presence of the choline group was considered, in fact, essential for the pretransition to occur¹¹⁵. Observation of pretransition temperatures implies either a different behavior of DODAC and liposome vesicles or the higher sensitivity of our method or both. Even more surprising is the observed sharp pretransition and transition temperatures for cholesterol containing vesicles. Conversely, addition of cholesterol initially broadens and ultimately eliminates the phase transition temperature of phospholipid liposomes¹¹⁶. Pronounced hystereses of the higher temperature transition were observed on determining positronium annihilation rates in DODAC vesicles by decreasing the temperature (Figures 43 and 44). Concomittantly,

the lower temperature phase transition disappeared. Hystereses have also been observed for the lower transition of multicompartment liposomes¹¹⁷. In contrast to DODAC, equilibrium cooling curves for liposomes were displaced to lower temperatures.

Thermal transitions of phospholipid liposomes have been rationalized in terms of morphological changes¹¹⁵. At temperatures below the pretransition, vesicles consist of one dimensional lamellas with the hydrocarbon chains fully extended and somewhat tilted. Transformations from one to two dimensional structures occur at the pretransition temperature. The fully extended lipid molecules are distorted by periodic undulations. At the transition temperature, the hydrocarbon chains "melt" by assuming mobile liquid-like arrangements and revert to one dimensional lattices. Phase transitions determined for DODAC vesicles can also be accommodated by analogous morphological changes. Detailed understanding of the temperature dependent structural changes of DODAC vesicles will become available upon additional experimentation.

CHAPTER VI: STUDY OF STYRENE-BUTADIENE-STYRENE BLOCK COPOLYMER
BY POSITRON ANNIHILATION TECHNIQUE

A. Introduction

The positron annihilation technique has been used successfully as a probe for detecting certain phase transitions and structural changes in molecular crystals¹¹⁸, liquids crystals⁶⁹⁻⁷², micellar systems⁷⁷⁻⁸², liposomes¹¹³ and polymers¹¹⁹⁻¹²¹. From the few studies on polymers, it was demonstrated that the thermal ortho-positronium lifetime (τ_2) depends on the physical and chemical structure of the polymers. It was found that this parameter may vary as a result of the changes which occur in the chain structure, configurations, conformations and molecular weight distributions of the samples.

The "free volume" theory is used in polymer chemistry in order to explain e.g. the glass transition. In this theory, it is postulated that the segments of a polymer chain can be represented by rigid bodies and the free volume as the holes between these segments as a result of packing requirements. It is assumed that the free volume reaches a constant value at the glass transition, T_g , which is too small to allow large scale conformational changes to occur. Above T_g , on the other hand, the free volume increases and becomes large enough to allow such motion to occur. Brandt¹²²⁻¹²³ et al. adopted similar interpretation to explain their results obtained in positron studies in molecular substances, including polymers. According to Brandt, the temperature and phase dependence of τ_2 in molecular substances is primarily a "free volume" effect in that the overlap between the positron component of

the o-Ps wave function and the wave function of the lattice electron involved in Ps formation depends on lattice spacing. We applied positron annihilation technique for studying the styrene-butadiene-styrene block copolymer.

Recent studies on styrene-butadiene-styrene block polymer types showed that the morphology and then the final properties can be influenced by the nature of the preparative conditions used for obtaining films. The effect of casting solvent on the bulk properties on linear styrene-butadiene-styrene block copolymers has been reported in the literature¹²⁴⁻¹²⁵. Because of a differing and controversial experimental results in these previous reports, it appeared worthwhile to investigate again this polymer by using a novel technique, and to determine the effect of the solvent used to produce the film, on the final properties. In these studies we investigated the styrene-butadiene-styrene block copolymer obtained by casting in toluene, carbon tetrachloride, ethyl acetate and methyl ethyl ketone.

B. Purity of Material:

The styrene-butadiene-styrene block copolymer used in these studies was Solprene[®] 416 (sample No. 52, 169). It was obtained from Phillips Petroleum Co. The nominal styrene content in the copolymer is 30%. The samples for measurements were obtained from solution by casting on glass plates and removing the solvent under vacuum at 80°C. The solvents such as toluene, carbon tetrachloride, ethyl acetate and methyl ethyl ketone were obtained from Fisher Scientific Co. and used without further purification.

C. Results and Discussion:

Positron annihilation parameters were determined as function of temperature. While I_2 , which is related to the thermal ortho-positronium formation probability, remained practically unaltered; λ_2 , the annihilation rate of the o-Ps atoms, exhibited abrupt changes at certain temperatures depending on the nature of the solvent (figure 45). Two distinct changes in the annihilation rate were observed at -70°C and $+85^\circ\text{C}$. In addition two other abrupt changes in λ_2 were observed at -14°C and $+10^\circ\text{C}$. The change at -14°C was observed in all films; whereas, the second at $+10^\circ\text{C}$ occurs only in films casted in solvents known to be poor for this polymer (ethyl acetate and methyl ethyl ketone). The first two changes in λ_2 , at -70°C and $+85^\circ\text{C}$, have been reported in the literature and were attributed to the onset of motion of polybutadiene and polystyrene segments, respectively¹²⁴⁻¹²⁵. However, at intermediate temperature, the question exists whether the styrene-butadiene-styrene block polymer exhibits changes in its properties as a function of temperature or whether it does not. Miyamoto¹²⁴ et al. reported the existence of a third peak in poor solvents (ethyl acetate and methyl ethyl ketone) in their studies by rheo-vibron technique and differential scanning calorimetry. The first technique demonstrated the existence of the peak at $+10^\circ\text{C}$; whereas, the second method at -14°C . The change observed by DSC was attributed to the one observed by rheo-vibron at $+10^\circ\text{C}$. Wilkes¹²⁵ et al. performed the same experiments with the rheo-vibron technique and did not observe any intermediate peak. In the present studies, we report the existence of two intermediate changes in λ_2 : the first only in the poor solvents ($+10^\circ\text{C}$) and the second in all

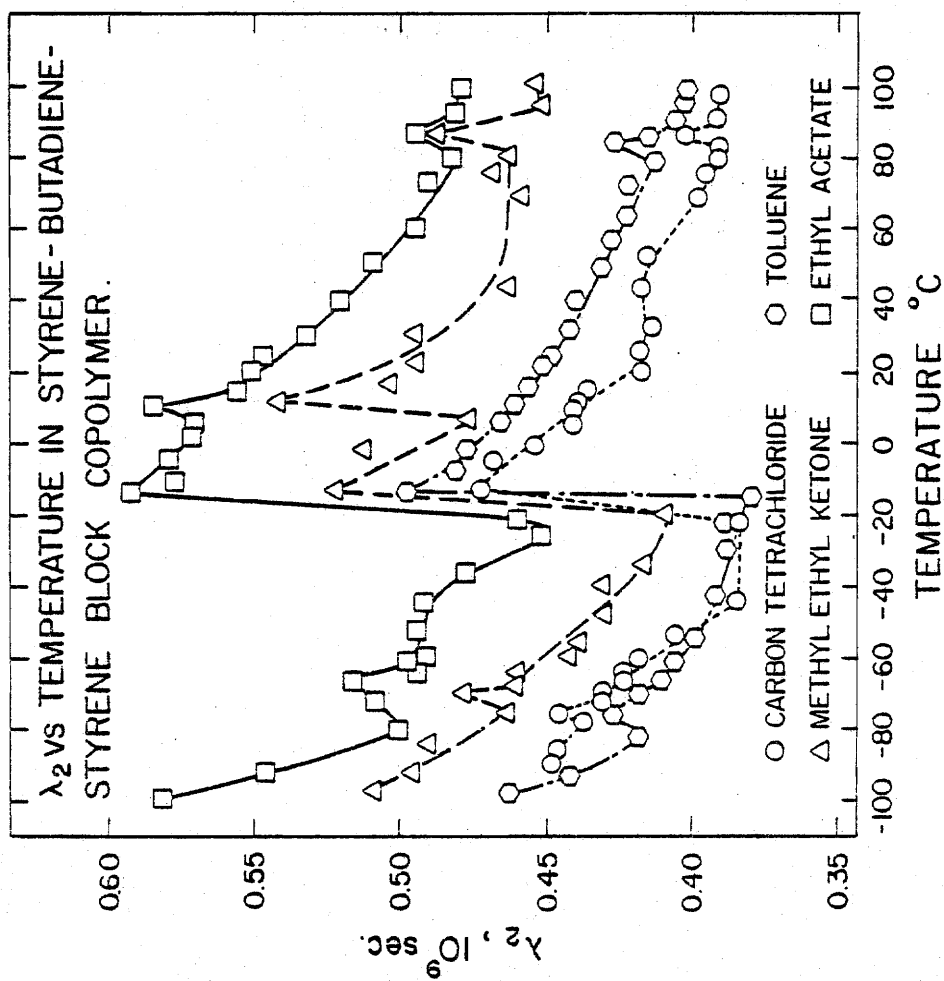


Figure 45. Plot of the Annihilation Rate as a Function of Temperature for Styrene-Butadiene-Styrene Block Copolymer Casted in Toluene, Carbon Tetrachloride, Ethyl Acetate and Methyl Ethyl Ketone

solvents (-14°C). The first change supports Miyamoto's results and a similar interpretation as given by this author can be adopted; namely, that the degree of phase separation in the poor solvents is not perfect. Consequently, a new phase, absent in toluene and carbon tetrachloride, should be present and therefore exert a certain influence on the properties of the polymer. This phase may consist of a mixture of polybutadiene and polystyrene. The second change, at +14°C, independent on the nature of the solvent, can be rationalized in terms of a major change in the morphological texture in the domain structure.

It is demonstrated in this investigation that changes in the styrene-butadiene-styrene properties are recognized by positron annihilation technique. The abrupt changes in the annihilation rate, λ_2 , can be interpreted of "free volume" effect postulated by Brandt¹²²⁻¹²³, in positron studies.

In summary, we believe that the data reported here provides new insights into the properties of polymer systems and also demonstrates the applicability of the positron annihilation technique for investigating polymer systems.

CONCLUSION

In the first part of this work we carried out several series of experiments, in which we further assessed the parameters responsible for changes in the thermal positronium formation probability, in various solutions of halogenated aliphatic and aromatic hydrocarbons. For these compounds, the electron attachment cross sections have been measured as function of electron energy and an attempt was made to correlate these parameters with the thermal Ps formation in order to further elucidate more accurately the exact mechanism responsible for the positronium formation.

In the second part, the positron annihilation technique was applied for studying systems such as micelle, liposome and polymers. The results obtained demonstrate clearly the applicability and, furthermore, the extreme sensitivity of the technique with respect to other conventional methods for the study of these systems.

In summary, the results presented in this thesis confirm the conclusion that the positron annihilation technique is very suitable for the investigation of microstructure changes in general.

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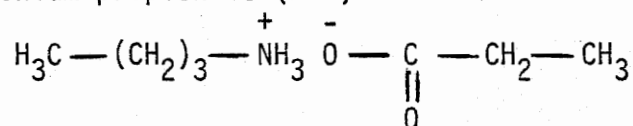
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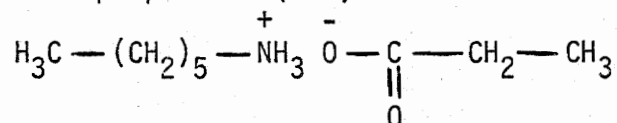
APPENDIX

Chemical Structures of Compounds Used

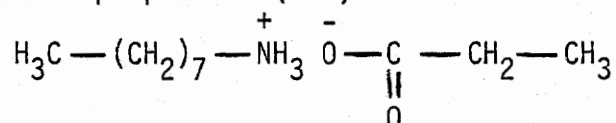
Butyl-ammonium propionate (BAP)



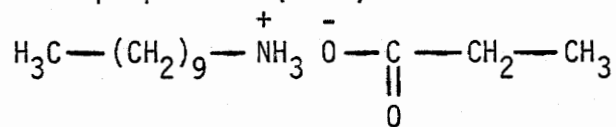
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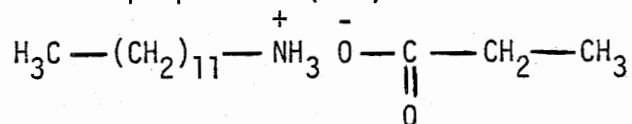
Octyl-ammonium propionate (DAP)



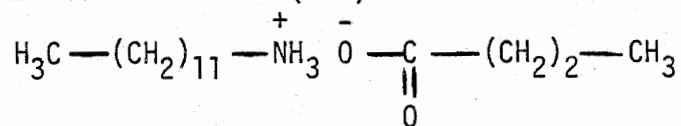
Decyl-ammonium propionate (DeAP)



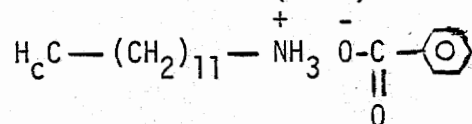
Dodecyl-ammonium propionate (DAP)



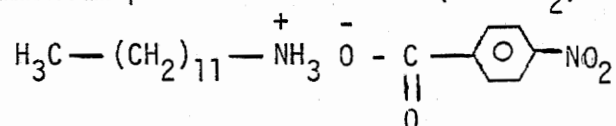
Dodecyl-ammonium butanoate (DAB)



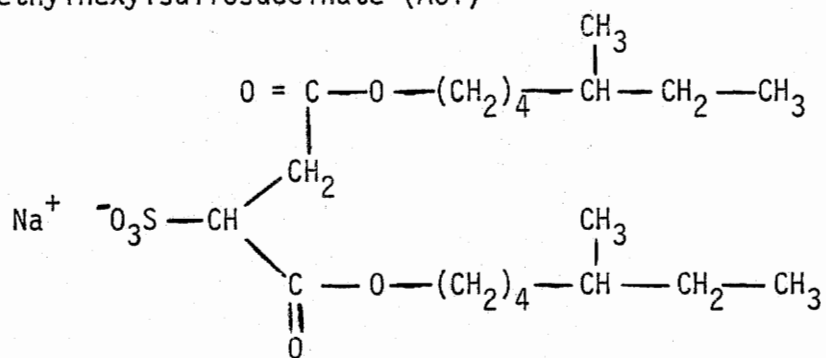
Dodecyl-ammonium benzoate (DABZ)



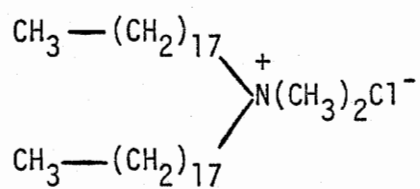
Dodecyl-ammonium para-nitrobenzoate (DABZNO₂)



Sodium-2-ethylhexylsulfosuccinate (AOT)



Dioctadecyldimethylammonium chloride (DODAC)



VITA

Belkacem Djermouni, the only son of Abdelkader Djermouni and Boukabrine Kheira, was born on January 22, 1950 at Sfisef, Algeria. He graduated from high school (Lycee Azza Abdelkader), Sidi-Bel-Abbes, in June 1968. He enrolled at Algiers University in the fall of that year; while there, he earned a licences ES-Sciences in Chemistry in June 1973.

Upon being awarded a scholarship from the French government, he traveled to France (Strasbourg) in the fall of 1973 to begin his graduate studies in radiochemistry at Louis Pasteur University under the direction of Professor J. P. Adloff and Dr. J. M. Friedt. In March 1976, he received the degree of Doctorate 3^e cycle.

In the fall of 1976, he was awarded a scholarship from the Algerian government to pursue his graduate studies in radiochemistry under the direction of Professor Hans J. Ache, at Virginia Polytechnic Institute and State University (USA). He completed the requirements for the degree of Doctor of Philosophy in radiochemistry in February, 1979. He is presently research associate in the same laboratory.



POSITRONIUM FORMATION IN ORGANIC LIQUIDS AND
STUDIES OF MICELLE, LIPOSOME AND POLYMER SYSTEMS
BY POSITRON ANNIHILATION TECHNIQUE

by

Belkacem Djermouni

(ABSTRACT)

The positron when formed as a result of nuclear decay process (β^+) can interact with an electron resulting in a positronium formation (Ps).

In the first part of this thesis the formation of positronium in benzene solutions containing various halogenated compounds was studied in the presence and absence of C_6F_6 additives. The observed I_2 values, which are indicative of the number of thermalized positronium atoms formed, showed a good correlation with the dissociative electron attachment parameters of the solute species.

The formation and the reactions of Ps were found to be very sensitive to structural changes and phase transitions. Therefore, the positron annihilation technique was applied for studying systems such as micelles, liposomes and polymers which have found widespread applications in today's chemical industry.

The micelle formation process was investigated in inverted micelles. A distinct cooperative effect of the solution resulting in abrupt changes in the number of thermal ortho-positronium atoms was observed and studied as a function of temperature, counter ion, length and structure of

the hydrocarbon chain in the cationic and anionic parts of the surfactant molecules. The results are being discussed in terms of existing models.

The thermotropic transition, which is an important parameter for all membranes and liposomes, was studied in sonicated dioctadecyldimethylammonium chloride vesicles (DODAC). The results obtained provide important information on fluidities and allow further assessments of cationic surfactant vesicles as membrane mimetic agents.

The third application deals with the study of styrene-butadiene-styrene block copolymers obtained by casting in toluene, carbon tetrachloride, ethyl acetate and methyl ethyl ketone. The temperature studies show the appearance of two distinct changes in the positron annihilation parameter λ_2 at -70°C and $+85^\circ\text{C}$. They were attributed to the onset of motion of butadiene and styrene respectively. In addition two other abrupt changes in λ_2 were observed at -14°C and $+10^\circ\text{C}$. The change at -14°C was observed in all films whereas the second at $+10^\circ\text{C}$ occurs only in films casted in poor solvents (ethyl acetate and methyl ethyl ketone). Their presence is discussed in terms of phase separation and morphological changes.