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Influence of Pressure on the Size of Free Volumes in Some Waxes

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Positron lifetime spectra were measured as a function of pressure for multicomponent mixtures of alkanes with an average carbon chain length of 19 atoms, and a varying width of length distribution. The range of rotator phase broadens with increasing the wax component distribution. When the number of wax components was five or more, we have observed the coexistence of rotator–rigid phases. The results of analysis of high statistics positron annihilation lifetime spectra by MELT program speaks in favour of an existence (in that range) of a single broad component, rather than two components corresponding to the separate rigid and rotator phases. In the mixtures of alkanes, the inter-lamellar gap size increases significantly due to the presence of various chain lengths of the components forming the mixture. For all investigated waxes the pressure of 360 MPa was sufficient to reduce the gap width to that one observed in pure alkanes.

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1. Introduction

The positron annihilation lifetime spectroscopy (PALS) has been successfully applied to estimate the size of free volume in hydrocarbons, which have a relatively simple structure in condensed phases (rigid crystal, rotator and liquid phase) [1–5]. In many applications (and in the nature) alkanes appear as a mixture (wax) composed of molecules of various chain length. It seems interesting to determine how phase transition points depend on the wax composition. The studies of this kind were performed up to now by classic methods [6–11] and were limited usually to the binary mixtures; the papers devoted to more complex compositions are rare. In our earlier work, we reported measurements of the PALS spectra as a function of temperature for various compositions of mixtures [12]. The aim of this paper was to compare the PALS spectra measured as a function of temperature with the analogous ones measured as a function of pressure. Comparing both these functions in alkanes one can assume that the decrease of temperature by 1 K is equivalent to the increase of pressure by 4 MPa [13].

The schematic phase diagram for binary mixtures is shown in Fig. 1 [14]. One can see that in these mixtures the range of rotator phase is broadened and the regions of coexistence of two phases are observed.

In the low temperature rigid phase n-alkanes have the form of straight chains (“all-trans” conformers) and they are arranged in a lamellar structure. In neat alkanes the long axes of molecules with an odd number of carbon atoms are perpendicular to the gap plane between the lamellae while these with an even number of carbon atoms — are oblique. The gap in the structure between the lamellae is larger for odd-numbered alkanes (0.195 nm) than for even-numbered ones (0.125 nm) [15]. Moreover, a rotary phase appears in the odd-numbered alkanes with $n \geq 9$ and even-numbered with $n \geq 22$, in the range of several degrees below the melting point. In this phase retaining the lamellar structure, some non-planar conformers: “end gauche”, “double-gauche” and “kink” ones exist [2, 15, 16]. Non-planar shapes lead, beside elongation of one of the crystal cell axis, to the formation of additional free volume in the vicinity of molecules. The kink conformers are dominant. A free volume near them is relatively larger in comparison to that one near “end-gauche" conformers, and it has the form of a channel running along the molecule.

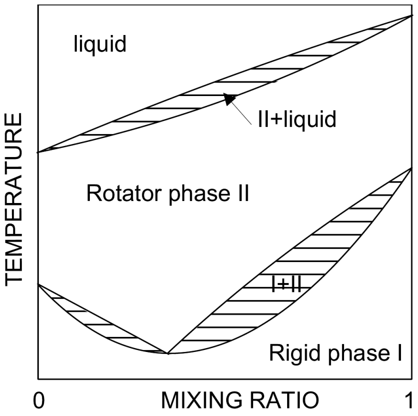

Fig. 1. Schematic phase diagram for binary mixture of alkanes. The regions of phase coexistence — dashed.

The positron entering the matter loses its energy and at the end of its ionization track can create positronium

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(Ps) — a bound state with one of the electrons from the medium. It can exist in two spin sub-states: singlet *para*-positronium (*p*-Ps), and triplet *ortho*-positronium (*o*-Ps). In vacuum, the average lifetime of *p*-Ps is short, 125 ps, while *o*-Ps lives much longer, 142 ns. In condensed matter, *o*-Ps interacts effectively with the surrounding medium, and its lifetime becomes shortened, mainly by the *pick-off* process. The lifetime of *o*-Ps trapped in free volumes is determined by the overlap of its wave function with the surrounding bulk; details of this relation are determined by the void geometry. The simplest relation between the *o*-Ps lifetime and the radius of spherical free volume is given by the Tao–Eldrup model [17, 18]; if the shape of the void is better approximated by a rectangular box, the modified models [19] can be used.

2. Experimental

The waxes investigated here were the mixtures of odd- and even-numbered paraffins, composed of 5 to 9 components (Table). The neat alkanes were from Sigma–Aldrich, of purity exceeding 99%. Selected n-alkanes in the required proportions were molten, carefully stirred, and solidified. The samples had the form of 2.5 mm thick pellets, between them the ^{22}Na (0.5 MBq) positron source in a kapton envelope was inserted. This sandwich was placed in a capsule, which was evacuated and closed by movable piston. The pressure was exerted via pistons and thin capsule walls. The capsule was placed in the chamber of gas compressor Unipress U-11. The temperature of the chamber could be regulated in a narrow range of temperatures from 270 K to 323 K, using a combination of heating coil and Peltier cell. The time resolution (FWHM) of lifetime spectrometer was better than 240 ps. About 10^6 coincidences per one spectrum were collected in 2 h. The spectra were processed by the LT 9.0 programme [20] fitting to the experimental data a sum of three exponential components, corresponding to *p*-Ps, *o*-Ps, and annihilation of free positrons, respectively, convoluted with the instrumental resolution curve. Some spectra were analyzed by the MELT program [21]; the statistics of 10–30 million coincidences, needed to this kind of processing, was obtained by summing up the spectra measured in the same temperature and pressure conditions.

TABLE

Composition of samples. An average chain length $\bar{n} = 19$.

Sample	c_n fraction of n-alkane									Distribution width Δn
	$C_{15}H_{32}$	$C_{16}H_{34}$	$C_{17}H_{36}$	$C_{18}H_{38}$	$C_{19}H_{40}$	$C_{20}H_{42}$	$C_{21}H_{44}$	$C_{22}H_{46}$	$C_{23}H_{48}$	
A			10%	10%	60%	10%	10%			1
B		8%	10%	10%	44%	10%	10%	8%		1.56
C	6%	8%	8%	10%	36%	10%	8%	8%	6%	2.05
D	11%	11%	11%	11%	12%	11%	11%	11%	11%	2.57

3. Results

The multicomponent mixtures can be described by two parameters:

— the average chain length

$$\bar{n} = \sum_{n} c_n n \tag{1}$$

(in our measurements $\bar{n} = 19$), and

— the distribution width

$$\Delta n = \sqrt{\sum_{n} c_n \left(n - \bar{n}\right)^2}, \tag{2}$$

where c_n — the fraction of alkane with a chain of n carbon atoms long (in our measurements $\Delta n = 1$, 1.56, 2.06, and 2.57).

In the rigid, rotator, and liquid phases the *o*-Ps lifetimes τ_3 and intensities I_3 are distinctly different, and therefore they are easy to distinguish in the PALS spectra. The longest-lived component in the spectrum is attributed to the *o*-Ps located in free volumes. In the rigid crystalline phase, Ps is located in the inter-lamellar gap, which in mixed structures is not smooth; one can talk about its average thickness only. In the rotator phase o-Ps resides in the vicinity of kinked molecules and respective free volumes represent a set of similar elongated voids. All what we have observed in the three--exponential fit to the spectrum corresponds to the average size of these voids. Even at a very high statistics in the spectrum it was not possible to split the *o*-Ps component into separate fractions belonging to all possible defects. Using the LT program one could find the width of distribution of lifetimes. However, for our purposes it was not necessary because adding an extra parameter would only increase the uncertainty of others.

The results of measurements as a function of pressure at 291 K for A, B, and C samples are shown in Fig. 2. For a comparison the PALS data from temperature dependences, respectively scaled, are also shown.

The measurements of the PALS spectra as a function of pressure began when the wax samples were in the ro-

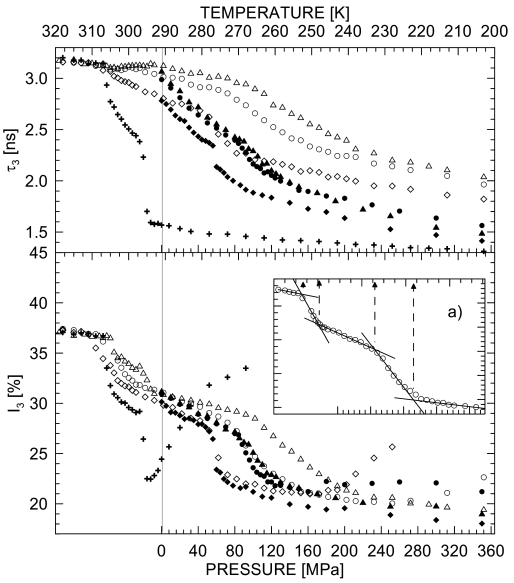

Fig. 2. Pressure dependence of *o*-Ps lifetime τ_3 and intensities I_3: diamonds — $\Delta n = 1$, full circles — $\Delta n = 1.56$, triangles — $\Delta n = 2.05$. Open symbols indicate respective temperature dependences. Crosses — temperature dependence for the neat *n*-nonadecane. Zero of the pressure scale corresponds to the temperature 291 K. The inset (a) shows how the points indicating the beginning and the end of pure phases were determined.

tator phase. Like in binary mixtures, the range of rotator phase increases with broadening of the mixture composition Δn. In the rotational phase the decrease of *o*-Ps lifetime τ_3 is faster than in the temperature measurements (if we accept the previously proposed scaling: 1 K corresponds to 4 MPa). The step of the annihilation parameters at the transition points is better visible in the intensity I_3 than in the lifetime τ_3. This is very clear for sample A, for other waxes we only see the broadening of phase coexistence (rotator and rigid) range. Such a phase coexistence region is well known in the temperature dependences.

Characteristic points on the curves τ_3, I_3 vs. p or T correspond to: the melting point, transition to pure rotator, end of pure rotator range, beginning of pure crystalline phase, respectively. We have determined the location of these characteristic points from the intersection of straight lines fitted to the experimental data below and above of these points (see Fig. 2a). For large Δn, the uncertainty of the points location can exceed 10 MPa.

The points found from the temperature and pressure dependences for various Δn are shown in Fig. 3. The ranges of rotator phase visible in the temperature and pressure dependences are quite similar. The relationships between the intensity I_3 and temperature or pressure are almost identical. However, the *o*-Ps lifetime at high pressures is distinctly shorter than the one measured at the equivalent temperatures.

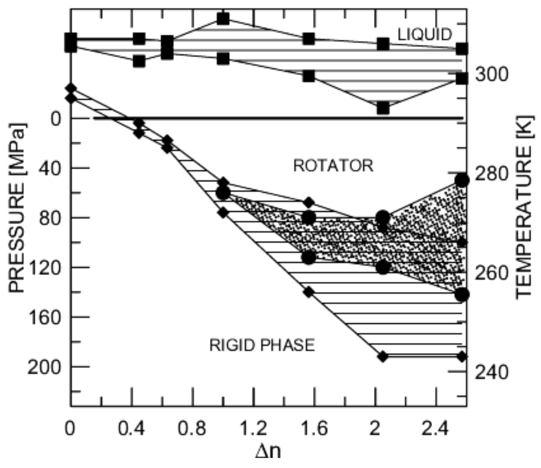

Fig. 3. Phase diagram for alkane mixtures of various Δn. The area of phase coexistence seen in the pressure (rotator-rigid, circles) and temperature measurements (rotator-rigid, diamonds and liquid-rotator, squares) is indicated by full and hatched area, respectively. The data for temperature dependences and for liquid-solid transition are taken from Ref. [12].

Contrary to the measurements as a function of lowering temperature, in the dependences on rising pressure the rise of intensity I_3 is not observed. At low temperatures the rise of I_3 means the positronium formation on trapped excess electrons [22]. Such a trapping is highly dependent on the temperature. Our measurements as a function of pressure were performed at 291 K which is too high to observe the electron trapping.

The range of pure rotator phase increases with Δn (for $\Delta n = 1$ it is about 30 K) and is similar in pressure and temperature dependences, except for the richest mixture. The region of phase coexistence seen in the temperature dependences is larger than the one in pressure dependences (in Fig. 3 this is indicated by hatched and full-filled area, respectively).

The widest area of phase coexistence is seen for the D mixture ($\Delta n = 2.57$, Fig. 4a). For this mixture, the relative deviation of length of the shortest and the longest molecules from the average is 1.27 and 1.21, respectively. The limit of miscibility of binary alkane mixtures is 1.22 (for multicomponent ones slightly more), thus extreme components of this wax are at the edge of forming a common structure.

It seemed interesting to check the long term stability of the spectrum parameters. The sources of possible instability can be either spontaneous de-mixing or change of relative content of two coexisting phases. For this mixture (D), the test measurements were performed at four selected pressures: 70, 80, 100 and 120 MPa. After the skip from 280 MPa (in rigid phase) to one of the selected four pressures (in coexistence region), a series of one-hour spectra was collected during several dozen hours (the measurements at 80 MPa took more than 140 h). The intensity I_3 has already stabilized after 2 h storage

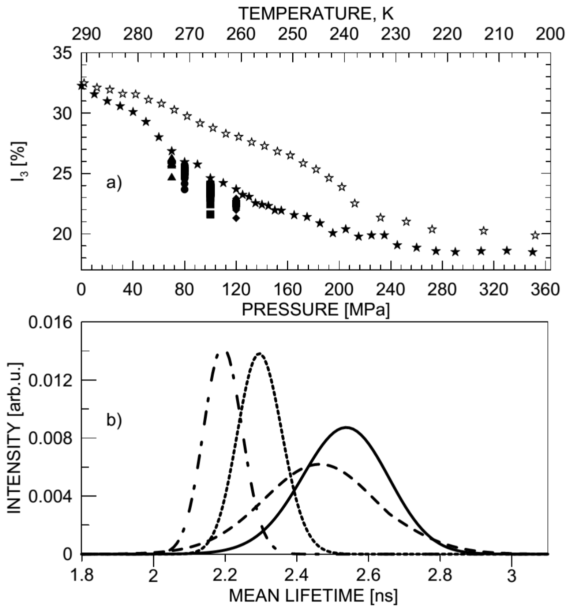

Fig. 4. (a) Pressure dependence of o-Ps intensities I_3 for 9-component wax $\Delta n = 2.57$ (D). Open symbols relate to respective temperature dependences. Full symbols — I_3 change with time for four selected pressure: 70 MPa — triangles, 80 MPa — circles, 100 MPa — squares and 120 MPa — diamonds. Zero of the pressure scale corresponds to the temperature of 291 K; (b) distribution of o-Ps lifetimes found by MELT; results for pressure: 70 MPa — solid line, 80 MPa — dashed line, 100 MPa — dotted line and 120 MPa — dotted-dashed line.

in selected pressure; the absence of instability in time (at the skips of temperature much longer relaxation times were observed [23]). The spectra were summed up (except these for first 10 h) to provide high statistics needed in the MELT program (Fig. 4b). The result of this analysis speaks in favour of the existence of a single component. No two lifetimes of o-Ps attributable to the rotational phase (about $2.7 \div 3.1$ ns) and the rigid phase (about $1.5 \div 2.2$ ns) were observed. At the pressures of 70 and 80 MPa, the lifetimes form a very broad distribution, which suggests that in the region of coexistence of both solid phases the grains of definite phases are very small and distorted; a rich variety of free volume defects exists, beside those found inside the grains, also the free volumes on grain boundaries appear. It makes a rich set of defects impossible to be separated in the PALS spectrum (note that PALS method does not see the crystalline structure, but only its defects).

4. Discussion and conclusions

Figure 3 shows that the range of rotational phase in the both temperature and pressure dependences is very similar. However, the crystalline structure formed in the rotational phase is much more sensitive to the pressure than temperature changes. Figure 5a shows the ranges of o-Ps lifetime variation in rotational phases of investigated waxes. The top value of τ_3 is indicated for the temperature of 291 K, as the pressure dependences were only measured at this temperature. The o-Ps lifetimes in the rotator phase of nine-component mixtures at 291 K are the same as in the liquid pure alkanes (about 3.15 ns). For these mixtures, it is possible to distinguish between the rotational and liquid phases only on the basis of changes in intensities I_3. The lower end of τ_3 bars in Fig. 5a corresponds to the lifetimes found at the end of the rotational phase range and the beginning of coexistence phase region. The free volume sizes in the rotator phase decrease strongly with increasing pressure (rapid decrease of the lifetime). This effect is clearly visible in the A mixture. The larger is the Δn, the smaller is the o-Ps lifetime reduction.

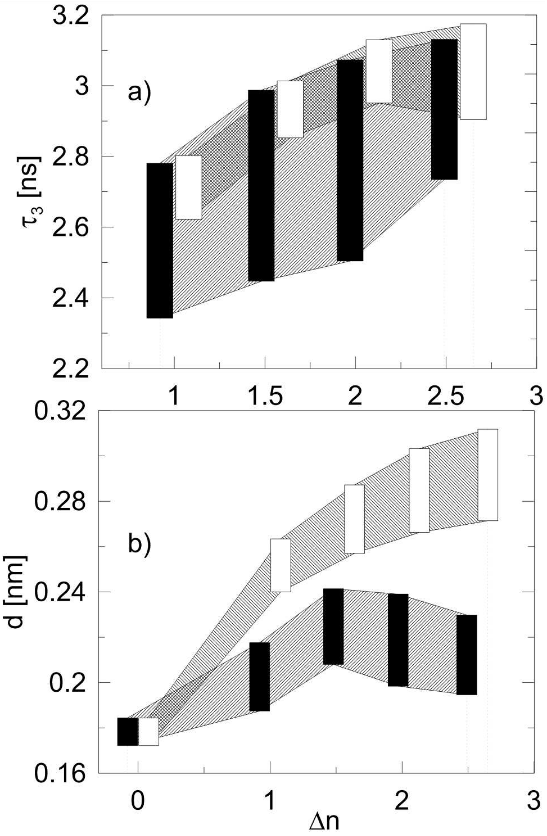

Fig. 5. (a) Differences of o-Ps lifetime τ_3 at the ends of rotator phase range as a function of distribution width Δn. Black bars — pressure dependences, white bars — temperature dependences. (b) Inter-lamellar gap width, d, as a function of the distribution width Δn in the equivalent ranges of temperature and pressure (200–240 K), (200–360 MPa); black bars — pressure dependences, white bars — temperature dependences.

This behaviour suggests that in the rotational phase:

1) the concentration of kink conformers is lower than in the absence of pressure, perhaps dominant conformers are end-gauche and double-gauche, leaving a much smaller free volume between the surrounding molecules,

2) the higher the pressure, the greater is the packing density of the crystal structure.

The latter conclusion is supported by the analysis of changes in the gap width between the lamellae. In the rigid phase, *o*-Ps locates itself in the gap, not inside the lamella, because all-trans conformers are tightly packed. It is found that in the mixtures the gap width increases, because of creating a common structure by the molecules of various hydrocarbon chain lengths (corresponding graphic representation can be found e.g. in [24]). Using the Tao–Eldrup model modified by Jasińska et al. for rectangular geometry [25] one can estimate the width of the gap between the lamellae. For a nine-component wax it reaches 0.31 nm in the measurements as a function of temperature (Fig. 5b). The gap width, d, in waxes under pressure does not exceed 0.24 nm at the beginning of the rigid phase range and is reduced even more when we increase the pressure further. For all investigated waxes the pressure of 360 MPa was sufficient to reduce the gap width to that observed in pure alkanes. It is also possible (especially with regard to the broadest mixture), that the re-segregation of components in the mixture can appear. Maybe one of factors reducing the gap width is the pressure forcing large concentration of end-gauche and double-gauche conformers of the longest molecules, in analogy to anomalous high concentration of these conformers in binary mixtures at low admixture of longer component [3].

Lowering the pressure to 0.1 MPa restores the lifetimes and intensities to the initial values, i.e. the pressure does not introduce permanent changes in the properties of waxes investigated.

References

[1] R.R. Nelson, W. Webb, J.A. Dixon, *J. Chem. Phys.* **33**, 1756 (1960).

[2] M. Marconcelli, S.P. Qi, H.L. Strauss, R.G. Snyder, *J. Am. Chem. Soc.* **104**, 6237 (1982).

[3] M. Maroncelli, H.L. Strauss, R.G. Snyder, *J. Chem. Phys.* **82**, 2811 (1985).

[4] F. Guillaume, J. Doucet, C. Sourisseau, A.J. Dianoux, *J. Chem. Phys.* **91**, 2555 (1989).

[5] T. Goworek, R. Zaleski, J. Wawryszczuk, *Chem. Phys. Lett.* **394**, 90 (2004).

[6] M. Maroncelli, H.L. Strauss, R.G. Snyder, *J. Phys. Chem.* **89**, 5260 (1985).

[7] R.G. Snyder, D. Clavell-Grunbaum, H.L. Strauss, *J. Phys. Chem. B* **111**, 13957 (2007).

[8] A. Sabour, J.B. Bourdet, M. Bouroukba, M. Dirand, *Thermochim. Acta* **249**, 269 (1995).

[9] A.R. Gerson, S.C. Nyburg, *Acta Crystallogr. B* **50**, 252 (1994).

[10] E.B. Sirota, H.E. King, Jr., G.J. Hughes, W.K. Wan, *Phys. Rev. Lett.* **68**, 492 (1992).

[11] M. Dirand, Z. Achour, B. Jouti, A. Sabour, J.-C. Gachon, *Mol. Cryst. Liq. Cryst.* **275**, 293 (1996).

[12] B. Zgardzińska, T. Goworek, *Chem. Phys. Lett.* **547**, 35 (2012).

[13] H. Forsman, P. Andersson, *J. Chem. Phys.* **80**, 2804 (1984).

[14] A. Craievich, J. Doucet, I. Denicolò, *Phys. Rev. B* **32**, 4164 (1985).

[15] J. Doucet, I. Denicolò, A. Craievich, *J. Chem. Phys.* **75**, 1523 (1981).

[16] A.F. Craievich, I. Denicolò, J. Doucet, *Phys. Rev. B* **30**, 4782 (1984).

[17] S.J. Tao, *J. Chem. Phys.* **56**, 5499 (1972).

[18] M. Eldrup, D. Lightbody, J.N. Sherwood, *Chem. Phys.* **63**, 51 (1981).

[19] T. Goworek, K. Ciesielski, B. Jasińska, J. Wawryszczuk, *Chem. Phys.* **230**, 305 (1998).

[20] J. Kansy, *Nucl. Instrum. Methods Phys. Res. A* **374**, 235 (1996).

[21] A. Shukla, M. Peter, I. Hofman, *Nucl. Instrum. Methods Phys. Res. A* **335**, 310 (1993).

[22] M. Pietrow, B. Zgardzińska, *Acta Phys. Pol. A* **110**, 641 (2006).

[23] B. Zgardzińska, T. Goworek, J. Wawryszczuk, K. Standzikowski, *Chem. Phys.* **379**, 116 (2011).

[24] B. Zgardzińska, T. Goworek, *Chem. Phys.* **368**, 101 (2010).

[25] B. Jasińska, A.E. Kozioł, T. Goworek, *J. Radioanal. Nucl. Chem.* **210**, 617 (1996).