MIR/NIR spectroscopic insight into the state of water in aliphatic esters

Autorzy

Mirosław Antoni Czarnecki

Kazimierz Orzechowski

Rok wydania

2026

Czasopismo

Spectrochimica Acta Part A-Molecular and Biomolecular Spectroscopy

Numer woluminu

348

Strony

127126/1-127126/9

DOI

10.1016/j.saa.2025.127126

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

This work is continuation of studies on the state of water in semi-hydrophobic solvents. For the first time, we performed systematic examinations of the binary mixtures of water with aliphatic esters. The main aim of this work was elucidation of hydrogen bonding between water and ester, as well as the possibility of water-water interactions. Since esters have two functional groups able to interact with water, it was of interest to study competition between these groups. Another interesting problem, not addressed before, was elucidation which of two alkyl groups has more important effect on the solubility of water in esters. To realize these aims we applied MIR/NIR spectroscopy and Karl Fischer titration. Interpretation of the experimental data was supported by the theoretical calculations of structure and binding energy of 1:1 and 2:1 ester:water complexes.Our results reveal that at room temperature, the molecules of water are mostly doubly bonded to esters, and only a small fraction of water is singly bonded. The temperature rise increases the population of singly bonded water at the expense of the doubly bonded species. Due to poor solubility of water in studied esters (<0.8 mol/dm^3) we did not observe water-water interactions in the studied mixtures. It was shown that water prefers the hydrogen bonding with the carbonyl group, while the interaction with the ester group is of minor importance. The solubility of water is related to molecular structure of the ester. The larger is the aliphatic part, the smaller solubility of water. In particular, bulky substituent near the C=O group effectively restricts the interaction with water. For this reason, the best solubility was observed in the acetate derivatives. The presence of few polar groups in the vicinity reduces the importance of the steric effects. Joining the spectroscopic data with Karl Fischer titration, we determined the molar absorptivity of the sum of ν_1 and ν_3 as well as $\nu_2 + \nu_3$ bands. These values appear to be constant for water dissolved in various aliphatic esters, allowing for determination of water content in esters by MIR and NIR spectroscopy.

Adres publiczny

http://dx.doi.org/10.1016/j.saa.2025.127126