

Microheterogeneity in binary mixtures of water with CH₃OH and CD₃OH: ATR-IR spectroscopic, chemometric and DFT studies.

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Rok wydania

2018

Czasopismo

Spectrochimica Acta Part A-
Molecular and Biomolecular
Spectroscopy

Numer woluminu

197

Strony

88-94

DOI

10.1016/j.saa.2018.01.068

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

Here we report ATR-IR spectroscopic study on the separation at a molecular level (microheterogeneity) and the degree of deviation of H₂O/CH₃OH and H₂O/CD₃OH mixtures from the ideal mixture. Of particular interest is the effect of isotopic substitution in methyl group on molecular structure and interactions in both mixtures. To obtain comprehensive information from the multivariate data we applied the excess molar absorptivity spectra together with two-dimensional correlation analysis (2DCOS) and chemometric methods. In addition, the experimental results were compared and discussed with the structures of various model clusters obtained from theoretical (DFT) calculations. Our results evidence the presence of separation at a molecular level and deviation from the ideal mixture for both mixtures. The experimental and theoretical results show that the maximum of these deviations appears at equimolar mixture. Both mixtures consist of three kinds of species: homoclusters of water and methanol and mixed clusters (heteroclusters). The heteroclusters exist in the whole range of mole fractions with the maximum close to the equimolar mixture. At this mixture composition near 55-60% of molecules are involved in heteroclusters. In contrast, the homoclusters of water occur in a limited range of mole fractions ($X_{ME} < 0.85-0.9$). Upon mixing the molecules of methanol form weaker hydrogen bonding as compared with the pure alcohol. In contrast, the molecules of water in the mixture are involved in stronger hydrogen bonding than those in bulk water. All these results indicate that both mixtures have similar degree of deviation from the ideal mixture.

Słowa kluczowe

Molecular structure, Clustering, Microheterogeneity, Liquid phase, Binary mixtures, Water, Methanol-d3, Methanol, ATR-IR, spectroscopy, Chemometrics, MCR, DFT, Excess absorption spectra

Adres publiczny

<https://doi.org/10.1016/j.saa.2018.01.068>

Strona internetowa wydawcy

<http://www.elsevier.com>

Plik został wygenerowany dnia 2026-04-25 04:27:01

Adres w repozytorium <https://old.chem.uni.wroc.pl/pl/repozytorium/u-haqYs>.