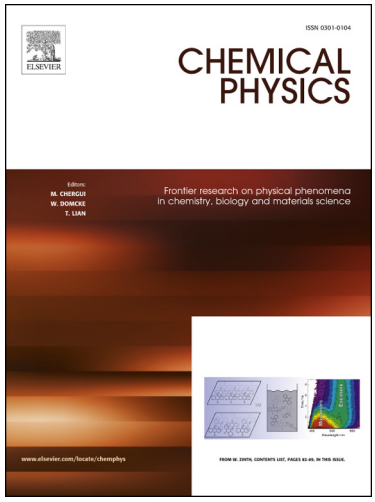
Accepted Manuscript



^{1}H and ^{17}O NMR study of H-bond dynamics in picolinic acid *N*-oxide solutions in acetonitrile-h_3 and acetonitrile-d_3: novel aspects of old casus

Arūnas Maršalka, Laurynas Dagys, Virginija Jakubkienė, Sigitas Tumkevičius, Vytautas Balevicius

PII: S0301-0104(18)30356-2
DOI: https://doi.org/10.1016/j.chemphys.2018.06.020
Reference: CHEMPH 10061

To appear in: *Chemical Physics*

Received Date: 15 April 2018
Revised Date: 25 June 2018
Accepted Date: 26 June 2018

Please cite this article as: A. Maršalka, L. Dagys, V. Jakubkienė, S. Tumkevičius, V. Balevicius, ^{1}H and ^{17}O NMR study of H-bond dynamics in picolinic acid *N*-oxide solutions in acetonitrile-h_3 and acetonitrile-d_3: novel aspects of old casus, *Chemical Physics* (2018), doi: https://doi.org/10.1016/j.chemphys.2018.06.020

^{1}H and ^{17}O NMR study of H-bond dynamics in picolinic acid *N*-oxide solutions in acetonitrile-h_3 and acetonitrile-d_3: novel aspects of old casus

Arūnas Maršalka[1], Laurynas Dagys[1], Virginija Jakubkienė[2], Sigitas Tumkevičius[2], Vytautas Balevicius[1*]

[1]*Institute of Chemical Physics, Vilnius University, Sauletekio av. 3, LT-10257 Vilnius, Lithuania*

[2]*Institute of Chemistry, Vilnius University, Naugarduko str. 24, LT-03225 Vilnius, Lithuania*

Abstract

Despite apparent similarity, two isotopomers of acetonitrile (ACN-h_3 and ACN-d_3) show unexpected differences in their structural and dynamic properties. These differences cannot be fully understood within the usual isotope effect and therefore called as unresolved casus. Sensing the solvent properties, the H-bond dynamics of picolinic acid *N*-oxide (PANO) in ACN was studied using ^{1}H and ^{17}O NMR. Several overlapping factors, like the presence of micro-traces of water, liquid-liquid equilibrium, effect of ionic ingredient, etc., which may cause the observed anomalies in the dependences of PANO chemical shift and signal width on temperature, were analyzed. The deuterium isotope effect on the phase separation in organic solute/water mixtures was deduced to be the crucial factor inducing those surprising differences between ACN-h_3 and ACN-d_3. Thus the casus could be resolved within the second-order phase transition model, in which the vibrational contributions to the intermolecular interaction energies would be properly taken into account.

Keywords: NMR spectra; hydrogen bond; isotopic effects; liquid-liquid phase separation; phase transitions

[*]Corresponding author. E-mail address: vytautas.balevicius@ff.vu.lt (V. Balevicius).