# Application of Positron Spectroscopy for the Detection of Nanostructures in Water–Alcohol Mixtures

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Analysis of the $o$-Ps lifetimes concentration dependences in water–propanol mixtures (with and without $CoCl_2$ additive) shows that this mixture looks like an emulsion of alcohol micelles in water at propanol mole fractions 0.1–0.4.

## 1. Introduction

In this paper we discuss applicability of the positron annihilation lifetime spectroscopy (PALS) for the determination of a nanoheterogeneity of water–alcohol solutions, relying mainly on the data published in [1]. We shall see that PALS is a promising method for detection of nanostructures in a condensed matter.
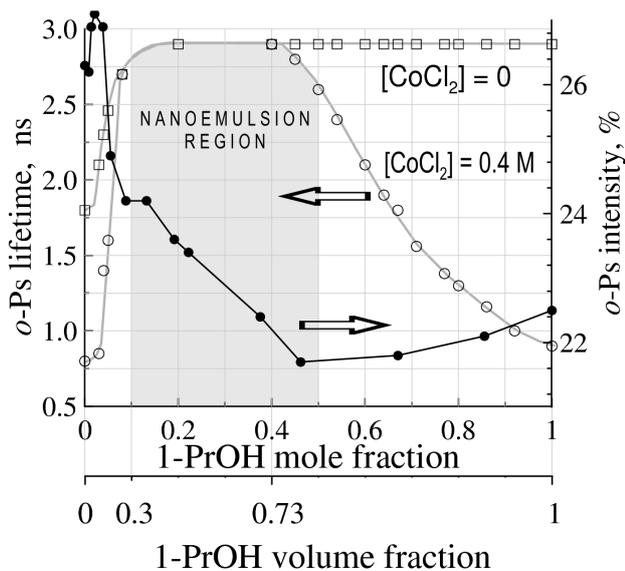


Fig. 1. $o$-Ps intensity (● [3]) and lifetime (□ — without $CoCl_2$, and ○ — with addition 0.4 M $CoCl_2$) in binary water–1-propanol mixtures at room temperature [1]. Statistical uncertainties are 5–10%.

Variations of the $o$-Ps lifetime in binary mixtures of water–1-propanol at room temperature are shown in

Fig. 1 [1]. At low alcohol mole fractions (m.f.) — from 0 to 0.1 — the $o$-Ps lifetime sharply increases from its value in pure water ($\approx 1.8$ ns), to the value in 1-PrOH ($\approx 2.9$ ns). It is noteworthy that the propanol value is reached when 1-PrOH m.f. is not a unity, but ten times less and remains unchanged throughout the following rise of the propanol content.

## 2. Discussion

What is the cause of the rapid rise of the $o$-Ps lifetime at small alcohol concentration?

The first reason could be a replacement of water molecules on the surface of the Ps bubble by alcohol molecules. Their adsorption leads to a three times reduction of the surface tension of the Ps bubble. It increases the bubble size and, therefore, increases $o$-Ps lifetime [2]. However, we shall see that this effect is mostly important at high alcohol concentration.

We attempt to show that a more likely reason for the sharp increase of the $o$-Ps lifetime is the nanoheterogeneous structure of the water–alcohol mixture in the range of propanol mole fractions from 0.1 to 0.4 where the mixture represents an emulsion (alcohol nanomicelles are suspended in water).

In PALS experiments such a structure of water–1-PrOH solutions can be revealed via specific variation of the $o$-Ps lifetime and $o$-Ps intensity vs. propanol concentration (with and without an addition of $CoCl_2$ salt into water–1-PrOH mixture). Paramagnetic $Co^{2+}$ ions efficiently interact with the $o$-Ps atoms, causing their conversion into short-lived $p$-Ps state [1]:

$$o\text{-Ps}(\uparrow\uparrow) + Co^{2+}(\downarrow) \rightarrow p\text{-Ps}(\uparrow\downarrow) + Co^{2+}(\uparrow). \qquad (1)$$

In water this *ortho–para* conversion process leads to a twofold reduction of the $o$-Ps lifetime (Fig. 1). However, with addition of the alcohol, the conversion rate rapidly decreases and at propanol mole fractions 0.1–0.4 the $o$-Ps lifetime becomes the same as in pure 1-PrOH. In this concentration interval $o$-Ps atoms do not "feel" the presence of neither $Co^{2+}$ ions, nor water molecules.

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This fact implies that $o$-Ps atoms and $Co^{2+}$ ions are located mostly in different phases — water and alcohol nanodroplets (nanomicelles).

This separation stems firstly from the fact that $Co^{2+}$ ions are known to be hydrophilic. Secondly, the sum of the Ps "zero" energy, $E_0 = \pi^2 \hbar^2 / 4m_e a_{Ps}^2$, and the surface energy $E_s = 4\pi a_{Ps}^2 \sigma$ of the Ps bubble, $E_s + E_0 \propto \sigma^{-1/2}$, decreases when the Ps atom transfers from the aqueous phase into the alcohol one. So alcohol micelles may trap Ps atoms.

Independence of the $o$-Ps lifetime vs. $Co^{2+}$ concentration at propanol m.f. = 0.1–0.4 is a manifestation of the emulsion structure of the water–propanol mixture as well as impossibility of $Co^{2+}$ ions to penetrate inside the propanol micelles. Formation of tightly bounded charged aqua-complexes $Co^{2+} \cdot (H_2O)_6$ at propanol m.f. $< 0.5$ [1] supports this conclusion.

As another confirmation of the emulsion structure comes from the concentration behavior of the intensity of the $o$-Ps component (Fig. 1). At m.f. = 0.04–0.1 the $o$-Ps intensity decreases, while the $o$-Ps lifetime rapidly increases due to migration of $o$-Ps atoms from water into alcohol micelles. Drop of the $o$-Ps intensity occurs due to spatial separation of the Ps precursors (the positron and track electrons). Electrons are mainly captured by micelles and get solvated therein, while a hydrophilic positron predominantly resides in an aqueous phase (outside micelles). Such a separation occurs due to specific orientation of polar molecules in the surface layer of the micelles [4].

Now we need to understand the reasons for the different behavior of the $o$-Ps lifetime in highly concentrated 1-PrOH solutions (m.f. $> 0.4$, the volume fraction $> 0.73$) with and without $Co^{2+}$ ions. In binary water–1-PrOH mixtures in the absence of the $Co^{2+}$ ions the $o$-Ps lifetime remains constant and its value is equal to the $o$-Ps lifetime in pure 1-PrOH. This means that only propanol molecules occupy the boundary of the $o$-Ps bubble, and water molecules have no chance to be adsorbed there because of their appearance would increase the total energy of the Ps bubble. It is notable that the intensity of $o$-Ps component is also close to its value in pure 1-PrOH (Fig. 1).

In mixtures with $Co^{2+}$ ions the reduction of $o$-Ps lifetime takes place. It is a result of renewed contacts between $Co^{2+}$ ions and $o$-Ps atoms.

The probable process which facilitates penetration of $Co^{2+}$ ions to the Ps bubble boundary is the following. At high concentrations of alcohol cobalt aqua-complexes gradually lose their charges by including chlorine anions in their solvation shells. The complexes replace also the water molecules with molecules of 1-PrOH [1]:

$$Co^{2+}(H_2O)_6 \rightarrow Co^{2+}(PrOH)_2(Cl^-)_2. \tag{2}$$

These electroneutral complexes of $Co^{2+}$ ions with alcohol solvation shells instead of aqueous ones may easily reach boundaries of Ps bubbles, decreasing $o$-Ps lifetime, Fig. 1.

Now let us estimate the number $N$ of alcohol molecules in a typical alcohol micelle in the above mentioned water–alcohol mixture. Motion of the Ps bubble in a liquid is of a diffusion character. Its diffusion coefficient may be estimated using the Hadamard–Rybchinsky formula $D_{Ps} = k_B T / (4\pi a_{Ps} \eta)$ [5]. Here $k_B$ is the Boltzmann constant and $a_{Ps}$ is the Ps bubble radius. In water at room temperature $a_{Ps} \approx 3.2$ Å [2], viscosity is $\eta \approx 1$ cP, so $D_{Ps} \approx 10^{-5}$ cm$^2$/s.

To obtain $N$, we equate the Ps diffusion length $\sqrt{6 D_{Ps}(1 \text{ ns})}$ (1 ns is the typical lifetime of the Ps atom in water) to the average distance between micelles, which is $(c_a/N)^{-1/3}$, here $c_a$ is the propanol concentration. Thus

$$N \approx c_a \left[6 D_{Ps}(1 \text{ ns})\right]^{3/2} \approx 40\text{–}60 \text{ molecules}. \tag{3}$$

To confirm findings, obtained by PALS, let us make use of additional, non-positron experimental data. From Fig. 2 it is seen that the viscosity of the mixture vs. 1-PrOH concentration has a non-monotonic behavior. It reaches a maximum at m.f. = 0.1–0.4. Appearance of the emulsion (with alcohol nanodroplets) may explain existence of this maximum. Einstein found the relation between relative viscosity $\eta(\phi)/\eta_0$ of suspension of particles and their volume fraction $\phi$: $\eta(\phi)/\eta_0 = 1 + A\phi$ [7]. Here $\phi \ll 1$ and $A$ is a numerical coefficient. In our case this relation looks like

$$\eta(\phi_{PrOH})/\eta_{H_2O} = 1 + A\phi_{PrOH}. \tag{4}$$

For spherical particles $A = 2.5$ and increases for both oblate and prolate spheroids, Fig. 3. Taking into account that the volume of a 1-PrOH molecule is four times larger than the volume of a water molecule, we obtain from Eq. (4) a quantitative prediction for the relative mixture viscosity growth at low propanol mole fractions, Fig. 2. At $A = 2.5$ the agreement with experimental data is only qualitative (dashed curve). For better fit it is necessary to adopt $A = 4.2$, which is suitable for the particles of
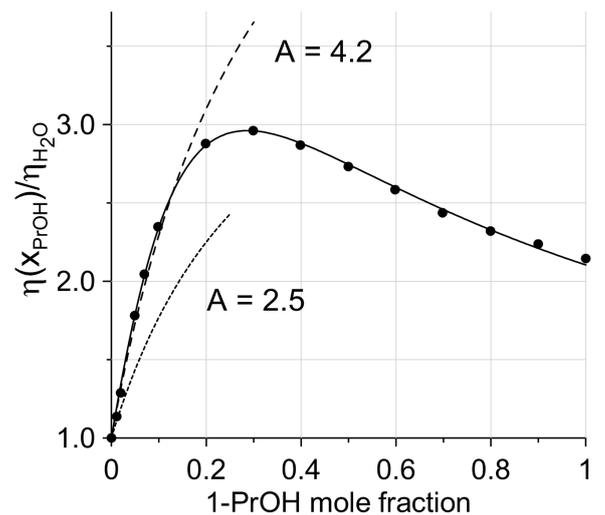


Fig. 2. Relative viscosity $\eta(x_{PrOH})/\eta_{H_2O}$ of water-1-propanol mixture at 298 K [6]. Dotted curve — viscosity predicted by Eq. (4) with $A = 2.5$; dashed curve is obtained with $A = 4.2$.
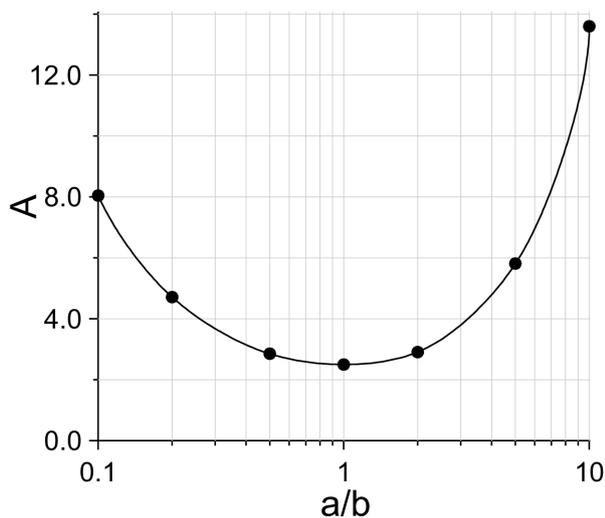
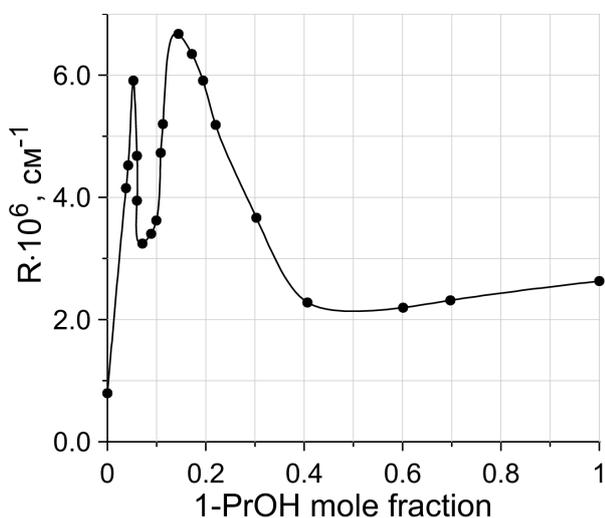Fig. 3. Values of $A$ coefficient in Eq. (4) for spheroidal particles, $a$ and $b = c$ are spheroidal axis [7].



Fig. 4. Coefficient of light scattering, $R$, in water–1-propanol mixtures [8].

ellipsoidal shape. This shape suits better to model the emulsion droplets, exposed to continuous deformations from the solvent molecules.

Another argument in favor of the nanoemulsion structure of the investigated mixture is the presence of a broad peak of the light scattering intensity, Fig. 4. In [8] it was found that this peak is due to large fluctuations of concentration of mixture components. Let us note that the narrow peak at propanol m.f. = 0.05 is not related to concentration fluctuations [8]. It is consistent with our view of a structure of the emulsion solution.

## 3. Conclusion

PALS experiments in water–1-PrOH mixtures with addition of paramagnetic ions give strong arguments in favor of nanoemulsion structure of the mixture (alcohol micelles) at propanol mole fraction from 0.1 to 0.4. Measurements of viscosity and light scattering in this system give independent confirmations of this conclusion.

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