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STRUCTURE OF CYCLOHEXANE + *t*-BUTANOL MIXTURES FROM POSITRON ANNIHILATION AND ULTRASONIC VELOCITY MEASUREMENTS

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The densities of and sound velocities in *t*-butyl alcohol solutions in cyclohexane were determined in the temperature range 25 to 45°C. From these data adiabatic compressibility coefficients of the solutions were calculated, as well as excess densities and compressibilities. The positron annihilation spectra of the solutions were measured at room temperature. The results plotted against alcohol concentration show structural processes, which can be attributed to dimerization of the solute molecules.

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1. Introduction

Previously, we tried to compare the ultrasonic results of measurements carried out on aqueous solutions of non-electrolytes (amines and alcohols) with those from positron annihilation experiment (see for example [1, 2]). It was found that both techniques applied, although different, led to consistent results explainable within the framework of liquid pseudocathrate structures. The next stage is to investigate non-polar-polar systems to test if these experimental methods are also able to monitor more subtle structural changes in liquids [3].

In this work we chose *t*-butanol as the polar associated component which was gradually diluted with a non-polar liquid (cyclohexane).

2. Experimental

Cyclohexane (pure for synth., POCh, Gliwice, Poland) and *t*-butanol (analytical grade, Ubichem, U.K.) were distilled under reduced pressure and stored over molecular sieve to avoid absorption of water from atmosphere. Weighed portions of liquids were mixed before measuring.

The ultrasonic velocity was measured with a sing-around equipment with an accuracy of about ± 0.05 m/s. The details of our apparatus can be found in [4].

Densities were measured with an accuracy of ± 0.5 kg·m⁻³ by weighing a calibrated sinker immersed into the liquid under test.

The lifetimes of positrons and positronium were measured using a standard system based on the "fast-slow" coincidence technique and described in details in [1]. The annihilation experiment was performed at room temperature (approximately 25°C).

3. Results

3.1. Acoustical measurements

From the measured densities and ultrasonic velocities, the adiabatic compressibility coefficients were calculated according to Laplace's equation, $\beta = (\rho c^2)^{-1}$, where ρ — density, c — sound velocity. The adiabatic compressibilities plotted against the mole fraction of *t*-butanol in cyclohexane are shown in Fig. 1.

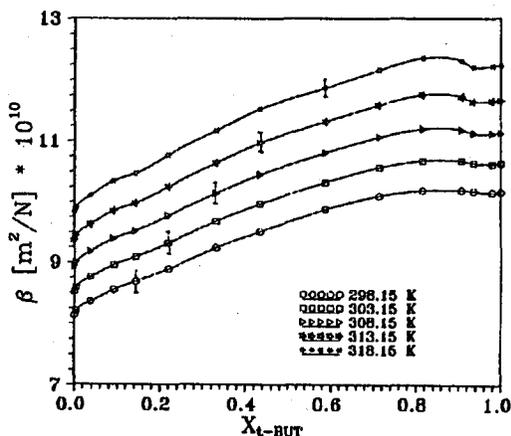


Fig. 1. The adiabatic compressibility coefficient of cyclohexane + *t*-butanol mixtures vs. alcohol concentration.

3.2. Positron annihilation measurements

The positron lifetime spectra were analysed into two components τ_1 and τ_2 (short- and long-lived), with intensities I_1 and I_2 . The details about data treatment can be found in [1]. The obtained values of τ_1 , τ_2 and I_2 are plotted in Fig. 2.

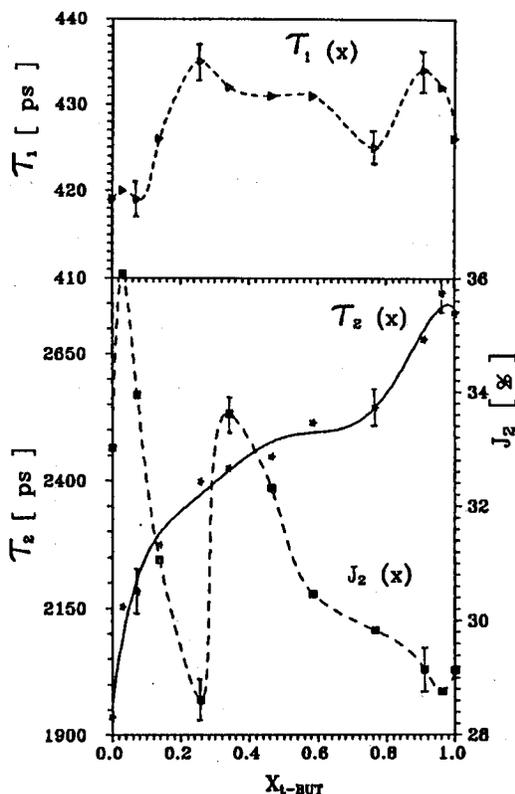


Fig. 2. The results of positron annihilation measurements vs. molar fraction of alcohol: τ_1 — lifetimes of the short-lived component, τ_2 — lifetimes of the long-lived component, I_2 — intensity of the long-lived component.

The annihilation parameters change rather smoothly with alcohol content in cyclohexane (except I_2). On the other hand, the changes in I_2 are very rapid in the region of low alcohol concentrations, suggesting strong structural rearrangements of the liquid under test.

4. Interpretation of the results

It was already noticed [5] that deviations from the "ideal" behaviour of a liquid mixture should be useful for studying molecular interactions and structural variations. The question of the mathematical representation of the "ideality" of

density, sound velocity, and compressibility of a liquid mixture was discussed in [4] on the basis of thermodynamic criterion of the ideality. The following definitions of ideal quantities were derived for density:

$$\rho^{\text{id}} = \sum x_{v,i} \rho_i^0, \quad (1)$$

and for adiabatic compressibility coefficient

$$\beta^{\text{id}} = \sum x_{v,i} \beta_i^0 \quad (2)$$

(where $x_{v,i}$ — volume fraction of i -th component in solution, superscript 0 denotes the value for the pure component).

Using these relations, the excess densities $\rho^{\text{E}} = \rho - \rho^{\text{id}}$ and the excess adiabatic compressibility coefficient $\beta^{\text{E}} = \beta - \beta^{\text{id}}$ were calculated for the mixtures under investigation. The results plotted against mole fraction of t -butanol in cyclohexane are shown in Figs. 3 and 4.

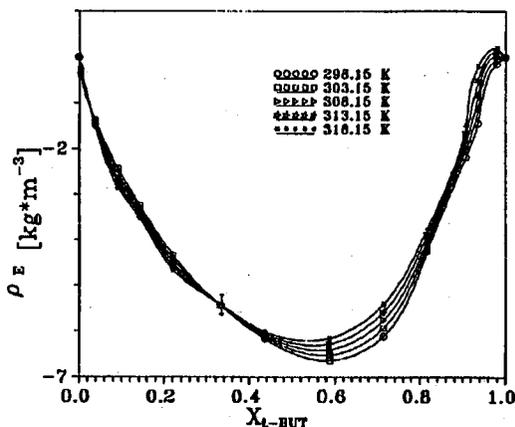


Fig. 3. The excess densities, ρ^{E} , of cyclohexane + t -butanol mixtures vs. alcohol concentration.

Because of great difference in densities of pure components, the excess density (shown in Fig. 3) is not sensitive for structural changes of their mixtures. However, the shape of curves in Fig. 4 (excess compressibility) suggests the existence of a structural change in the region of low concentrations of t -butanol (mole fraction of alcohol approximately equal to 0.1).

Our recent papers concerning the correlation between acoustic and annihilation results in interpretation of the liquid solution structure show that in aqueous non-electrolyte mixtures the region of structural changes is usually reflected by fast changes in τ_1 and τ_2 . On the other hand, in the region where the changes of the liquid structure are slow (i.e. there exists any definite quasi-crystalline structure), the changes of the annihilation parameters with organic solute concentration are much slower. Although every comparison between aqueous solutions of non-electrolytes and their solutions in cyclohexane is rather risky, the general idea, in our opinion,

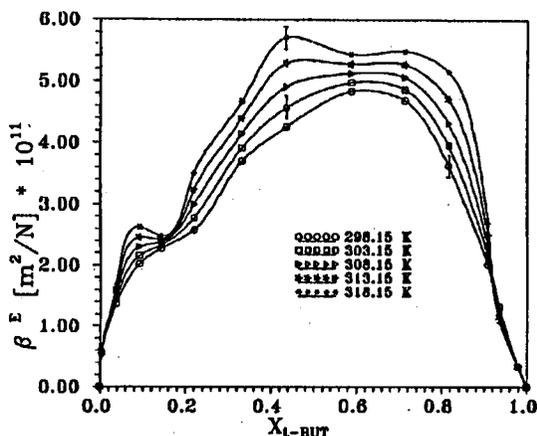


Fig. 4. The excess adiabatic compressibility coefficient, β^E , of cyclohexane + *t*-butanol mixtures vs. alcohol concentration.

should be conserved. Moreover, it seems clear that almost no solvation of alcohol in cyclohexane solution should be expected.

No direct relation should be expected between τ_2 and I_2 : the former depends mainly on local (microscopic) surface tension of liquid and lifetime of microscopic structures, and the latter — on the number of stable voids in the structure, which are able to accommodate the positronium atoms.

Assuming that the dimerization process of *t*-butanol molecules starts at low alcohol concentrations (below 0.1 mole fraction), the changes in I_2 (Fig. 2) and in β^E (Fig. 4) can be attributed to the dimerization, not solvation. This hypothesis implies the explanation of the process observed in high concentration range of alcohol (I_2 , Fig. 2, mole fraction between 0.2 and 0.5). It may be possible that almost pure *t*-butyl alcohol forms (in liquid state) structures more complicated than the simple mixture of dimers and monomers. It is worthy noting that the results obtained in this work are essentially different from those found for the mixtures of *t*-butanol in carbon tetrachloride [3].

The experimental results used and the results obtained do not allow us to describe the structure of cyclohexane + *t*-butanol mixtures. The small maximum of β^E in Fig. 4 can be attributed to dimerization of alcohol molecules, and the sharp changes in I_2 in Fig. 2 (below mole fraction of alcohol equal to 0.5) to specific interactions between non-polar solvent and the alcohol dimers. However, this interpretation needs support of other experimental methods.

Acknowledgments

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