

STUDY OF STRUCTURAL CHANGES
IN MICELLAR SOLUTIONS AND MICROEMULSIONS
BY POSITRON ANNIHILATION TECHNIQUES:
THEIR RELEVANCE TO LIQUID
SCINTILLATION COUNTING PHENOMENA¹

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The mechanism of the formation of the positronium atom, which is the bound state of a positron and an electron, as well as its subsequent reactions are highly dependent on the physical and chemical microstructure of the environment in which they occur.

Since positronium formation and positronium reactions can be easily identified by positron lifetime measurements this technique has been applied to the study of micelles, reversed micelles, microemulsions, liquid crystals, and microphase changes occurring in these systems. By adding probe molecules to these solutions it is also possible to study their location in e.g., micelles.

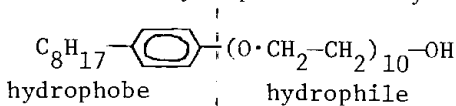
According to the currently accepted theory of positron interactions with the entities present in these solutions, trapping of positrons by the aggregates, micelles, etc. would be the process responsible e.g. for the reduction in positronium formation observed upon micelle formation. They would therefore very closely resemble interactions of electrons in solution or gels used as solvents in liquid scintillation counting.

Thus an attempt was made to correlate (liquid scintillation) counting efficiency determined as a function of the composition of the solution with structural changes occurring in the solution as reflected in positron annihilation parameters.

I. INTRODUCTION

Emulsion counting utilizing toluene based counting solutions which can accommodate milliliter quantities of aqueous samples has become an important technique in liquid scintillation spectroscopy (2-11). This technique is based on the fact that in the presence of non-ionic surfactant, such as Triton X-100, in toluene solution, relatively large volumes of aqueous radioactive samples form homogenous solutions, which allow measurement of the radioactivity under well reproducible conditions.

Triton X-100, a non-ionic surfactant molecule which is composed of a hydrophobic and hydrophilic part:



as well as other surfactants, form if dissolved in larger quantities, in an apolar solvent, inverted micelles. These inverse (or reversed) micelles (12-14) can be described as spherical aggregates with the polar head group pointing to the inside of the aggregate while the hydrophobic part of the molecule is directed toward the surrounding apolar solvent (Fig. 1).

SCHMATIC REPRESENTATION OF A REVERSE MICELLE
IN NONPOLAR MEDIA

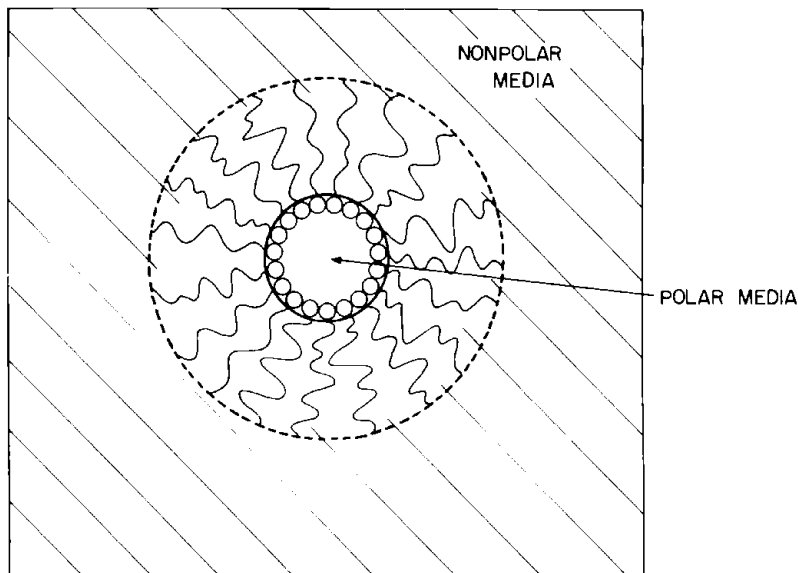


FIGURE 1. Reversed micelles.

Small amounts of water can be solubilized inside the micelle via interaction between the polar groups and the water molecules which stabilize these aggregates. If the water contents increase above a certain limit further stabilization via increased interaction between the hydrophobic part and the apolar solvent is necessary to stabilize the system, which is then called a microemulsion (15-18). In any case, the increased water contents may lead to significant changes of the micellar solution not necessarily limited to the size of the aggregates if more water molecules are incorporated but also to structural rearrangements of these aggregates.

The effect of the size of the aggregates on the counting efficiency in liquid scintillation spectrometry has been previously pointed out. Assuming that a beta emitter (tritium) is present in the aqueous phase in these aggregates, Kobayashi and Mandsley (19) argue, that since the maximum range of a tritium beta particle is typically 6 microns and 1.2 microns on the average, the beta particles will effectively leave the aqueous environment and interact with the fluoro- dissolved in the apolar solvent as long as the size of the micelles is less than about 1 microns. In the case of more energetic beta emitters, such as Carbon-14 or Sodium-22, this effect should be less pronounced.

More recently we have investigated the fate of the positron (20), e^+ , which is the antiparticle of the negatron, e^- , and found that not only the size but as suggested above also the presence of structured aggregates have a definite effect on the fate of the particle (21-24).

One important feature of the positron interaction with matter is the formation of the positronium, which is the bound state of an electron and a positron. We have found that the presence of various types of surfactant aggregates, such as micelles, leads to a reduction of (thermalized) positronium formation and suggested (24) that trapping of energetic positrons (or positronium atoms possessing excess kinetic energies) by the surfactant aggregates is responsible for the reduced formation of thermalized positronium. Because of the similarity of the species, positron and electron, particle and antiparticle, one could postulate that the behavior of the positron in liquid scintillator solutions would resemble very much that of the beta particle (e^-).

Thus an attempt was made to correlate the phenomena which affect the liquid scintillation counting efficiency determined as a function of the composition of the solution with structural changes occurring in the solution as reflected in positron annihilation parameters and thus to obtain a clearer picture of the processes responsible for changing the counting efficiency of weak beta emitters.

II. EXPERIMENTAL

A. *Materials*

Triton X-100 purchased from Amersham Corp. was scintillation grade quality. Toluene was spectroscopic grade from Fisher Co.; it was further dehydrated by distillation. PPO and Dimethyl-POPOP (DMPOPOP) as well as Sodium-22, in the form of carrierfree NaCl, ^3H -toluene, ^3H - H_2O and ^{14}C -sodium carbonate were also obtained from Amersham Corp. Bidistilled water was used.

B. *Liquid Scintillation Counting*

The liquid scintillation spectrometry was performed on a Beckman LS-100 counter. Energy discrimination for tritium, carbon-14 and sodium-22 betas was achieved in the usual way by selecting appropriate window settings.

1. *Experiments Designed to Determine the Effect of Water Additives on Count Rates.* The composition of the scintillator solution was 70 Vol % toluene and 30 Vol % Triton to which 7g/l PPO and 0.35g/l DMPOPOP were added. To each vial containing 10 ml of this solution was added the desired amount of water followed by the addition of 10 μl of the radioactive sample, ^3H -toluene, ^3H - H_2O , ^{14}C -cyclohexane, ^{14}C -sodium carbonate and $^{22}\text{NaCl}$, the two latter compounds dissolved in a microamount of H_2O . The counting solutions prepared in this way were vigorously shaken and counted at room temperature.

2. *Experiments Designed to Determine the Effect of Triton Concentration on the Count Rate.* To scintillator solutions of low concentrations of Triton X-100 (3-160mM), containing 7g/l PPO and 0.35g/l DMPOPOP, 0 to 2 Vol % H_2O were added. The tritium activity was added in form of 10 μl ^3H - H_2O or ^3H -toluene.

C. *Positron Lifetime Measurements*

Positron lifetime measurements were carried out by the usual delayed coincidence method (25). The resolution of the system, as measured by the prompt time distribution of ^{60}Co source and without changing the 1.27- and 0.511-MeV bias, was found to be 0.390 ns fwhm. Corrections for the source component, which had an intensity of less than 4%, were made in the usual way by using conventional computational methods.

1. *Data Analysis.* The resulting positron-lifetime spectra were analyzed into two or three components by using the PAL (26), POSITRONFIT, and POSITRONFIT EXTENDED (27) computer programs. No significant differences were observed between the results obtained by each of these programs. Thus, the PAL program was consistently used to separate the spectra into two components. In agreement with previous work, the intensity of the long-lived component, I_2 , was considered to be directly related to the number of thermal o-Ps atoms formed in the substance.

2. *Preparation of Sample.* Specially designed sample vials (cylindrical glass tubes 100 mm long and 10 mm i.d.) were filled with 1 ml of sample. In the first series of experiments (solutions of Triton and toluene containing various amounts of H_2O) 20 μCi in form of aq. $^{22}\text{NaCl}$ was used. The samples were gently stirred during the measurements. In all the other experiments the positron sources were 5-20 μCi ^{22}Na , prepared by diffusing carrierfree $^{22}\text{NaCl}$ into a thin soft glass foil.

The sources were placed inside the vials and completely immersed in the liquid sample. The vials were degassed and subsequently sealed off and counted at room temperature.

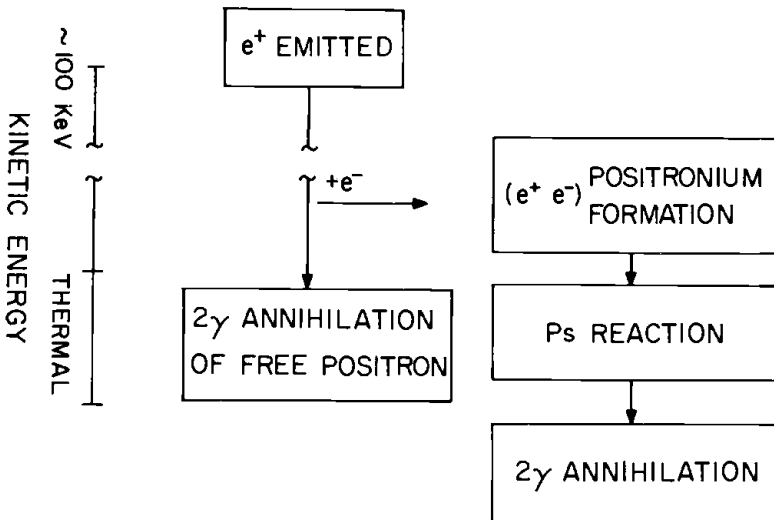


FIGURE 2. Fate of positrons emitted as a result of nuclear decays.

III. GENERAL ASPECTS OF POSITRON ANNIHILATION IN CONDENSED MATTER

Positrons (20) are most commonly emitted as a result of the radioactive decay of a neutron deficient nuclide. They lose their high kinetic energy in collisions with the surrounding matter until they reach thermal or near thermal energies at which point the cross section for mass annihilation with an electron assumes a maximum value (Fig. 2).

A certain fraction of these positrons, however, may enter the bound state of the positronium (Ps), by combining with an electron. Ps can be formed in two ground states either in the triplet or ortho state, with parallel spin orientation and an intrinsic average annihilation lifetime of 1.4×10^{-7} s, or in the singlet or para state with antiparallel spin orientation, which has an intrinsic average lifetime of 1.25×10^{-10} s (Fig. 3).

The chemical information about the environment in which the positron or Ps is formed and subsequently annihilates can basically be extracted from the observation of two processes:

Firstly, the positronium formation and secondly the reactions of the positronium atom.

A. Basic Aspects of Positronium Reactions

Quantum chemistry predicts that the annihilation lifetime of a positron species is generally determined by the degree of overlapping of positron and electron wave functions, which leads e.g. to the intrinsic lifetime of the ortho-Ps of 1.4×10^{-7} sec. In a condensed matter it is obvious that the electron density at the position of the positron will greatly depend on the macroscopic and microscopic (mass) density and thus on parameters such as phase and temperature. This rather simple approach has led to the development of the "free volume" or "excluded volume" model (20, 28-29), whose basic feature it is that the lifetime of a positron or Ps trapped in such a material will depend on the free volume which it has available.

These models have been quite useful as a means of explaining some of the phenomena associated with the rate of positron annihilation. Other experiments, however, seemed to indicate that the "free volume" model includes far too few properties apart from the factor of density as to satisfactorily explain variations in the positron lifetimes which occur as a result of phase transitions. It would appear that in this case an important part in the positron annihilation process is played by the nature of the intermolecular interaction and by the internal order of the structures of the molecular substance.

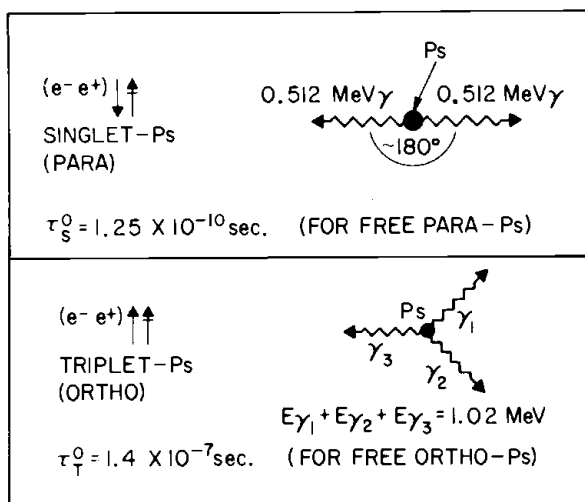


FIGURE 3. Positronium annihilation.

In most cases different degrees of order are accompanied with large changes in the state of matter of the sample, which may cause a definite change in the mechanism of the annihilation process. To establish whether the degree of order has any bearing on the annihilation process, measurements have been made on samples of unchanged density but of different degree of order. Liquid crystals proved to be a good material for this kind of study. Previous work by Walker et al. (30-31) in liquid crystalline systems has borne out the fact that the lifetime of the longlived component in the positron lifetime spectra, which they attributed to ortho-positronium, varies not only during fusing (i.e. solid-smectic or nematic transitions), but also during transitions between the smectic and cholesteric phase. Since these latter phase transitions are accompanied only by very small density changes but involve very definite rearrangements of the molecules in the substance at the transition point, these results supported the above contention that internal structural ordering affects the positron lifetimes.

These findings were further confirmed in a series of investigations on liquid crystal systems carried out in our own laboratory (32) and it was concluded that the mechanism of positron annihilation is extremely sensitive not only to variations in the free volume but also to slight changes in the arrangements of molecules in a condensed matter and thus to changes in the nature and magnitude of intermolecular interactions.

Another model which describes positron or positronium annihilation in terms of the interactions of the Ps with individual molecules has been recently developed in our laboratory (33). It has been found extremely useful for the evaluation of the interaction between Ps and those molecules which display high reactivity towards Ps. It is based on simple gas kinetic principles and includes schematically the following reactions.

As shown in Fig. 4 the basic assumption is that in a collision between o-Ps and another molecule a more or less long-lived collision complex is formed, in which the electron density at the position of the positron is drastically increased (Fig. 4). The average time that the Ps spends in this complex will depend on the stability of this complex. If only weak (van der Waals) forces are operative in holding this complex together, the Ps will spend only very little time in this environment, and the positron experiences only for a short time the effect of the increased electron density. Thus the average lifetime of o-Ps is only slightly reduced. On the other hand, if this Ps collision complex undergoes stabilization involving genuine chemical forces, e.g., bond formation, then the positron will find itself for a prolonged period in an environment of high electron density, and its lifetime will be substanti-

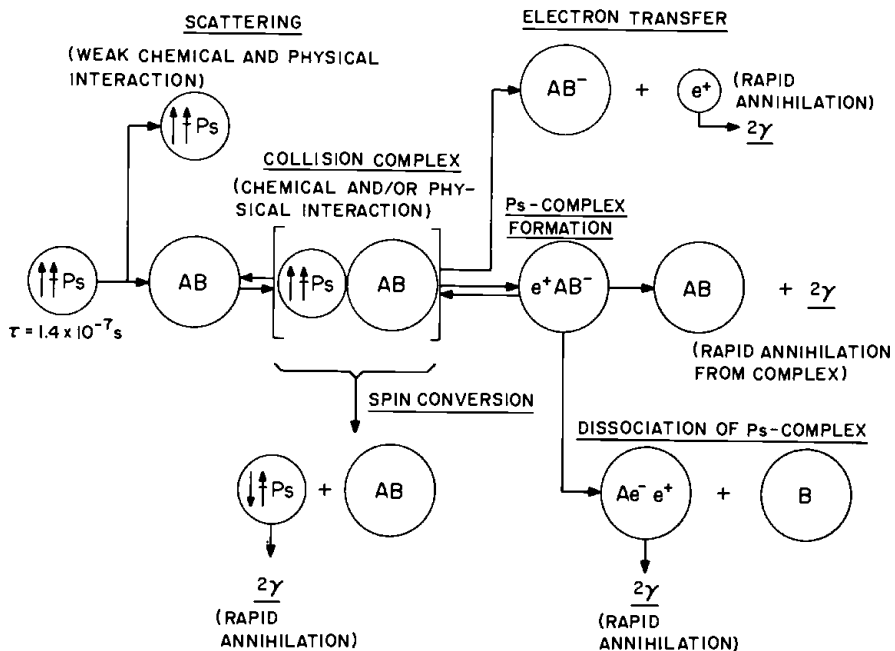


FIGURE 4. Schematic representation of possible o-Ps interactions with matter.

ally reduced. In other cases this complex may be just a transition state leading to electron transfer from Ps to substrate, i.e. oxidation of Ps. The product of this latter process is a free positron, whose lifetime in condensed matter is considerably shorter (0.1 - 0.5 nsec) than that of the o-Ps. If the substrate is paramagnetic the collision can result in a spin conversion from ortho to para Ps, whose intrinsic lifetime is only 1.25×10^{-10} sec. (Because of the extremely short intrinsic lifetime of the para Ps, reactions of this species can be neglected.) Thus, one can generally state that all interactions of the o-Ps with matter lead to a shortening of its apparent lifetime.

For accurate determination of the reactivity of thermal Ps towards various substrates these qualitative predictions had to be developed to a quantitative method which allows the calculation of the chemical rate constants for the reactions between Ps and substrate.

This can be accomplished by setting up appropriate kinetic equations and subsequent integration of the resulting differential equations, from which the population of the various states in which the positrons exist o-Ps and PsM can be found as a function of time. From these values and the positron annihilation constants for these states, an equation for the time dependent two photon annihilation rate can be obtained, which in turn allows the determination of the chemical reaction rate constants by utilizing sophisticated nuclear chemical lifetime measurement techniques.

It was found that the rate constants observed between a reactive molecule and Ps are not only determined by the nature and the chemical properties of the molecule itself but depend also on the environment, type of solvent, nature and magnitude of intermolecular (solute - solvent) interactions which the molecule undergoes with the surrounding molecules (34-35).

B. Basic Aspects of Positronium Formation

Two basic models, the Ore gap model (20) and the spur reaction model (36), have been invoked to describe the Ps formation process. More recently several versions of a modified spur reaction model have been suggested (37-38).

The Ore model postulates that positrons generated in the radioactive decay of certain nuclides are slowing down from higher energies and pass through an energy gap in which they can abstract an electron and form Ps (e^+e^-) (Fig. 5).

The lower boundary of this "Ore gap" is defined by the expression $V - I_{Ps}$, where V is the ionization of the surrounding molecules and I_{Ps} the ionization potential of Ps, 6.8eV. If the kinetic energy of the positrons exceeds V it is assumed

Energetics of Positronium Formation

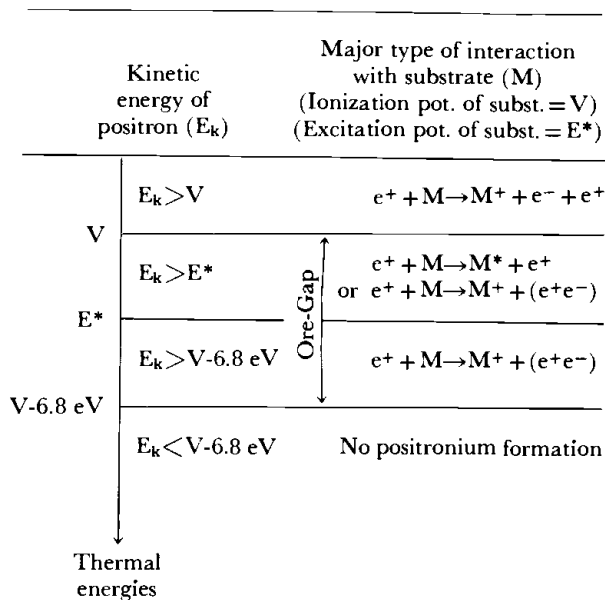
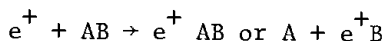


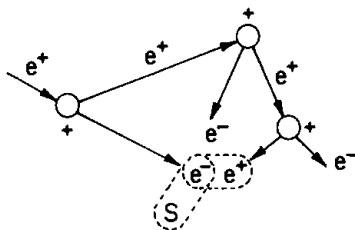
FIGURE 5. Energetics of positronium formation.

that ionization of the surrounding molecules ($e^+ + M \rightarrow M^+ + e^- + e^+$) becomes more probable than Ps formation ($e^+ + M \rightarrow M^+ + \text{Ps}$), so that V constitutes the upper boundary of the "Ore gap". Ps atoms can be formed in the Ore gap with Kinetic energies of up to 6.8 eV and react as such or after being thermalized.

The experimental results, however, suggest that not all positrons form Ps and several factors have been discussed which could interfere with and inhibit this process.

The Ore model is based on the simplified assumption that all positrons whose kinetic energy lies in the Ore gap produced Ps. In practice, however, the Ps formation process in the Ore gap has to compete with all other processes that can cause moderation of the positron to energies below the lower Ore Limit. The most important of these are elastic and inelastic collisions with substrate molecules, the energy transferred in the second case possibly stimulating molecular vibrations and rotations. This category also includes processes that lead to positron capture by addition of positrons to the substrate molecule AB.



END OF e^+ TRACK (POSITRON SPUR)

Ps FORMED BY COMBINATION OF e^+ WITH e^- GENERATED IN e^+ SPUR. Ps FORMATION HAS TO COMPETE WITH OTHER RADIATION-CHEMICAL PROCESSES, e.g. e^- ATTACHMENT TO SOLVENT OR SOLUTE SPECIES (S).

FIGURE 6. Spur reaction model for positronium formation.

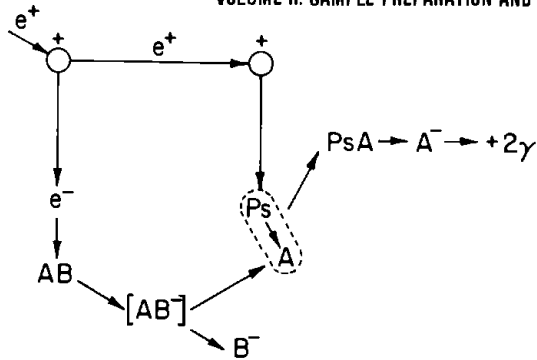
If the compound formation occurs above or within the Ore gap, the captured positrons are no longer available for the formation of Ps , whose yield is therefore decreased.

A second model for Ps formation which has been recently suggested by Mogensen et al. (36) is the spur reaction model. They assume that Ps is formed as a result of a spur reaction between the positron and a secondary electron in the positron spur (Fig. 6). In this model a correlation should exist between the Ps formation probability and the availability of the electrons in the spur, that is to say that Ps formation must compete with electron - ion recombination and with electron and positron scavenging by the surrounding molecules, as well as with other processes.

A model which combines certain features of both models is Tao's "modified spur model" (37). In this model Tao considers both the possibility of combination of a positron with an electron created in the spur as well as the "direct" formation of a positronium, similar to the mechanism discussed in the Ore model, if the total kinetic energy of the resulting electron-positron pair is less than the potential energy between them.

More recently, Ache et al. (38) suggested that Ps is predominantly formed by the interaction of energetic positron with electrons, however subsequent rapid reaction of the Ps with radicals or other reactive species produced in the spur leads to a reduction of thermalized Ps and thus to changes in I_2 which is indicative of the number of thermal Ps (Fig. 7).

Regardless which model one wants to adopt for the Ps formation process, it is clear that factors such as ionization and excitation potentials, electron attachment cross sections, the



Ps FORMED VIA ABSTRACTION OF e^- BY AN ENERGETIC e^+ REACTS BEFORE IT REACHES THERMAL ENERGIES WITH REACTIVE SPECIES PRESENT OR GENERATED VIA DISSOCIATIVE e^- ATTACHMENT AND OTHER RADIATION CHEMICAL PROCESSES

FIGURE 7. Modified spur reaction model.

factors which control them, i.e. degree of order in the structure of dipolar molecules, intermolecular forces, polarization etc., will govern to a great extent the positronium formation.

C. Experimental Measurements of Ps Reactions and Ps Formation

In order to observe changes in Ps reaction rates and in the Ps formation probability the most common method is the lifetime measurement (39).

In order to obtain rate constants for the reaction of Ps (or positrons) with substrate molecule or to follow changes in the reactivity of a certain medium towards Ps the two photon annihilation rate (see above) has to be determined. This is accomplished by positron lifetime conventional fast-slow γ - γ coincidence methods.

The positron emitter used is ^{22}Na , which decays under emission of a positron to the excited state of ^{22}Ne , which in turn

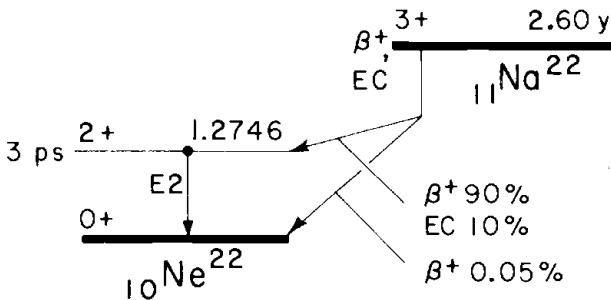


FIGURE 8. ^{22}Na decay scheme.

undergoes deexcitation under emission of a 1.27 MeV photon. The lifetime of the excited ^{22}Ne is only 3 psec, so that for all practical purposes the emission of the positron and 1.27 MeV photon can be considered to occur simultaneously (Fig. 8).

Thus the positron lifetime distribution can be determined by observing the time elapsed between the generation of the 1.27 MeV photon and the appearance of the 0.51 MeV photons resulting from the annihilation of the positron. These time measurements can be carried out by conventional fast-slow coincidence techniques as previously described (39).

A positron lifetime spectrum, as shown in Fig. 9, can usually be dissolved into two components. As indicated schematically in Fig. 10, the short-lived component with an associated lifetime τ_1 and intensity I_1 can be attributed to the annihilation of the free positron, the annihilation of the products formed in the reaction of "hot" ortho Ps and the self annihilation of para-Ps, whereas the long-lived component displaying a lifetime τ_2 and intensity I_2 is attributed to the annihilation of thermalized o-Ps.

The intensity (I_2) of the long-lived component can be correlated as previously discussed to the o-Ps formation yields.

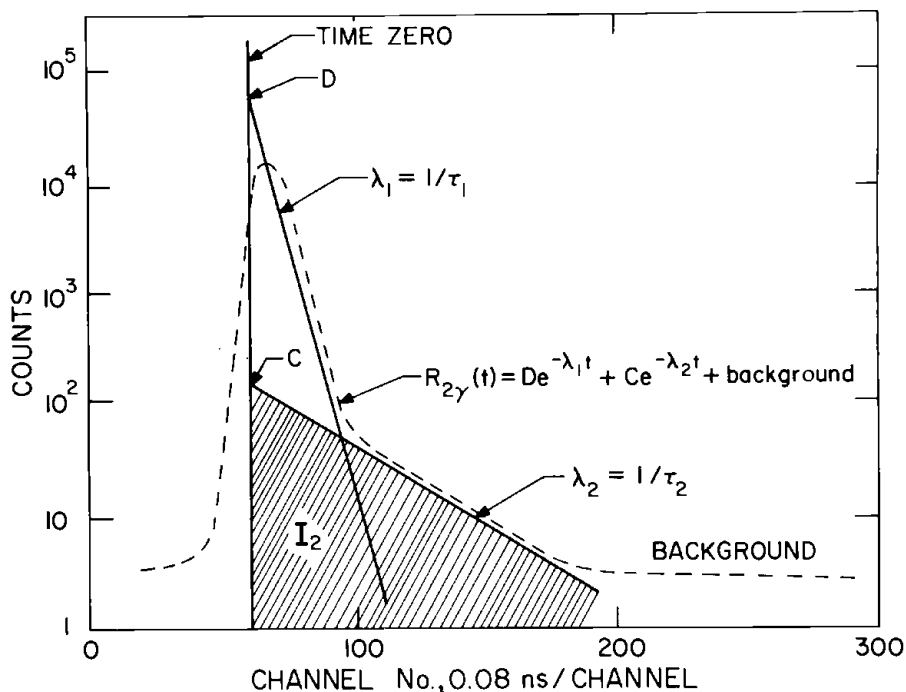


FIGURE 9. Typical positron lifetime distribution curve as acquired by fast-slow coincidence techniques.

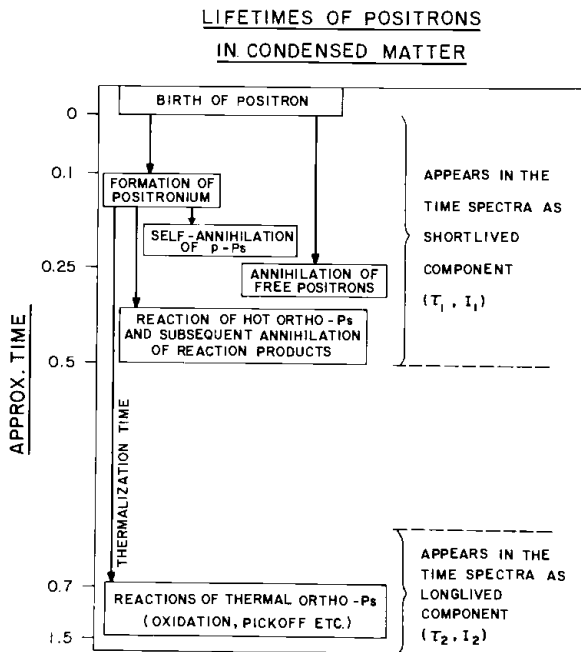


FIGURE 10. Time scale for the progress of the various types of interactions between e^+ or P_s and solute or solvent species in aqueous solution.

IV. RESULTS AND DISCUSSION

In order to determine the effect of the microstructure of the solution on the beta counting efficiency in toluene - Triton mixtures in a first series of experiments the positron annihilation parameters were determined in toluene - Triton mixtures containing various amounts of water. As can be seen from Figs. 11 and 12, where the Parameter I_2 , which is correlated to the formation probability of thermal positronium, is plotted as a function of Triton (in the presence of 0 and 2 % water) concentration, increasing amounts of Triton reduce I_2 to a semi-plateau value, while λ_2 , the annihilation rate of the thermal positronium, changes only slightly. A more detailed plot of I_2 at lower Triton concentration reveals that I_2 remains constant up to 20 mM or 10 mM Triton in solutions containing 0 or 2 % water, respectively.

In previous investigations we have been able to correlate this abrupt break in the I_2 - surfactant concentration plots with the formation of micelles or surfactant aggregates (24). An analysis of the present data in terms of the previously

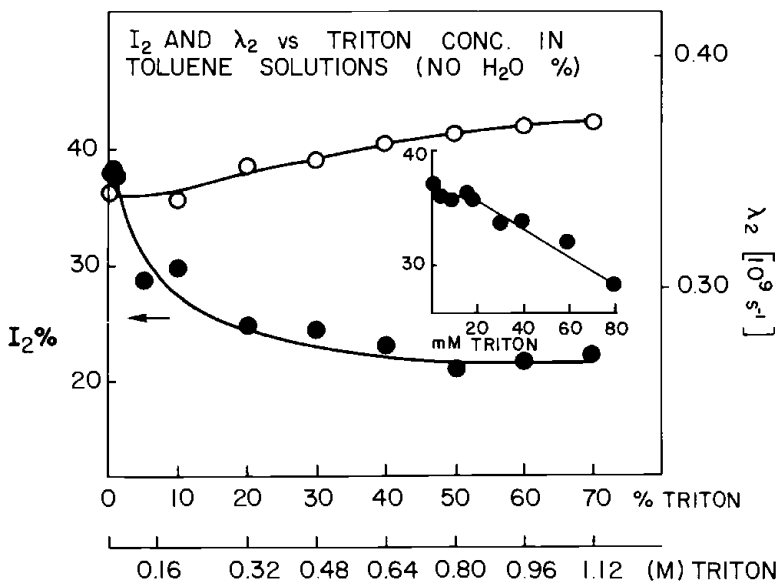


FIGURE 11. I_2 and λ_2 vs. Triton concentration in toluene solutions (no H_2O_2 added).

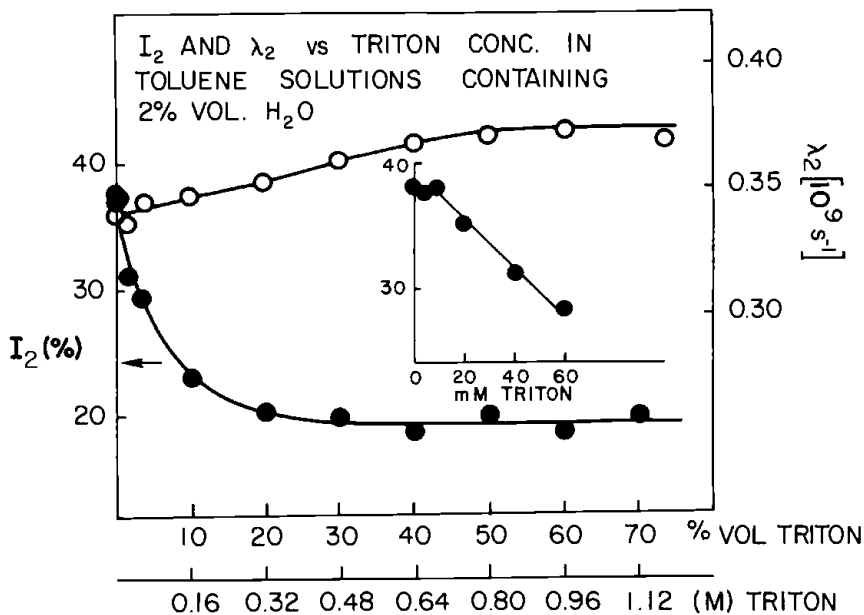


FIGURE 12. I_2 and λ_2 vs. Triton concentration in toluene solutions containing 2% Vol. H_2O .

described assumption that energetic positrons become trapped in these aggregates, in this case reverse micelles, reducing their chance to form thermal positronium atoms, leads to the following correlation between the plateau value, I_2^m , I_2^o , the value observed in the pure solvent, I_2 measured at a given surfactant concentration, and the surfactant concentration:

$$-\ln \left[\frac{I_2 - I_2^m}{I_2^o - I_2^m} \right] = K(S - \text{CMC}) / N$$

where K is the so-called inhibition constant (for positronium formation), CMC is the critical micelle concentration and N the aggregation number.

The corresponding plots in Fig. 13 show that at the higher water contents (1-2%) the CMC is shifted from about 19 mM to 11 mM Triton, and that inhibition is more effective in the presence of a small amount of water than in its absence, $K \sim 10 \text{ M}^{-1}$ vs. 4 M^{-1} .

In order to evaluate which effect the formation of reversed micelles might have on the counting efficiency of tritium beta particles, in a second series of experiments the (tritium) counting efficiencies of toluene solutions containing PPO - POPOP fluors and 0 or 2 % water, respectively, were

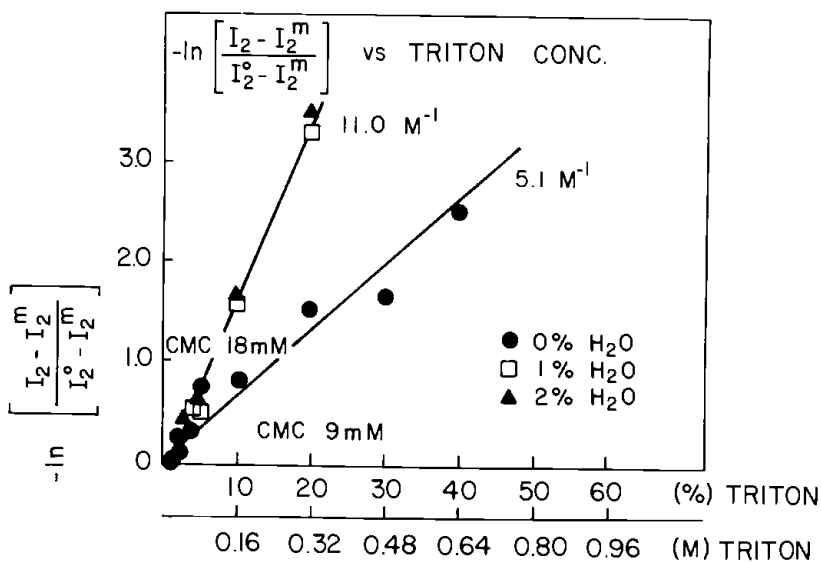


FIGURE 13. $-\ln \left[\frac{I_2 - I_2^m}{I_2^o - I_2^m} \right]$ vs. Triton concentration.

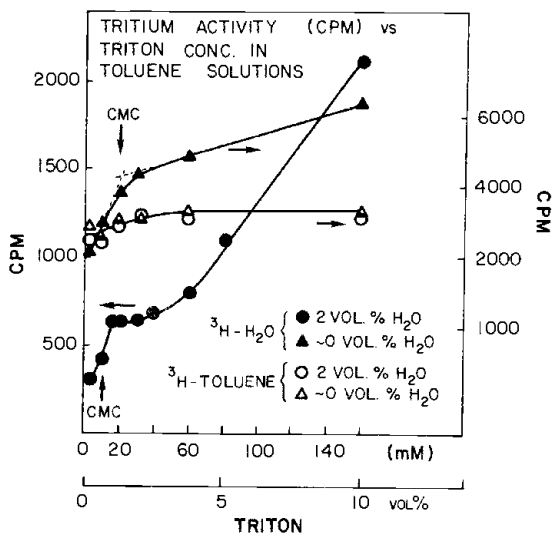


FIGURE 14. Tritium activity (CPM) vs. Triton concentration in toluene solutions.

studied as a function of Triton concentration. In Fig. 14 the results of these investigations were plotted in terms of cpm as a function of Triton concentration. In both systems, where the same amount of tritium activity in form of $^3\text{H-H}_2\text{O}$ was used, the counting efficiency steeply increases as a function of Triton additive, up to 20 or 10 mM, respectively, in which case a distinct break in the curves can be observed, coinciding with the formation of reversed micelles, followed by further increase at higher surfactant concentration. No such discontinuities can be seen if the tritium beta source is $^3\text{H-toluene}$.

These results clearly indicate that the interaction between the beta particles (and the resulting delta rays) and the *monomeric* surfactant molecules leads to a more efficient energy transfer resulting in higher count rates, than in a system where the surfactant aggregates are present in form of reversed micelles. One might argue that this could be caused by the fact that the water (and tritiated water) becomes incorporated in the center of the reversed micelles and that only the tritium beta particles at the interface between the organic and aqueous layer have sufficient energy to penetrate into the organic layer and interact with the fluor. However, the size of the reversed micelles is too small (<0.05 micron) as compared with the range of the tritium betas to make this a viable explanation. It appears that some yet to be defined specific interaction between the beta emitter in the micelle and the micelle aggregates lead to a reduced counting efficiency.

This is further supported by the results of a second series of experiments in which samples of beta emitters of various energies were counted in mixtures of 70% toluene and 30% Triton X-100 containing increasing amounts of water. As can be seen in Fig. 15 where the activity of tritium, either in form of ^3H -toluene or ^3H - H_2O , is determined as a function of the water contents of the solution, the counting efficiency drastically decreases in both samples. However, there are distinct differences depending on the chemical form of the tritium source. While in the case of ^3H - H_2O a small amount of water, less than 2%, reduces the counting efficiency by more than a factor of two, only a relatively small reduction can be seen if the tritium is present in form of ^3H -toluene. In addition to this initial sharp drop a maximum can be observed at about 10% water contents, whereas the ^3H -toluene system shows one at about 14% water and a plateau in the region between 22 and about 40% water.

If the data are represented in form of the EM value (which is product of counting efficiency multiplied by the water volume) curves result showing maxima at about 30% water for ^3H - H_2O and at 40% water in the case of ^3H -toluene (Fig. 16).

A different picture develops if a beta emitter of higher energies such as carbon-14 (E_{max} 160 KeV vs 18 KeV for ^3H) is employed (Fig. 17). In the case of a water soluble molecule, such as ^{14}C -sodium carbonate, the addition of a small amount of water (2%) results again in a drastic drop of counting efficiency, followed by an increase and subsequent drop in the region between 12 and 18%. If carbon-14 activity is incorporated into an organic molecule such as cyclohexane the initial drop is much less pronounced and a minimum is reached at about 20%. In both cases, however, additional water increases the counting efficiency to a plateau value which remains constant up to 50% water, which was the largest amount added in these experiments. The EM values for these systems as demonstrated in Fig. 18 increase rather smoothly with the amount of water added.

For comparison a high energetic positron emitter (E_{max} 545 KeV), sodium-22, in form of carrierfree $^{22}\text{NaCl}$, was also included in this investigation. As the results in Fig. 19 show, where the relative number of counts was plotted as a function of water contents, after an initial drop at about 2-3%, the counts reach very rapidly a plateau value, if the energy window of the liquid scintillation spectrometer is set to accept pulses corresponding to the range of phosphorous-32 betas. If only lower energy pulses are accepted (carbon-14 window), the plateau value is reached at a somewhat higher water concentration. The corresponding EM values are plotted in Fig. 20.

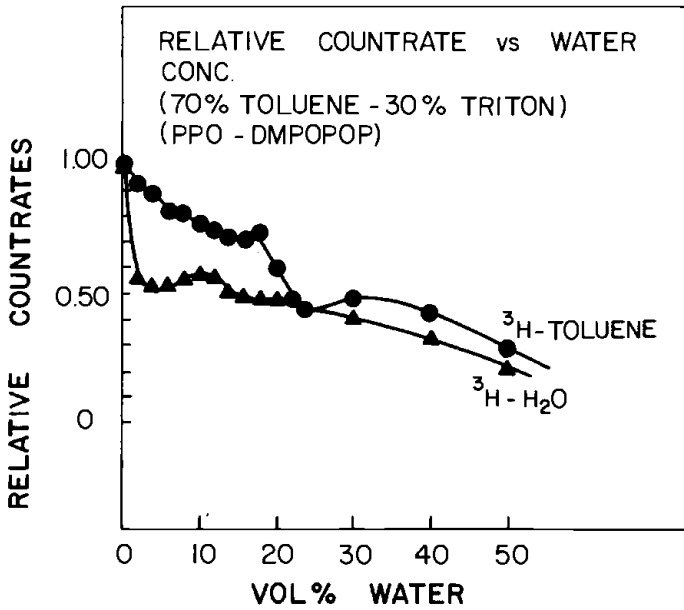


FIGURE 15. Relative count rate vs water concentration (70% Toluene-30% Triton - PPO-DMPOPOP).

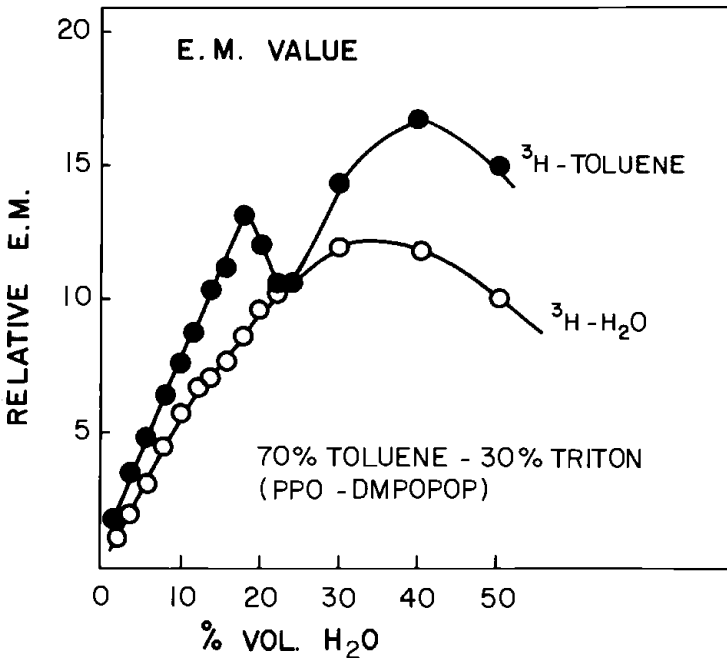


FIGURE 16. E.M. value vs water concentration.

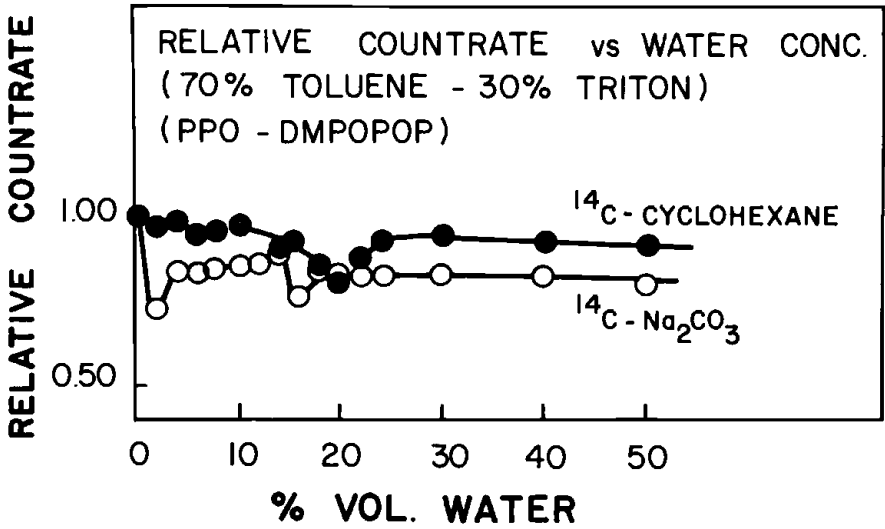


FIGURE 17. E.M. value vs % Vol H_2O .

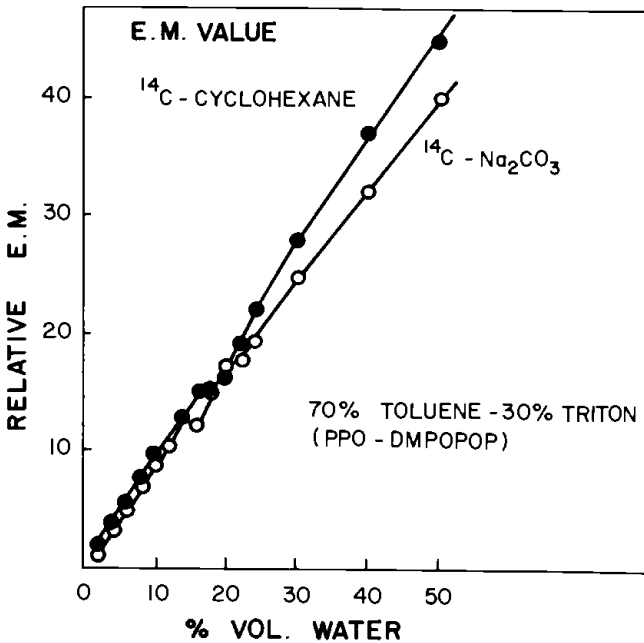


FIGURE 18. Relative count rate vs water concentration (70% toluene-30% Triton - PPO-DMPOPOP).

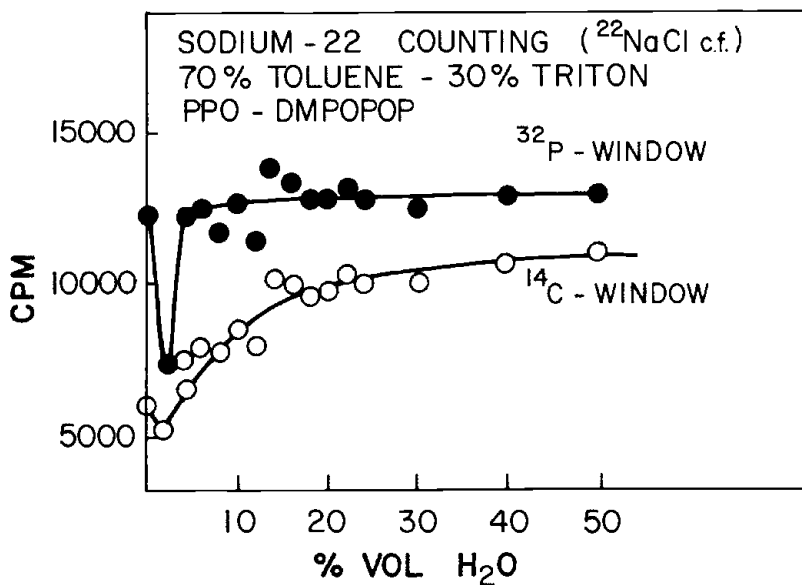


FIGURE 19. Sodium-22 counting ($^{22}\text{NaCl}$ c.f.) (70% toluene-30% Triton - PPO-DMPOPOP).

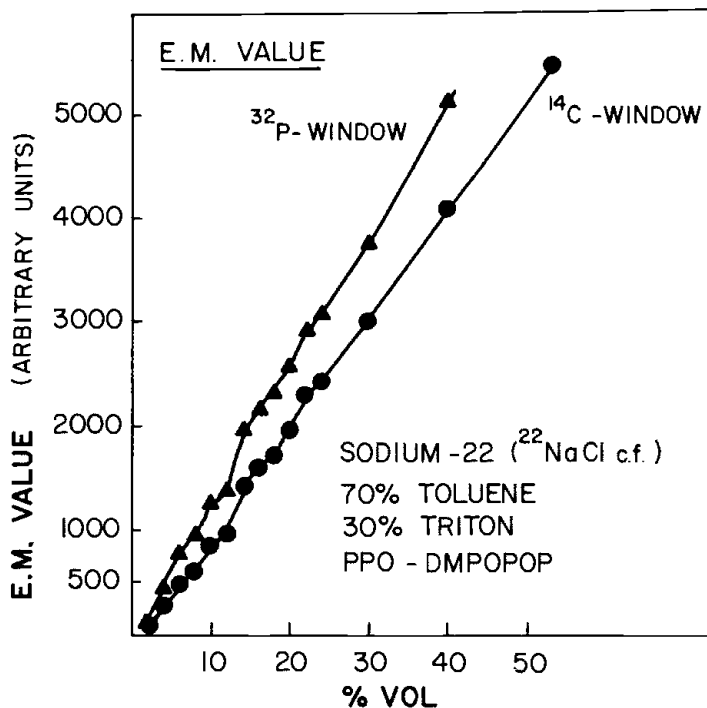


FIGURE 20. E.M. value vs H₂O concentration.

In Fig. 21 the positron annihilation parameters are shown for a solution of 70% toluene and 30% Triton X-100 containing increasing amounts of water. Again a distinct discontinuity is observed at about 3% H₂O (region I) followed by a plateau (II) and an intermediate maximum in region III before λ_2 and I_2 increase abruptly at about 26% followed by a slighter monotonous increase from 30% to 50%.

In an effort to interpret these results we would like to associate the minimum at 3% H₂O contents with a change in the structure of the reversed micelles. It appears that the reversed micelle can accommodate about 2-3% water which interacts strongly with the polar head groups and displays therefore as discussed by various authors (40) quite different properties than "normal" water. As the results indicate this strongly bound water system seems to be capable of suppressing somewhat the positronium formation or when it contains tritium interferes with the counting of the betas, possibly by effectively absorbing the kinetic energy of the beta particle as evidenced by the fact that the counting efficiency is reduced only when the beta source is water or a strongly water soluble substrate.

A further increase of the water contents leads to plateau values in region II, which we associate with the formation of microemulsions; that is to say, reversed micelle systems containing larger amounts of water. This causes an opening of

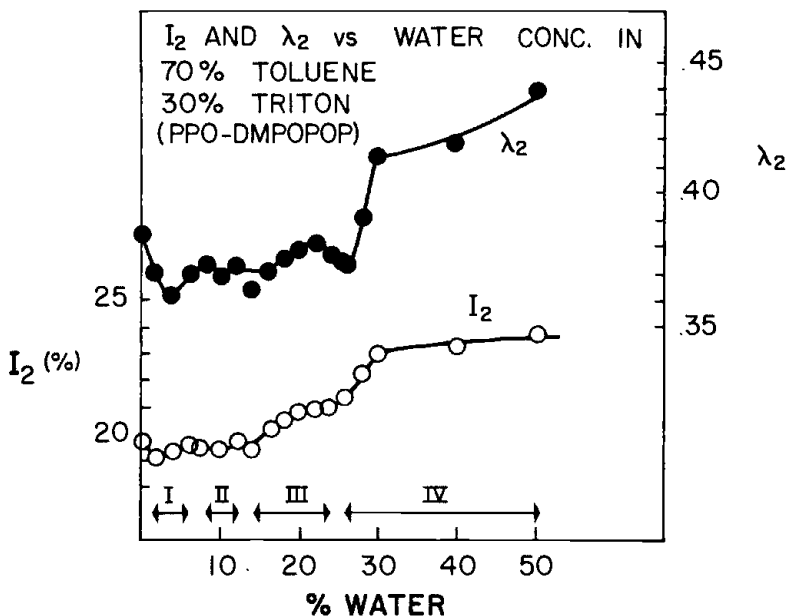


FIGURE 21. I_2 and λ_2 vs water concentration in 70% toluene-30% Triton (PPO-DMPOPOP).

the rigid reverse micellar environment, thus allowing the betas or positrons more freely to interact with the fluors or to form positronium. The results in region III are difficult to interpret, since separation in two phases occurred. The further sudden increase of λ_2 and I_2 at 20% eventually approaching the values observed in pure water seem to indicate that at these concentrations the positrons experience basically a waterlike environment, i.e. after they have lost most of their energy they are trapped in a water environment which determines their probability for positronium formation and its lifetime. Thus the abrupt change at 26% seems to signal a drastic structural change in the solution, probably the transition from a water in oil microemulsion to an oil in water microemulsion.

These transitions observed by this method are also reflected in the tritium counting efficiency which decreases strongly at higher water concentrations and indicate a preferential trapping of the weaker beta particles in the water environments. Consistent with these assumptions, this effect is less pronounced when beta particles are more energetic and are therefore capable of sampling the whole solution.

While the amount of water which can be solubilized in a surfactant-hydrocarbon is relatively small the addition of a co-surfactant, commonly an alcohol, resulting in the formation

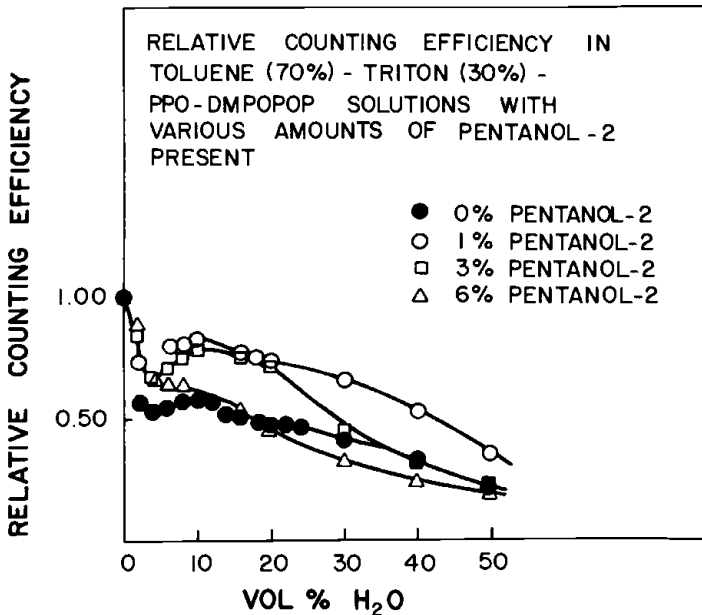


FIGURE 22. Relative counting efficiency in toluene (70%) - Triton (30%) - PPC-DMPOPOP solutions with various amounts of pentanol-2 present.

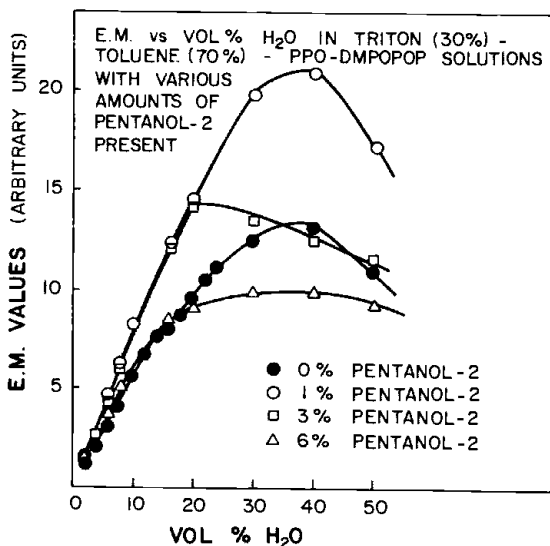


FIGURE 23. E.M. vs Vol. % H₂O in Triton (30%)-Toluene (70%)-PPO-DMPOPOP solutions with various amounts of pentanol-2 present.

of microemulsions, can be used to accommodate larger water quantities (41). We therefore studied the effect of alcohol additives on the relative counting efficiency in samples containing $^3\text{H-H}_2\text{O}$ in 70% toluene - 30% Triton mixtures (PPO and DMPOPOP fluors present). As can be seen in Fig. 22 where the relative counting efficiency in systems containing 0-6% pentanol-2 are plotted as a function of water contents, small amounts of pentanol-2 (1%) definitely improve the counting efficiency. This is more clearly expressed in Fig. 23 which shows the relative figure of merit. Larger alcohol additions on the other hand (>6%) result in a decrease of the counting efficiency in the critical region between 10 and 40% water contents.

From these results one might have to conclude that the formation of a clear phase as achieved by the addition of about 20% pentanol-2 to solutions containing approximately 10% water is not necessarily associated with increased counting efficiency. The increased number of alcohol molecules present in the interface seem to overcompensate the positive effect which the formation of a clear phase might have on the counting mechanism.

While these investigations are still in their infancy, the results clearly demonstrate that interactions of betas, especially of those with lower kinetic energies, with the various species of different structures present in the solution, can

strongly affect the counting efficiency and it appears that the combination of positron annihilation technique with conventional liquid scintillation counting can contribute to a better understanding of the reactions involved.

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