

Positive and Negative Contributions in the Solvation Enthalpy due to Specific Interactions in Binary Mixtures of C1-C4 n -Alkanols and Chloroform with Butan-2-one

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Abstract

© 2015 American Chemical Society. In the paper, results of calorimetric measurements, IR spectra, and calculated ab initio stabilization energies of dimers are reported for binary systems butan-2-one + (methanol, ethanol, propan-1-ol, butan-1-ol, and chloroform). Changes in the total enthalpy of specific interactions due to dissolution of butan-2-one in the alcohols, calculated using equations derived in previous works, are positive. That results from the endothermic breaking of the O-H...O-H bonds not completely compensated by the exothermic effects of formation of the O-H...O - C ones. Moreover, the concentration of nonbonded molecules of butan-2-one is significant even in dilute solutions, as is evidenced by the shape of the C - O stretching vibrations band in the IR spectra. Apart from that, the spectra do not confirm 1:2 complexes in spite of two lone electron pairs in the carbonyl group of butan-2-one capable of forming the hydrogen bonds. The changes in enthalpy of specific interactions are negative for dilute solutions of alcohols and chloroform in butan-2-one and of butan-2-one in chloroform, because no hydrogen bonds occur in pure butan-2-one. The experimental results are positively correlated with the enthalpies estimated from the ab initio energies using a simple chemical reaction approach.

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