Analele Universităţii de Vest din Timişoara
Vol. LI, 2007
Seria Fizică

CAPILLARY CONDENSATION IN POROUS ALUMINA OBSERVED BY POSITRONIUM LIFE TIME SPECTROSCOPY (preliminary results)

Eugeniu Ivanov[a,b], Ion Vata[a], Stefan Toderian[a],Dorin Dudu[a], Ion Rusen[a], Nitisor Stefan[a]

[a] *Nat.l Institute for Nuclear Physics and Engineering- Horia Hulubei,Bucharest- Magurele CP MG 06, Atomistilor Street 407*
[b]*Center for Adv. Studies in Physics of the Rom. Academy. Casa Acad. Rom., C. 13 Septembrie 13, Bucharest Romania*

Abstract
Positronium annihilation life time spectroscopy (PALS) has been used to study capillary condensation of different gases adsorbed in mesoporous alumina powder. The isotherms exhibit features which are associated with a shifted gas-liquid transition. The isotherm data suggest that pore filling occurs via progressive layer formation at the pore surface followed by an abrupt gas-liquid phase transition at some pressure below the bulk saturated vapour pressure.
Key words: capillary condensation, hysteresis, positronium annihilation

1. Introduction

The behavior of a fluid confined in a porous material has been since long a problem of interest theoretical and experimental .The phase diagram of confined fluids present characteristics as the gas condensation in pores in liquid-like phase at partial pressure below the bulk saturated vapor pressure, due to finite pore size and pore geometry. During the isotherm transformation the mass of condensed liquid in pores show a rapid variation at at lower pressure than bulk saturated gas pressure. The sorption and desorption process are irreversible presenting a hysteresis effect. The PALS can be used, in some favorable circumstances (porous dielectric materials or polymers), to study the gas condensation dynamics. The positrons emitted by a source are rapidly thermalized in solid. A fraction of positrons reach the pores, forms Positronium (Ps) and subsequently annihilate. Long lived ortho-Positronium atoms (o-Ps, $\tau\approx$ 100 ns) are copiously produced in porous alumina. As these atoms spend all time in the free volume by knocking the pores walls (about 10^6 times) o-Ps is potentially an attractive probe to observe, “from inside the pore”, gas ad sorption and gas condensation phenomena. In small pores a fraction of positrons undergo 2γ annihilation via quenching with the electrons from the pores walls [1]. This process is amplified by the gas introduced in pores. If the gas – liquid transformation occurred in pores, the intensity of 2γ annihilation increase substantial. So the $3\gamma/2\gamma$ ratio depends on amount and the density of any confined fluid. Experimentally the $3\gamma/2\gamma$ ratio can be determined measuring energy or time spectra distribution. The results presented here were obtained measuring time

distribution spectra. The evolution of $3\gamma/2\gamma$ ratio, during an isotherm transformation, is similar to classic isotherms.

2. The experimental arrangement

We have investigated the gas-liquid equilibrium for several condensable gases, like butane, ethylic ether and n-hexane in porous alumina, by using PALS.

A $^{22}NaCl$ source (about 1 μCi) was encapsulated in a sandwich geometry with alumina powder (0,5 cm^3 at a density of about 1g/cm^3) and mounted into a vacuum chamber provided with controlled gas filling and manometer accessories.

A conventional time fast-fast spectrometer [2] based on a time to amplitude converter (TAC) having a time resolution of 0,5 ns was used. The 1275 keV photon (start signal) was detected using a barium fluoride (BaF_2) scintillator (2 inch diameter,2 inch thickness) with a photomultiplier tube XP1200 and the 140-511 keV photons (stop signal) was detected by another BaF_2 detector. The resolution was selected to observe ortho-Positronium annihilation. Delay spectra up to 800 ns (distributed on 8192 channels) were registered at different gas pressure in a sequence corresponding to sorption and de sorption isotherms for rapid and very lent process. For rapid sorption–de sorption process (1 minute measuring time for a pressure value) we registered two rate of annihilation intensity ; the one in the 5-20 ns range , called short isomer and the second one in the 50-300 ns range called long isomer (fig.1).

3. Results and discussions

The time spectra (fig. 1) were analyzed with LT9.0 program [3]. Generally the spectra were fitted with three components: a very short and constant one (≈ 0.5 ns), a short one with the intensity and value (5- 20 ns) dependent on partial pressure and a long one with the intensity and value (50-120 ns) dependent on partial pressure .Two kind of o-Ps can be explained by two kind of “cages” for o-Ps atoms. We have investigated the gas-liquid equilibrium for several condensable gases, like butane, ethylic ether, n-pentane and n-hexane in porous alumina.

We present in details the result for n-pentane condensation in alumina powder. The N_{long} rates decrease with increasing partial pressure of the gas partial pressure and in mean time the N_{short} is increasing (fig. 2). We observed that long and short annihilation rates present hysteresis effect but the two evolutions are in opposites directions. At a partial pressure lower than saturation value the isomers rates suddenly change. The isomers rates for sorption and de sorption process are different presenting an hysteresis effect .This effect is

visible and in fig.1 were two spectra measured at same partial pressure are shown. Similar results are obtained analyzing time distribution spectra.

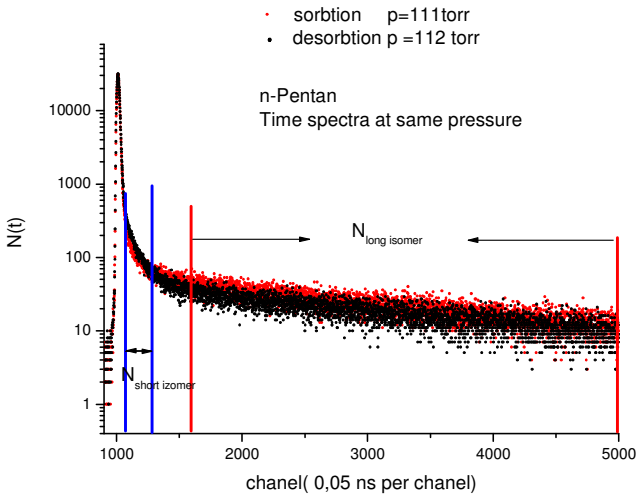

Fig. 1 Annihilation time spectra for n-pentane and range for $N_{short\ isomer}$ and $N_{long\ isomer}$.

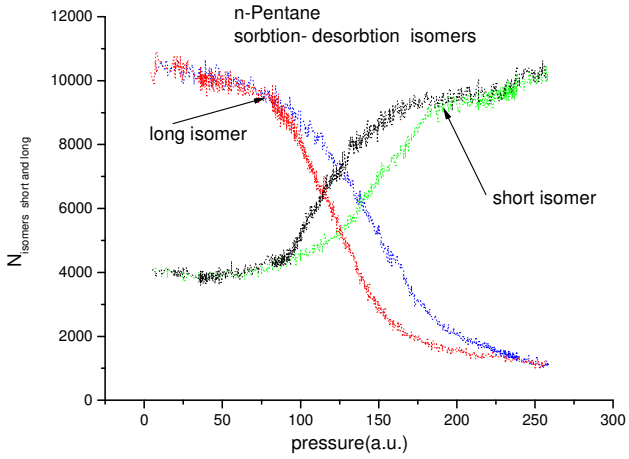

Fig. 2. Hysteresis effect in gas-liquid phase transition of n-pentane adsorbed on porous alumina.

The intensities of the short and long life time have similar dependence like short and long rates (fig.3).

The short and long intensities of o-Ps annihilation were determined with LT9.0 program on time distribution spectra measured in slow sorption - de sorption process. The long life time is decreasing with increasing of partial pressure of the gas. This can be explained by reduction of pore radius by liquid condensation on the pores walls .We have not

a clear explanation for the evolution of short life time o-Ps. It is possible that short life time o-Ps to be produced in liquid condensed in pores.

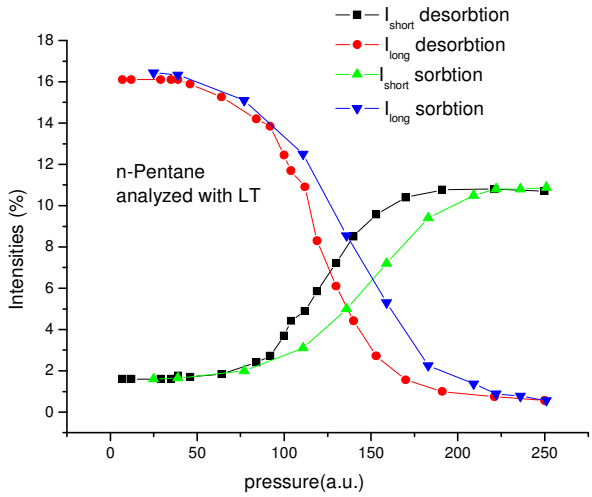

Fig. 3. Hysterezis effect observed in capillary condensation of n-pentane on alumina powder

4. Conclusions

The preliminary results shown that time spectra characterizing positron and Positronium annihilation provides a valuable technique for monitoring phase transitions of confined fluids. In some cases the new technique can provide new insight into capillary condensation dynamics .

Acknowledgements

This research was supported under Romanian Ministry of Education and Research contract no:6-15 /2006 (ARPA).

References

1. Positron Annihilation Study of Capillary Condensation of Nitrogen Gas in a Mesoporous Solid by N.J. Wilkinson,M.A. Alam, J.M. Clayton, R.Evans, H.M. Fretwell and S.G.Usmar in Phys. Rev. Let. Vol 69, number 24 (1992) 3535.
2. Gunter Schatz, Alois Weindinger " Nuclear Condensed Mater Physics; Nuclear Methods and Application (ch.5) ed John Wiley &sons 1996
3. J. Kanys "*Microcomputer program for analysis of positron annihilation lifetime spectra*" Nucl. Instr. and Meth in Physics Research A 374 (1996) 235-244