



UNIVERSITI PUTRA MALAYSIA

**STRUCTURES OF SURFACTANT SYSTEM
STUDIED BY POSITRON ANNIHILATION LIFETIME
SPECTROSCOPY**

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**STRUCTURES OF SURFACTANT SYSTEM
STUDIED BY POSITRON ANNIHILATION LIFETIME
SPECTROSCOPY**

By

Rosdi Bin Haji Ibrahim

A Thesis Submitted in Fulfilment of the Requirements for
the Degree of Master of Science in the
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LIST OF ABBREVIATIONS

ABS	-	Alkyl Benzene Sulphonate
ACAR	-	Angular Correlation of Annihilation Radiation
ADC	-	Analog to Digital Converter
AOT	-	Diocetyl Sulfosuccinate
ARC	-	Amplitude and Rise Time Compensated
bcc	-	Body-Centred Cubic
BDTAC	-	BenzylDimethylTetradecylAmmonium Chloride
C ₁	-	Cubic Phase
C ₂	-	Cubic Phase
CFA	-	Zero-Crossing Pickoff
CF ckt	-	Constant Fraction Circuitry
CFDD	-	Constant Fraction Differential Discriminator
CMC	-	Critical Micelle Concentration
CTAB	-	CetylTrimethylAmmonium Bromide
D	-	Diamond
DAC	-	Digital Analogue Converter
DAP	-	DodecylAmmonium Prepionate
DBS	-	Doppler Broadening Spectroscopy
DDAB	-	DidodecylDimethylAmmonium Bromide
DHBS	-	Podihexylbenzene Sodium Sulphonate
DVM	-	Digital Voltmeter
eV	-	Electron Volts
FWHM	-	Full Width at Half Maximum



H	-	Hexagonal Phase
H ₂ O	-	Water
I ₂	-	Intensity
I-WP	-	Monolayer Structure
keV	-	Kiloelectron Volts
LEAD	-	Leading Edge Arming Discriminator
MCA	-	Multichannel Analyzer
²² Na	-	Sodium-22 Radioactive
NaCl	-	Sodium Chloride
NALS	-	Sodium Lauryl Sulfate
NIM	-	Nuclear Instrumentation Modules
NMR	-	Nuclear Magnetic Resonance
O/W	-	Oil/Water
PAL	-	Positron Annihilation Lifetime
PAS	-	Positron Annihilation Spectroscopy
PATFIT	-	Positronium Fit
Ps	-	Positronium
PMT	-	Photomultiplier Tube
OPC	-	Ortho-Para Converter
o-Ps	-	Orthopositronium
p-Ps	-	Parapositronium
SANS	-	Small Angle Neutron Scattering
SAXS	-	Small Angle X-ray Scattering
s.c.	-	Single Cubic
SCA	-	Single Channel Analyzer
SDS	-	Sodium Dodecyl Sulfate



Surfactant	-	Surface Active Agent
TAC	-	Time to Amplitude Converter
TTAB	-	Tetradecyl Trimethyl Ammonium Bromide
W/O	-	Water/Oil
τ_2	-	Lifetime



Abstract of the thesis .submitted to the Senate of Universiti Pertanian Malaysia in fulfilment of the requirements for the Degree of Master of Science.

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January 1996

Chairman : Prof. Mohd. Yusof Sulaiman, PhD

Faculty : Science and Environmental Studies

Surfactant system has many applications in industry. Many investigations have been carried out on surfactants using various methods such as small-angle neutron scattering (SANS), small-angle x-ray scattering (SAXS), conductivity freeze-fracture electron microscopy and nuclear magnetic resonance (NMR). In the positron annihilation lifetime spectroscopy technique, the lifetime (τ_2) of positron that interacts with surfactant medium is measured using fast coincidence system. The intensity of formation of orthopositronium(I_2), when positron interact with aggregate of surfactant system are sensitive to phase changes. In amphiphilic system with



bicontinuous character geometry of periodic phase can be explained using minimal surfaces. Factors influencing the topology includes the length of surfactant and cosurfactant tails and the aqueous volume fraction. Positron are readily attracted to these centres. Changes in the geometry of the interfacial layer thus will influence the lifetime and intensity of the orthopositronium atom formed. These parameters are obtainable using the POSITRONFIT programme.

In this study, three surfactant systems were investigated. Firstly, the intensity (I_2) and lifetime (τ_2) of the DidodecylDimethylAmmonium Bromide (DDAB) - Water - Octane system were measured at various amount of water content in the surfactant system in the diamond and body centred cubic phases. A symmetry transitions from diamond phase to body-centred cubic phase was observed in this system.

Secondly, the equivalent data were measured against ratio of (BDTAC/TTAB) of cubic phase area of BenzylDimethylTetradecylAmmonium Chloride (BDTAC) / TetradecylTrimethylAmmonium Bromide (TTAB) - Water - Octane system. Thirdly, for the TetradecylTrimethylAmmonium Bromide (TTAB) / Butanol ~ 2 - Water - Octane system, the

intensity (I_2) and lifetime (τ_2) were measured against different composition ratio of Octane/Water.

In all the three systems, an attempt was made to explain the behaviour of the positronium atom in the bicontinuous phase of the surfactant.



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**KAJIAN KE ATAS SISTEM SURFAKTAN
DENGAN MENGGUNAKAN KAEDAH MASA HAYAT
MUSNAHABISAN POSITRON**

oleh

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Januari 1996

Pengerusi : Prof. Mohd. Yusof Sulaiman, PhD

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Sistem surfaktan mempunyai pelbagai kegunaan dalam industri. Banyak kajian mengenai surfaktan telah dijalankan dengan menggunakan pelbagai kaedah seperti kaedah serakan sudut kecil neutron (SANS), kaedah serakan sudut kecil x-ray (SAXS), spektroskopi pengaliran elektron "freeze-fracture" dan nuklear magnetik resonan (NMR). Dalam teknik spektroskopi masa hayat musnah-habisan positron (PALS), masa hayat positron yang berinteraksi dengan medium surfaktan diukur dengan menggunakan sistem kesekenaan. Perubahan Pembentukan Keamatan o-Ps (I_2) bila positron berinteraksi dengan sistem agregat surfaktan adalah

sensitif terhadap perubahan fasa. Dalam sistem amfifilik dengan geometri bersifat "bicontinuous", fasa berkala dapat diterang dengan menggunakan perkalaan permukaan terkecil. Faktor yang mempengaruhi topologi adalah panjang surfaktan dan ekor kosurfaktan dan fraksi isipadu akuas. Positron adalah tersedia tertarik kepusat ini. Perubahan geometri lapisan antara muka akan mempengaruhi masahayat dan keamatan pembentukan atom orthopositronium. Parameter-parameter diperolehi dengan menggunakan program POSITRONFIT.

Dalam kajian ini , tiga sistem surfaktan akan digunakan. Pertama, keamatan (I_2) dan masahayat (τ_2) diukur untuk sistem DidodecylDimethyl Ammonium Bromide (DDAB) - Air - Oktana, bagi kandungan air yang berbeza-beza dalam sistem surfaktan yang berada pada fasa intan sehingga terjalin transisi fasa intan kepada kubus berpusat jasad.

Keduanya, keamatan (I_2) dan masahayat (τ_2) diukur terhadap nisbah (BDTAC/TTAB) dalam kawasan fasa kubus didalam sistem BenzylDimethyl TetradecylAmmonium Chloride (BDTAC) / TetradecylTrimethylAmmonium Bromide (TTAB) - Air - Oktana, dan akhir sekali, sistem yang

ketiga adalah TetradecylTrimethylAmmonium Bromide / Butanol ~ 0.2 - Air - Oktana. Keamatan (I_2) dan masahayat (τ_2) diukur terhadap perubahan komposisi Oktana/Air.

Bagi ketiga-tiga sistem surfaktan diatas, usaha telah dibuat untuk menjelaskan pemerhatian secara teori.

CHAPTER I

INTRODUCTION

The lepton, positron, is the antiparticle of the electron. Its existence was predicted by Dirac (1930). In condensed matter, initially fast positron annihilates after having reached equilibrium with the surroundings. The characteristics of the quantum electrodynamic annihilation process depend almost entirely on the state of the positron-electron system of the medium. Discoveries of new features in the positron interaction with matter have maintained continuous interest and increasing activity in the field. A striking feature is thus the great diversity of the fields in which positron annihilation method is now applied. In addition to solid-state and material physics, there are intensive activities in atomic physics and radiation chemistry, the latter extending even into biochemistry and biology.

The Positron Method

The positron method can be established by discussing the annihilation process of free positrons. The positron - electron annihilation is a relativistic



process where the particle masses are converted into electromagnetic energy - the annihilation photons. From the invariance properties of quantum electrodynamics, several selection rules can be derived. Firstly, one-gamma annihilation is possible only in the presence of a third body absorbing the recoil momentum and its relative probability is negligible. The main process is the two-gamma annihilation, since the spin-averaged cross section for the three-gamma annihilation is 0.27% of that for the two gamma annihilation. The three-gamma annihilation is important only in a spin-correlated state like orthopositronium, where the selection rules forbid the two-quantum process.

From the non relativistic limit of the two gamma annihilation cross-section derived by Dirac (1930), one obtains the annihilation probability per unit time or the annihilation rate

$$\lambda = \pi r_0^2 c n_e \quad [1.1]$$

which is independent of the positron velocity. Here, r_0 is the classical electron radius, c the velocity of light and n_e is the electron density at the site of the positron. By measuring the annihilation rate λ , the inverse of which is the mean lifetime t , one directly obtains the electron density n_e encountered by the positron.

The kinetic energy of the annihilating pair is typically a few electron volts. In the centre-of-mass frame the photon energy is exactly $m_0c^2 = 511$ keV and the photons are moving into opposite directions. Because of the non zero momentum of the pair, the photons deviate from collinearity in the laboratory frame. As illustrated in Figure 1, the momentum conservation yields a result,

$$\theta \approx p_T/m_0c^2 \quad [1.2]$$

where $180^\circ - \theta$ is the angle between the two photons in the laboratory frame and p_T is the momentum component of the electron-positron pair transverse to the photon emission direction.

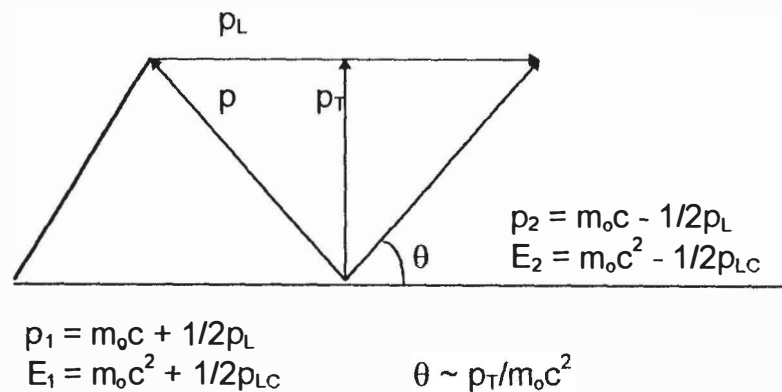


Figure 1 : The Vector Diagram of the Momentum Conservation in the Two Gamma Annihilation Process.

Usually θ is very small ($\theta < 1^\circ$) and equation 1.2 is valid. Because the momentum of the thermalised positron is almost zero, the measured angular