

POSITRON ANNIHILATION IN AND ADIABATIC
COMPRESSIBILITY OF WATER-ORGANIC
SOLUTIONS. THE SYSTEM
WATER-DIMETHYLSULFOXIDE*

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The results of positron lifetime and ultrasonic velocity measurements in dilute aqueous dimethylsulfoxide (DMSO) solutions show the usual extreme characteristic for polar organic solutes. The results obtained suggest that strong structural changes occur in the system, in the region of low DMSO concentrations. Liquid clathrate hydrates forming in the system are supposed, with unusual stoichiometry and untypical geometry of the hydrates.

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It is a well established fact now that the thermodynamic properties of aqueous solutions of apolar compounds or molecules having both polar and polar components (polar organic molecules) at low concentrations are predominantly determined by hydrophobic interactions which result in an enhancement of water structure. The stabilization of water structure also gets support by NMR [1] and infrared spectroscopy [2], by X-ray diffractions [3] as well as by studies on molecular dynamics [4].

Because of the fact that many of these organic compounds form clathrate hydrates in the solid state, attempts to explain the characteristic behaviour of liquid solutions in terms of clathrate-like structures seem to be more legitimate than interpretations based on other concepts.

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As regards the ultrasonic properties of dilute aqueous solutions of polar organic compounds they usually show absorption maxima with increasing solute concentration, whereas their adiabatic compressibility isotherms intersect before reaching minimum values. Measurements on a number of polar organic compounds show [5] that both the intersection concentration and the absorption maximum are shifted to lower concentrations with increasing hydrophobic character of the solute and that the concentration of maximum absorption is somewhat higher than that of the intersection. According to Endo [6] the intersection of the compressibility isotherms should be related to the formation of pseudocathrate (cathrate-like) structures, while Baumgartner and Atkinson [7] relate the formation of such structures to the minima of the compressibility isotherms. According to Andreae et al. [8] the compressibility minimum (maximum velocity) can be explained using a quasi chemical model, where these extremes are interpreted in terms of solute-solvent complex formation.

In the present work, using dimethylsulfoxide (DMSO) as solute we have tried to examine these interpretations comparing the ultrasonic and positron annihilation behaviour of this system.

1. Experimental

1.1 Materials

Dimethylsulfoxide pure for synthesis (POCh, Gliwice, Poland) was purified by fractional distillation. Water was doubly distilled and freshly prepared chemicals were used for measurements. The concentrations of the solutions were determined by weighing the components.

1.2 Density measurements

Density was measured using a calibrated sinker method at the temperature range from 15° to 35°C. Calibrations were determined daily using the known densities of air and H₂O. The reproductibilities of the densities were $\pm 0.01 \text{ kg/m}^3$.

1.3 Sound velocity measurements

The ultrasonic velocity was measured with an accuracy of $\pm 0.1\%$ using a sing-around equipment. The details of the apparatus and measurement techniques applied in this study are given in [9].

1.4 Positron annihilation measurements

The annihilation measurements were carried out at room temperature (approx. 25°C) with a standard measuring device based on the "fast-slow" coincidence technique and described elsewhere [10].

2. Experimental results

2.1 Ultrasonic properties of the system water-DMSO

The adiabatic compressibility coefficients β were calculated from the Laplace's equation:

$$\beta = (dc^2)^{-1}, \quad (1)$$

where c is the ultrasonic velocity and d the density of the liquid. The concentration dependence of the compressibility in the low DMSO concentration region, which is of interest for the further discussion, is shown in Fig. 1.

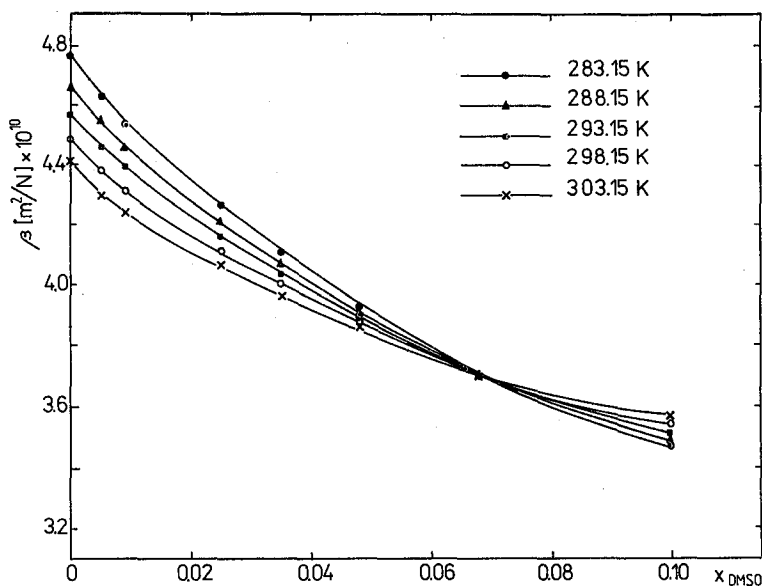


Fig. 1. Dependence of the adiabatic compressibility coefficient on the dimethylsulfoxide concentration.

The adiabatic compressibility plotted against the mole fraction of DMSO (Fig. 1) shows that in the DMSO concentration range covered by our measurements the isotherms intersect approximately at a common point corresponding to the concentration $X_{DMSO} = 0.068$.

It should be noted that the authors have repeated the measurements a few times, obtaining in all cases very similar results.

2.2 Positron mean lifetimes

Two components are expected in the time spectrum: a short-lived component τ_1 , with the intensity I_1 and a long-lived component τ_2 , with the intensity I_2 , distinctly separated from the former one and assigned to the pick-off process of the ortho-positronium.

The short-lived component is connected with the free positron annihilation (τ_0 and I_0) and with the para-positronium (τ_S and I_S). These two short-lived components are very difficult to distinguish from each other. We therefore consider the short-lived component as a "resultant" time related to τ_0 and τ_S and the corresponding intensities I_0 and I_S by the following equation:

$$\lambda_1 = I_0\lambda_0 + I_S\lambda_S, \quad (2)$$

where $\lambda_1 = \tau_1^{-1}$, $\lambda_0 = \tau_0^{-1}$, and $\lambda_S = \tau_S^{-1}$. Thus τ_1 is a weighed average of times.

According to the above consideration, the time spectra obtained, after making allowances for the "source" contribution as described in [10], were analysed with regard to the two components τ_1 and τ_2 . The latter one of the intensity I_2 , was attributed to ortho-positronium annihilating in the pick-off process [11-13]. The short lifetime component (with subscript 1) is ascribed to the free positron annihilation and to para-positronium annihilation. In this treatment the condition $I_1 + I_2 = 100\%$ is fulfilled.

From the analysis of the time spectrum of the DMSO solutions the decay constants $\lambda_1 = \tau_1^{-1}$ and $\lambda_2 = \tau_2^{-1}$ were determined. The results are presented in Fig. 2.

Usually two of the annihilation parameters, the intensity I_2 and lifetime τ_2 , are interpreted in terms of liquid structure. The annihilation parameters of the pick-off process of an ideal mixture of classical liquids are a simple function of concentration [10]:

$$\lambda_{2AB}^{1/2} V_{AB} = \lambda_{2A}^{1/2} V_A - (\lambda_{2A}^{1/2} V_A - \lambda_{2B}^{1/2} V_B) X_B, \quad (3)$$

where λ_{2AB} — the ortho-positronium decay constant in the pick-off process in the mixture of liquids A and B, λ_{2A} and λ_{2B} — the molar volumes of the components A and B, X_B — the molar fraction of the B component, V_{AB} — the mean molar volume of the mixture A-B:

$$V_{AB} = (X_A M_A + X_B M_B)/d, \quad (4)$$

where M_A — the molecular mass of water, M_B — the molecular mass of DMSO, d — the measured density of the mixture.

Taking into consideration the formula (3) and the positron annihilation data, we obtained the values of "ideal" τ_{2AB} . Through the relation (3) τ_{2AB} is connected with $d(x)$. The smooth dependence of $d(x)$ results in a smooth concentration dependence of τ_{2AB} . The experimental values of τ_{2AB} differ significantly from those obtained from the relation (3). So the latter formula is evidently incorrect for DMSO-water mixtures.

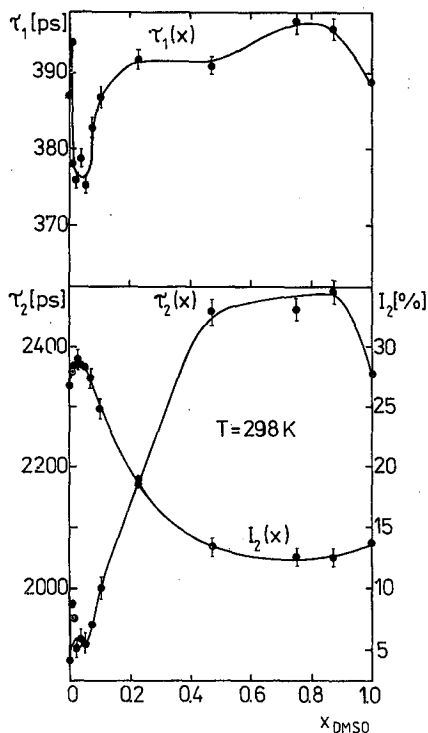


Fig. 2. The results of positron annihilation measurements: τ_1 — lifetimes of the short-lived component, τ_2 — lifetimes of the long-lived component, I_2 — intensity of the latter vs. molar fraction of dimethylsulfoxide.

It should also be stressed that the short lifetime component τ_1 decreases rapidly over the concentration region $0 < x_{\text{DMSO}} < 0.03$ and achieves a minimum value at 0.05 mole fraction of DMSO. A further increase in DMSO concentration generates a rapid increase of τ_1 .

3. Discussion

3.1 Adiabatic compressibility

To the best of our knowledge, the formation of clathrate hydrates of DMSO has not been reported in literature including the most representative reviews on clathrate type compounds [14, 15]. This suggests that either DMSO does not form inclusion compounds of this type with water or they are too unstable to be isolated.

According to the concept of iceberg formation of Frank and Evans [16] or to that of hydrophobic hydration formulated by Franks [17], when an organic compound is dissolved in water, the water structure is modified around the nonpolar

parts of the solute molecule in the direction of greater "crystallinity", whatever the actual quasi-solid water structure induced in this way. Thus, the water structure in the vicinity of an organic molecule is determined mainly by the hydrophobic moiety of the guest, the latter being accommodated in the cavities of the open hydrogen-bonded water network which in pure water are occupied most probably by "monomeric" water molecules [18-21]. This physical picture seems to interpret reasonably some properties of aqueous solutions of non-electrolytes, e.g. of p-dioxan [22], tetrahydrofuran [23], ethanol [24] and some amines [25].

According to Endo [6], the intersection point of the adiabatic compressibility isotherms should be attributed to the formation of clathrate-like structures in liquid water-organic systems at low concentrations of the organic component. A similar structural interpretation of the concentration dependence of compressibility of aqueous solutions of non-electrolytes was suggested in [25] and [26]. Thus, the intersection point concentration indicates a clathrate stoichiometry of 1 DMSO : 13.7 H₂O.

Most of the water-soluble polar compounds form in solid state cubic lattices of two types: I of CsCl type (with the lattice dimension $a = 1.2$ nm) and II of diamond type (with the lattice dimension $a = 1.7$ nm) [14, 15, 27, 28]. The unit cell of structure I consists of 46 lattice water molecules (vertices) that form 2 pentagonal dodecahedra with a free diameter of 0.5 nm and 6 tetrakaidecahedra which are approximately oblate with free diameters of 0.3 and 0.64 nm. The unit cell of structure II contains 136 lattice water molecules that form 16 pentagonal dodecahedra and 8 nearly spherical hexakaidecahedra with a monooccupied diameter of 0.66 nm.

Taking into account the above clathrate structures with dimethylsulfoxide (DMSO) accommodated in the voids, the following stoichiometry could be expected:

	structure I	structure II
(*) All voids occupied by DMSO	DMSO : 5.75 H ₂ O	DMSO : 5.67 H ₂ O
(**) Larger voids occupied by DMSO, smaller voids empty	DMSO : 7.67 H ₂ O	DMSO : 17 H ₂ O
(***) Larger voids occupied by DMSO, smaller voids occupied by monomeric water molecules	DMSO : 8 H ₂ O	DMSO : 19 H ₂ O

The crossing point concentration $x_{\text{DMSO}} = 0.068$ does not correspond to any of the above stoichiometries. However, the geometry of DMSO molecule is not as simple as that of the compounds investigated by us before (simple alcohols and amines). Because of this geometry, it is possible, for example, that one DMSO molecule forms with water a quasi-clathrate structure which is not known in solid state. It is worth noting that the compressibility value at the crossing point ($3.7 \times 10^{-10} \text{ m}^2 \text{N}^{-1}$) is even lower than that found by von Stackelberg for the solid clathrates of structure II ($4.0 \times 10^{-10} \text{ m}^2 \text{N}^{-1}$) [27, 28]. As the DMSO concentration is increased upwards of $x_{\text{DMSO}} = 0.068$, the compressibility is decreasing and achieves finally a minimum value at a concentration depending on temperature. The increasing water shortage leads to the formation of larger water cavities [28],

in which two or even more organic molecules associated in a hydrophobic sense may be accommodated. Those clathrate structures may exist in a temperature dependent equilibrium. The accommodation of two organic molecules in a common water envelope at organic component concentrations higher than 0.2 was suggested by Gorbunov et al. [29] on the basis of IR and NMR spectra of the water-dioxane system. A variety of structures existing simultaneously in equilibrium seems to be supported also by the results of freezing point measurements reported by Ennan and Lapshin [30] for the system water-tetrahydrofuran.

Concluding, the structure of dilute solutions of DMSO in water is untypical. It does not correspond to the two structures known for solid clathrates. The above interpretation was made mainly by comparison of the ultrasonic properties of the system under investigation with the systems investigated before. The ultrasonic velocity data give not enough information for proper interpretation and one needs more experimental data to it.

3.2 Positron annihilation

The concentration dependencies of positron annihilation parameters remain a bit that of the systems water-alcohols [5]. The concentration of the I_2 maximum or τ_1 minimum are close to the concentration of the organic solute corresponding to the intersection point of compressibility isotherms. The results indicate a remarkable structural variation with composition in the water-rich region. In this system different structures are probably formed, involving the hydrate structures of clathrate type with significant perturbations due to untypical geometry and/or interactions of the DMSO molecule. The lifetime of the ortho-positronium is markedly affected by the surface tension coefficient σ . According to the "bubble" model of the pick-off annihilation process [31, 32]:

$${}^* \tau_2^{-1} = A\sigma^\gamma, \quad (5)$$

with the A and γ parameters fitted so as to obtain ${}^* \tau_2 = \tau_1$ for $x = 0$ and $x = 1$. We measured the surface tension coefficients at 298.15 K and calculated the A and γ parameters. They are $A = 0.06978$ and $\gamma = 0.4735$. The similarity of the concentration dependence of τ_2 to that of ${}^* \tau_2$ calculated from (5) confirms, at least qualitatively, this annihilation model. If it is assumed that the surface tension is the main lifetime controlling factor in the pick-off annihilation, the difference $\Delta\tau_2 = {}^* \tau_2 - \tau_2$ may be attributed to structural effects. The dependence of $\Delta\lambda_2 = 1/\Delta\tau_2$ on DMSO concentration is shown in Fig. 3, with a sharp maximum at concentration very close to 0.068. That fact indicates that an important structural change of the solution occurs at this concentration of DMSO in water.

4. Conclusions

The experimental results obtained for the system water-dimethylsulfoxide using two methods (ultrasonic velocity and positron annihilation) and interpreted

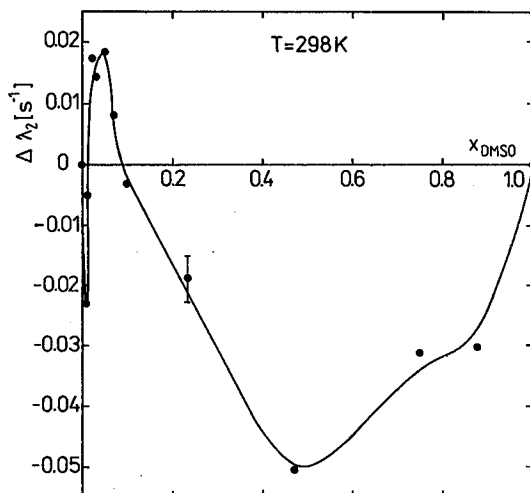


Fig. 3. The "excess" decay constant $\Delta \lambda_2$ calculated from surface tension vs. dimethylsulfoxide concentration.

independently are both explicable within the framework of liquid pseudo clathrate structure. The results clearly show that in the investigated system liquid quasi crystalline hydrates are forming in the region of low DMSO concentrations. The stoichiometry of the liquid hydrates is approximately 1 DMSO : 13.7 H₂O and does not correspond to the most common clathrate structures. It may therefore be concluded that the structure formed by DMSO in its dilute aqueous solutions is different from those known in solid state. Thus, it can be considered as a clathrate hydrate of unusual structure and stoichiometry. Similar unusual structures were reported for some amines (n-propylamine, diethylamine). This is probably the result of the specific geometry of the DMSO molecule, especially of the fact that the hydrophobic groups (methyls) are very small.

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