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BOOK OF ABSTRACTS

Self-association of Dimethylarsinic Acid: Optical, NMR, and Calculation Study of Solid State and Solutions

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Dimethylarsinic acid ($Me_2AsPOOH$, DMA) also known under trivial name Cacodylic acid has two centers capable of forming Hydrogen bond: AsOH can act as a proton donor and As=O can play role of a proton acceptor. Thus, DMA can form H-bond associates like at was found for different carboxylic and phosphinic acids. In crystals, the latter can form cyclic dimers or infinite chains depend on the substituents. However, crystals of DMA growing from protic or aprotic solvents form either cyclic dimers (polymorph I) or infinite chains (polymorph II). These polymorths were studied by X-ray diffraction analysis, IR and Raman spectroscopy. The parameters of the unit cell and intermolecular distances were obtained. The results of DFT calculations with periodical boundary conditions performed for both polymorphs are closed to the experimental values. Attenuated total reflection (ATR) spectra of polymorphs I and II recorded in the range of 4000 – 550 cm^{-1} are rather similar to each other. Particular the broad ABC structure of the ν(OH) band is observed in these spectra. This is typical for the spectra of systems with very strong hydrogen bond. Despite similarity there is some region that allows one to discern the polymorphs by spectrum. The Raman spectra of DMA crystals were obtained in the region of 4000 – 100 cm^{-1}. The intrigues feature of these spectra is weak but well distinguishable ABC-like ν(OH) band. DMA is rare example were such a band was recorded in Raman spectra of the system with the strong hydrogen bond. Again, the Raman spectra of both types of DMA crystals are similar at high frequency shift region, however, at shifts below 500 cm^{-1}, they are differ markedly.

NMR spectra of the solution of partially deuterated DMA in a mixture of liquefied freonic gasses (CDF_3/CDF_2Cl) were recorded at temperature of T = 100 K. It was found that DMA under such conditions forms only cyclic dimers. IR spectra of the solution of DMA in different aprotic solvents were obtained at room temperature at concentrations $2.5\cdot10^{-2}$ – $5\cdot10^{-4}$ mol/L. The spectra have signature of the strong hydrogen bond. In the mentioned concentration range, the spectra are the same for each solution. It is indicating that self-associates exist in solution even at quite low concentrations and the equilibrium does not shift to monomers. These results have been recently published.[1]

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References
1. V.V. Mulloyarova, A.M. Puzyk et al. *J. Mol. Struct.* **2021**, 1234, 130176