UNIVERSITI PUTRA MALAYSIA

POSITRON ANNIHILATION LIFETIME STUDY OF THE CUBIC PHASES IN THE TERNARY SYSTEM OF DIDODECYLDIMETHYLAMMONIUM BROMIDE/WATER/ HYDROCARBON

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By

ABD. HALIM BIN BAIJAN

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Untuk Mak, Pn. Tini bt. Sidal
dan Abah, En. Baijan Salaman,
adik Imah
dan
abang-abang, Abd. Rahim, Abd. Latif,
Abd. Aziz, Abd. Wahid dan Abd. Rahman
...ini semua adalah untuk kalian

... perjalanan ini telah pun bermula,
dan yang pastinya tiada titik akhirnya.....

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"Fikiran tanpa dipergunakan adalah pemikiran yang hampa" - Sayidina Ali

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LIST OF ABBREVIATIONS

2D-ACAR	-	Two Dimensional Angular Correlation of Annihilation Radiation
CF	-	Constant Fraction
CFA	-	Constant Fraction Amplifier
CF ckt	-	Constant Fraction Circuitry
CFD	-	Constant Fraction Discriminator
CMC	-	Critical Micelle Concentration
D	-	Diamond
DDAB	-	Didodecyldimethylammonium Bromide
FWHM	-	Full Width at Half Maximum
D_2O	-	Deutrium Oxide
LE	-	Leading Edge
LEAD	-	Leading Edge Arming Discriminator
MCA	-	Multichannel Analyzer
MeV	-	Mega Electron Volts
NIM	-	Nuclear Instrumentation Modules
NMR	-	Nuclear Magnetic Resonance
O/W	-	Oil/Water
o-Ps	-	Ortho-positronium
PAL	-	Positron Annihilation Lifetime
PAS	-	Positron Annihilation Spectroscopy
PAT	-	Positronium Annihilation Technique

PATFIT	-	Positronium Fit
PET	-	Positron Emission Tomography
PMT	-	Photomultiplier Tube
p-Ps	-	Para-positronium
Ps	-	Positronium
SANS	-	Small Angle Neutron Scattering
SAXS	-	Small Angle X-ray Scattering
SCA	-	Single Channel Analyzer
Surfactant	-	Surface Active Agent
SR	-	Slow Risetime Reject
TAC	-	Time to Amplitude Converter
TPHC	-	Time to Pulse Height Converter
TSCA	-	Constant Fraction Timing of Single Channel Analyser
UV	-	Ultra Violet
W/O	-	Water/Oil
Z	-	Atomic Number

Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Master of Science.

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March 1999

Chairman : **Professor Hj. Mohd Yusof Sulaiman, PhD**

Faculty : **Science and Environmental Studies**

Positron annihilation lifetime technique (PAL) has become a standard technique especially for the investigation of defects in solids, fermi surface, phase transitions etc. The effectiveness of the method lies on the ability of the positron to sample selectively electron states in the media and highlighting them via its annihilation photons. It is now known that in amphiphilic system positron forms para and ortho-positronium atoms. The former has a lifetime of 125 ps and annihilates via two photons while the ortho-positronium atom has a lifetime of 140 ns and annihilates via three photons. Any localised factors such as those found during rearrangement of microstructures in amphiphilic systems can influence the ortho-positronium to annihilate prematurely.

In this project Positron Annihilation Lifetime Method was used to study the cubic phases in the ternary system of didodecyldimethylammonium bromide (DDAB)/water /hydrocarbon. Three different systems of DDAB were measured i.e DDAB/ D_2O/ Octane, DDAB/ D_2O/ Tetradecane, and DDAB/ D_2O/ Toluene. These systems were expected to provide information on the effect of molecular size and degree of penetration of the oil into the hydrophobic tail region and to influence the structure of the cubic phase. A fast-slow coincidence technique was used to measure the lifetime of positron that interacts with the surfactant medium. The result was analysed using POSITRONFIT programme. An attempt was made to identify the various symmetries by referring to alternative work on the same system.

The inhibition constants, k' for the D-Schwarz of the mixtures of DDAB/ D_2O/ Octane and DDAB/ D_2O/ Toluene were found to be 2.54 and 0.92 respectively. On the other hand the P-Schwarz minimal surfaces for the mixtures of DDAB/ D_2O/ Octane gave an inhibition constant of 1.89 and for the mixtures of DDAB/ D_2O/ Tetradecane an inhibition constant is 1.63. For other space groups such as the Ia3d space group in the DDAB/ D_2O/ Toluene mixtures, k' was found to be 5.03. Although the results is not constant from one sample to another, the positron method shows the sensitiveness of the changes in the microstructure phases. Thus the Positron Annihilation Lifetime Technique can be used as an alternative method in resolving phases in ternary surfactant systems.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk memperolehi ijazah Master Sains.

KAJIAN MASAHAYAT MUSNAHABISAN POSITRON KE ATAS FASA KUBIK DI DALAM SISTEM TERNARI DIDODECYLDIMETHYLAMMONIUM BROMIDE/ AIR/ HIDROKARBON

Oleh

ABD. HALIM BIN BAIJAN

Mac 1999

Pengerusi : Profesor Hj. Mohd Yusof Sulaiman, PhD

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Teknik Masahayat Musnahabisan Positron (PAL) telah menjadi teknik yang piawai terutamanya terhadap kajian ke atas kecacatan bahan, permukaan fermi, perubahan fasa dan lain-lain lagi. Keberkesanan kaedah ini bergantung kepada keupayaan pemilihan keadaan elektron sampel di dalam media dan mengetengahkannya melalui musnahabisan photonnya. Diketahui bahawa di dalam sistem amphifilik, positron akan membentuk atom para dan ortho-positronium. Para-positronium mempunyai masahayat selama 125 ps dan musnahabisan melalui dua foton manakala atom ortho-positronium mempunyai masahayat selama 140 ns dan musnahabisan melalui tiga foton. Sebarang faktor-faktor tempatan seperti yang didapati semasa penyusunan semula mikrostruktur di dalam sistem amphifilik akan mempengaruhi ortho-positronium untuk pra-matang musnahabisan.

Di dalam projek ini Teknik Masahayat Musnahabisan Positron telah digunakan untuk mengkaji fasa kubik di dalam sistem ternari didodecyldimethylammonium bromide (DDAB)/ air/ hidrokarbon. Tiga sistem DDAB yang diukur adalah DDAB/ D_2O/ Oktana, DDAB/ D_2O/ Tetradekana, dan DDAB/ D_2O/ Toluena. Sistem-sistem ini dijangkakan akan memberikan maklumat tentang kesan saiz molekul dan darjah penembusan minyak di dalam kawasan ekor hidrofobik dan mempengaruhi struktur kepada fasa kubik. Teknik kesekenaan cepat-lambat digunakan untuk mengukur masahayat positron yang berinteraksi dengan bahantara surfaktan. Hasil dapatan kemudiannya dianalisis dengan menggunakan program POSITRONFIT. Suatu cubaan dilakukan untuk mengenalpasti kepelbagaian simetri dengan merujuk kepada hasil kerja lain ke atas sistem yang sama.

Pemalar penyekatan, k' bagi D-Schwarz untuk campuran DDAB/ D_2O/ Oktana dan DDAB/ D_2O/ Toluena telah didapati masing-masing sebagai 2.54 dan 0.92. Manakala pemalar penyekatan untuk permukaan minimal P-Schwarz bagi campuran DDAB/ D_2O/ Oktana pula adalah 1.89 dan untuk campuran DDAB/ D_2O/ Tetradekana pula adalah 1.63. Bagi lain-lain ruang kumpulan seperti kumpulan Ia3d di dalam campuran DDAB/ D_2O/ Toluena pula, k' memberikan nilai 5.03. Walaupun hasil keputusan tidak sekata dari satu sampel ke sampel yang lain, kaedah positron telah menunjukkan kepekaan terhadap pertukaran fasa mikrostruktur. Dengan itu Kaedah Masahayat Musnahabisan Positron boleh digunakan sebagai kaedah alternatif di dalam kajian fasa sistem surfaktan ternari.

CHAPTER I

INTRODUCTION

In 1930 Dirac predicted that the electron should have a positively charged counterpart. First experimental indications of an unknown particle were found in cloud-chamber photographs of cosmic rays by Andersons in 1932. This particle was identified later as the positron, which was thus the first antiparticle in physics. When a particle meets its antiparticle, they can annihilate each other. That is, the particles can disappear, their combined rest energies becoming available to appear in other forms. For an electron annihilating with its antiparticle, this energy appears as two gamma-ray photons.

$$e^- + e^+ = \gamma + \gamma \quad (Q = 1.02 \text{ MeV}) \qquad [1]$$

If the two particles are stationary when they annihilate the photons share equally between them and to conserve momentum and because photons cannot be stationary - they fly off in opposite directions. It was discovered soon that the energy and momentum conservation during the annihilation process could be utilised to study properties of solids.

The Positron Annihilation Technique (PAT) has recently emerged as a powerful technique for studying defects in metal or non-metal. It has been well established that positrons entering metals are thermalised in a very short time ($\sim 10^2$s), tend to be trapped by lattice defects such as vacancies, vacancy clusters, voids, and dislocations, and are annihilated with observable characteristics which directly reflect the electronic structure of the type of defect in which they are trapped.

The Positron Method

When energetic positrons from a radioactive source are injected into a condensed medium the positron looses rapidly (a few ps) its kinetic energy until it reaches near thermal energies. The mean implantation range varying from 10 to 1000 μm guarantees that the positrons reach the bulk of the sample material. Finally, after living in thermal equilibrium, the positron annihilates with an electron from the surrounding medium dominantly into two 511 keV gamma quanta. The average lifetime of positrons is characteristic of each material and varies from 100 to 500 ps. The above picture is distorted in molecular media, where positronium formation may occur during the slowing down process.

The positron annihilation rate, which is the inverse of the positron lifetime, in the independent particle model, is given by

$$\lambda = \sigma_{2\gamma}\, v\, n_e = \pi\, r_o^2\, c\, n_e \qquad [2]$$

where $\sigma_{2\gamma}$ is the cross section for two photon annihilation, v the velocity of the positron, r_o the classical electron radius and n_e the electron density.

Figure 1 shows schematically the positron annihilation experiment, where the most commonly used radioisotope Na^{22} is implied. Within a few picoseconds after the positron emission the nucleus emits an energetic 1.274 MeV photon which serves as a birth signal. The lifetime of the positron can thus be measured as the time delay between the birth and annihilation gammas.

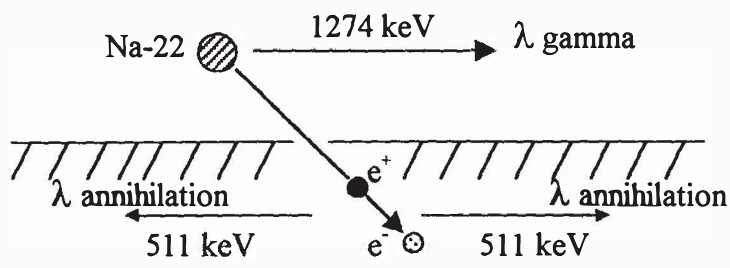

Figure 1: Positrons (e^+) from a radioactive isotope like ^{22}Na annihilate in the sample material. Positron lifetime is determined from the time delay between the birth gamma (1274 keV) and the two annihilation quanta.

The momentum of the annihilating electron-positron pair is transmitted to the annihilation quanta and it can be detected as a small angle deviation from collinearity between the two 511 keV photons. The motion of the pair also produces a Doppler shift to the annihilation radiation and this is seen in an accurate energy measurement of one of the photons.

There are three conventional experimental methods to study positron annihilation.

1. Positron Lifetime
2. Angular Correlation
3. Doppler Broadening

A schematic representation of the experimental methods used in conventional positron measurement is presented in Figure 2. The full lines on the typical spectra denote the defect-free bulk whereas the dashed spectra correspond to the presence of defects. The emission of one gamma ray in coincidence with the positron makes the ^{22}Na a quite suitable source for positron lifetime experiments.

The thermalised positron contributes very little extra momentum to the centre of mass of the annihilation pair. The electron, by contrast has a significant momentum because of the effect that the Pauli exclusion principle has on an electron sea with $\approx 10^{22}$ electrons/cm^3 . The conservation of momentum implies then a small deviation from the colinearity of the two annihilation gamma rays.

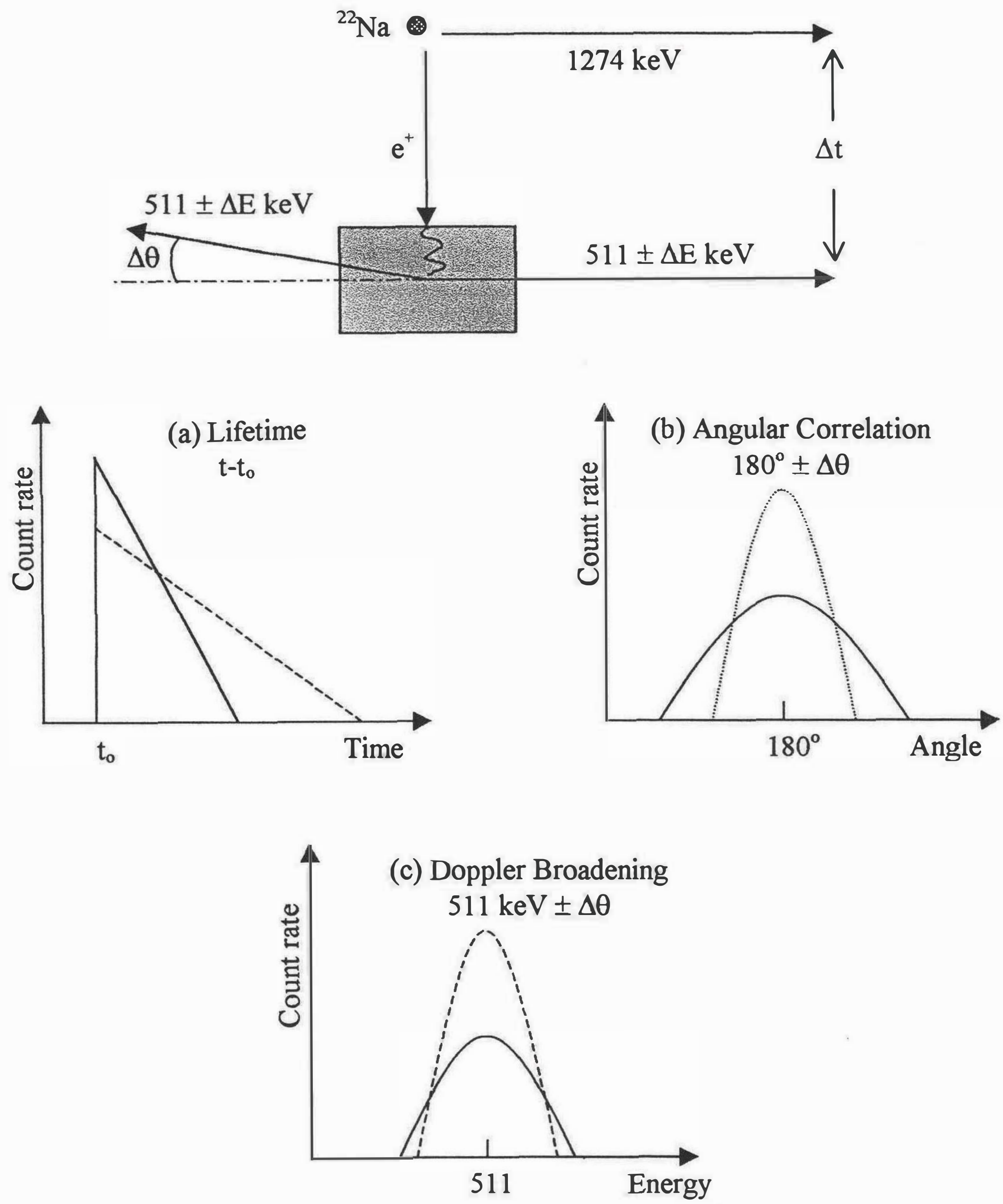

Figure 2 : Schematic representation of the experimental methods used in conventional positron measurements.

The deviation can be determined by angular correlation measurements which are performed by placing detectors on both sides of the samples and measuring the count rate as a function of the angle between the emission directions. Nowadays, two-dimensional angular correlation measurements (2D-ACAR) are performed using arrays of detector placed at both sides of the source/sample arrangement. Given the high sensitivity of this technique it can be used on the identification of Fermi surfaces of metals and alloys.

Phase Structures of Surfactant Studied by Positron Annihilation Lifetime

Positron is a useful probe on the order of nano-meter (so called nano-meter probe) to investigate molecular and atomic structures of substances like polymer or surfactant. Positrons form positronium (Ps) in substances by picking electrons from surrounding structures. Ps has a hydrogen-like atom and there are two states: the triplet or ortho-positronium (o-Ps) and the singlet or para-positronium (p-Ps).

The singlet Ps (p-Ps) with antiparallel spin orientation has a self annihilation lifetime in free space of 125 ps and decays by two photon emission. The triplet Ps (o-Ps) with parallel spin orientation has a self annihilation lifetime of 140 ns in free space and decays by three photon emission. Ortho and para Ps are normally formed in the ratio 3:1 . Thus ortho-Ps can have longer life in larger holes and annihilates with electrons located on the walls of the holes. The life and intensity are affected by surfactant and chemical structures and thus it is a good measure of surfactant characteristics.

Objectives

The aim of this project are;

1. To determine the resolution of the Lifetime System
2. To determine the lifetime of the lifetime and intensity of positronium atoms in ternary system of DDAB/ D_2O/ Octane, DDAB/ D_2O/ Tetradecane , and DDAB/ D_2O/ Toluene.
3. To analyse for different phases in the above system.

Reason for Study

The purpose of this study is to provide an alternative method of resolving phases in ternary surfactant system since such information is useful in material characterisation for specific use such as cosmetic, detergent, oil recovery and etc.

CHAPTER II

SURFACTANT SYSTEM

Introduction

Surfactant is a contraction for *surface-active-agent*. A surface-active substance - including detergents, wetting agents, and emulsifiers - that when added to water will lower the surface tension and increase the "wetting" capabilities of the water. Reduced surface tension allows water to spread and penetrate fabric of other substances to be washed or cleaned.

Surfactants are special molecules which are made up of two sections:

1. The hydrophilic part (usually ionic or nonionic) which likes water
2. The hydrophobic part (usually a hydrocarbon chain) which likes oil (see Figure 3.)

It is this dual nature which causes these molecules to adsorb at the interfaces between two immiscible liquids, like oil and water. The interfacial layer formed as a result of this is usually a monolayer and is responsible for allowing oil and water to mix (Binks, 1993). Surfactants find numerous applications in industries as well as home use for personal hygiene, washing and cleaning; these uses include