



Positronium in solid phases of n -alkane binary mixtures



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ARTICLE INFO

Article history:

Received 18 April 2015

In final form 8 June 2015

Available online 15 July 2015

Keywords:

Even alkanes

Binary mixtures

Positronium

Rotator phase

Trapped electrons

ABSTRACT

Binary mixtures of even-numbered normal alkanes C_nH_{2n+2} and $C_{n+2}H_{2n+6}$ with $n \leq 18$ were investigated by positron annihilation spectroscopy. Formation of the rotator phase was observed in mixed structures, while no such a phase in neat alkanes in this range of n was found. Phase diagrams for $n = 18$ and $n = 16$ are very similar to the diagrams for binary mixtures of odd-numbered alkanes. The effect of positronium formation with trapped excess electrons weakens with decreasing n , at low n values the time constant of Ps rise contains the component much shorter than 1 h.

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1. Introduction

1.1. Alkanes

Normal alkanes C_nH_{2n+2} (shortly C_n) represent a homologous series of saturated hydrocarbons in the form of linear chains. Alkanes and their mixtures are widely distributed in the natural environment; they are the main constituents of oil, lubricants, they appear as the building components of lipids, surfactants and liquid crystals. So far they have been the object of numerous studies by X-ray diffraction [1–4], DSC [1,5–7], infrared and Raman spectroscopy [1,8,9], neutron scattering [10], positron annihilation [11–15] etc. If $n < 25$, only two solid phases of these compounds are observed: a rigid crystal and a waxy rotator phase. At low temperatures the molecules have the shape of straight zig-zag chains of carbon atoms (*all-trans* configuration). With the increase of temperature, the concentration of non-planar conformers: *end-gauche*, *double gauche*, *kink* grows. X-ray diffraction studies have shown that the odd-numbered alkanes with $13 \leq n \leq 41$ crystallise in the orthorhombic structure, while even-numbered ones with $14 \leq n \leq 26$ are triclinic. The crystals have a lamellar structure; the molecules are packed in parallel, odd numbered ones obliquely to the lamella surface, even-numbered – perpendicularly. According to the crystallographic data, the interlamellar gap d_0 is 0.195 nm and 0.125 nm in odd and even numbered alkanes, respectively. In odd-numbered alkanes with $n \geq 9$ and even-numbered with $n \geq 22$ in the range of temperatures of several K below the melting point the hexagonal rotator phase is formed, the

molecules can rotate around their long axis. This structure contains a large concentration of *kink* and other non-planar conformers.

In natural conditions the alkane mixtures predominate. The composition of alkane mixture can be described by two parameters: an average chain length \bar{n} and the width of distribution Δn :

$$\bar{n} = \sum_n c_n n \quad (1)$$

$$\Delta n = \sqrt{\sum_n c_n (n - \bar{n})^2} \quad (2)$$

where c_n is the fraction of alkane with the chain composed of n carbon atoms.

The most published papers on mixed alkanes deals with binary ones [16–20]. Typical features of these binary compositions, compared to neat compounds, are:

- broadening of the temperature range of the rotator phase;
- appearance of phase coexistence ranges liquid-rotator and rotator-rigid crystal;
- increase of the interlamellar gap.

1.2. Positronium in alkanes

Positron annihilation lifetime spectroscopy (PALS) is commonly used in determination of free (electronless) volume sizes in solids, particularly in polymers [21,22]. In alkanes such a free volume exists in the form of an interlamellar gap, or inside a lamella if there is a large concentration of nonplanar conformers (like in the rotator phase).

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Positron entering matter loses its energy and at the end of its ionisation track can form with one of electrons in the medium a hydrogen-like bound structure called positronium (Ps). Depending on mutual spin orientation of particles positronium exists in a singlet (para-positronium, p-Ps) or a triplet (ortho-positronium, o-Ps) state. The singlet state is a short-lived species with the lifetime of 0.125 ns, while the lifetime of the triplet one in vacuum is 140 ns. Except of rare cases of delocalization (Bloch states) Ps in condensed matter needs an empty volume to be trapped there owing to its negative work function. The decay rate of o-Ps located in a free volume is a sum of self-annihilation rate (negligible) and the rate of the pick-off process consisting in positron annihilation with one of electrons from the surrounding bulk. Pick-off rate is determined by degree of overlap of Ps wavefunction with the bulk, thus by the size of free volume. The larger the trap is – the longer is the lifetime; details of this relationship are determined by the void geometry. Usually the spherical shape of free volume hole is assumed [23,24]. However, due to the peculiar shape of free volumes in the crystalline alkane structure, as described above (interlamellar gap, elongated free space adjacent to kinked molecules), an assumption of the rectangular geometry is more appropriate [25]. In the case of para-Ps the role of pick-off is marginal, but the decay rate can be changed (usually reduced) due to modified contact electron density [26].

The value of o-Ps lifetime allows for an easy identification of alkane solid phase. In the rigid crystal Ps locates in the interlamellar gap, the o-Ps lifetime is determined by the gap width (other two dimensions one can approximate as infinite) and amounts slightly above 1 ns. In neat even-numbered alkanes the width 0.125 nm is smaller than average distance electron–positron in free Ps atom, however in such quasi-twodimensional space the size of Ps atom is much smaller than in vacuum [27]. In the rotator phase Ps locates in the free channel along the kinked molecule and its lifetime is longer, over 2.5 ns, increasing with the length of the molecule. In liquid alkanes the o-Ps lifetime does not depend on the molecule length and it amounts to (3.1–3.2) ns near the melting point.

A specific feature of neat alkanes at low temperature is the rise of Ps intensity with the time of irradiation by the positrons (essentially, with the dose of radiation absorbed by the sample). There are no changes of o-Ps lifetime following this rise. Such an effect, observed earlier in many polymers, is explained by trapping the excess electrons produced at ionisation of the medium [28]. The number of trapped electrons rises with time, and next free positrons entering the sample have an increased possibility to pick them from the traps and form additional Ps atoms. At the temperatures roughly about 250 K, the traps are emptied (or destroyed) by thermal motion. The excess electrons can be also thrown out the traps by illumination with visible light or near IR.

In our earlier works on positronium in odd-numbered alkane mixtures C19 + C21 and C19 + C23 [29–31], and in multicomponent mixture with $\bar{n} = 19$ [32] we have observed that:

- in the rigid crystal the o-Ps lifetime in binary mixtures rises with Δn , which reflects the broadening of the interlamellar gap;
- in the rotator phase the dependence of o-Ps lifetime on Δn is weak, as the free volume hole near the kinked molecule accommodating Ps depends on the molecule length but not on Δn ;
- probability of Ps formation with trapped excess electrons decreases with Δn , at Δn over 2 no trapped electron effects at all [32].

In this paper similar measurements were performed with binary mixtures of even-numbered alkanes with relatively short chains, where in neat samples there is no rotator phase and the only solid phase is the rigid one. The PALS measurements were

done for C18 + C20 as a function of mixing ratio, a series of measurements was also performed for the set $C_n + C(n+2)$ with $n \leq 16$ for equimolar mixing composition 1:1.

2. Experimental

The values of \bar{n} and Δn for binary mixtures investigated in this paper are given in Table 1.

The samples of pure alkanes were from Sigma–Aldrich, 99% nominal purity. The respective amounts of mixture components were molten, stirred well and poured into the measurement chamber, in which the positron source holder was placed in the centre. The sample was degassed by the standard freeze–thaw technique and solidified by lowering the temperature. The chamber volume over the sample was evacuated, so it contained the alkane vapour only. The sample chamber was fixed to the cold finger, whose lower end was cooled by liquid nitrogen or its vapour; just below the chamber a heating coil was placed. The temperature was measured by a thermocouple and regulated by a control unit. The positron source was 0.7 MBq of ^{22}Na in a sealed Kapton envelope absorbing about 10% of positrons. The chamber was viewed by a pair of BaF₂ scintillation counters connected to a standard fast–slow delayed coincidence spectrometer. The time resolution of the spectrometer was about 260 ps. The PALS spectra were assumed to consist of three exponential components convoluted with the instrumental resolution curve, approximated by a single Gaussian. The correction for positron absorption in Kapton was taken into account (lifetime 374 ps; minute temperature dependence of that lifetime [33] was neglected). The number of counts collected per one spectrum was 1.4×10^6 .

The lifetimes τ_i and relative intensities I_i (i.e. the fraction of positrons forming *i*th component) were determined using the LT program [34]. The shortest lived component ($\tau_1 \approx 120$ ps) was ascribed to singlet *para*-Ps decay, an intermediate one ($\tau_2 \approx 340$ ps) to the annihilation of free (unbound) positrons and the longest-lived component τ_3 to the decay of *ortho*-Ps.

For each mixture composition the spectra were measured as a function of temperature. If the rotator phase exists in the mixed sample, five regions in the τ_3 vs. temperature dependence should be observed: rigid crystal, coexistence rigid–rotator, pure rotator, coexistence rotator–liquid, liquid. The limits of particular regions were determined as inflexion points i.e. at the intersection of straight lines fitted to the fragments of $\tau_3(T)$ and $I_3(T)$ dependences (Fig. 1).

3. Results and discussion

3.1. *n*-Octadecane + *n*-eicosane

The o-Ps lifetime in the low temperature region, where only the rigid crystal phase exists, is shown in Fig. 2. One can see a systematic rise of the lifetime with Δn . The dependence $\tau_3(T)$ for the same Δn but with dominant content of shorter and longer molecules looks almost identical, with slightly smaller slope $d\tau_3/dT$ when the longer molecules predominate. In order to estimate the width

Table 1

Selected information about the samples: the percentage of *n*-octadecane (C18) and *n*-eicosane (C20), the average length of the molecules in the mixture \bar{n} and distribution width Δn .

C18	100	96	90	80	50	30	20	10	4	0
C20	0	4	10	20	50	70	80	90	96	100
Symbol	◇	✕	■	▲	+	◆	★	●	*	○
\bar{n}	18	18.1	18.2	18.4	19	19.4	19.6	19.8	19.9	20
Δn	0	0.41	0.6	0.8	1	0.92	0.8	0.6	0.39	0

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