



Euroopa Liit
Euroopa Sotsiaalfond



Eesti tuleviku heaks

Toetab TÜ ja TTÜ doktorikool “Funktsionaalsed
materjalid ja tehnoloogiad”(FMTDK)

ESF projekt 1.2.0401.09-0079

INFLUENCE OF WATER CONTENT ON THE ACIDITIES IN ACETONITRILE

Karl Kaupmees (presenting author)¹, Ivari Kaljurand¹, Ivo Leito¹

¹Institute of Chemistry, University of Tartu, Ravila 14a Str, 50411, Tartu, Estonia

e-mail: karl.kaupmees@ut.ee

Experimentally measured acid and base strength of molecules (usually expressed as pK_a values) in different media are among the most important chemical characteristics of molecules. Acetonitrile (AN) is one of the most popular non-aqueous solvents for acid-base chemistry. The best known and most often reported impurity in solvents is water. It is well known that amphiprotic water as a cosolvent in an aprotic solvent influences physico-chemical properties of compounds and chemical equilibria substantially.

The goal of this work was to quantify the influence of water on acid-base equilibria in AN.

The recently published comprehensive acidity scale of neutral Brønsted acids in acetonitrile [1,2] was taken as a reference. All together 10 different acid pairs differing by strength and acidity centre were studied, quantifying the influence of water on their relative strength (ΔpK_a). The $\Delta pK_{a,exp}$ of each pair was measured in four AN-water mixtures having water contents of approximately 10, 100, 1000 and 10000 ppm. To aide the interpretation and to assess the predictive power the COSMO-RS [3] computations of relative acidities were also carried out. Because no good characteristic to describe the charge delocalization in anions was found in the literature the Weighted Average Positive Sigma (WAPS) parameter was introduced. The WAPS parameter uses the so called sigma profile – distribution of charge density (σ) on molecular surface.

As a general trend, water has markedly higher influence on the acidities of weaker acids ($pK_a > 20$), in particularly on the acidities of OH acids (unless with a strongly sterically shielded acidity centre) compared to NH and CH acids. From the experimental point of view the water content for acidity determination experiments in AN should be as low as possible, especially for acids with WAPS values higher than 4.5. The COSMO-RS method was found to satisfactorily describe the trends in ΔpK_a values.

References

1. Kütt, A.; Leito, I.; Kaljurand, I.; Sooväli, L.; Vlasov, V. M.; Yagupolskii, L. M.; Koppel, I. A. *J. Org. Chem.* **2006**, *71*, 2829-2838.
2. Leito, I.; Raamat, E.; Kütt, A.; Saame, J.; Kipper, K.; Koppel, I. A.; Koppel, I.; Zhang, M.; Mishima, M.; Yagupolskii, L. M.; Garlyauskayte, R. Yu.; Filatov, A. A. *J. Phys. Chem. A* **2009**, *113*, 8421-8424.
3. Klamt, A. COSMO-RS: From Quantum Chemistry to Fluid Phase Thermodynamics and Drug Design; Elsevier Science Ltd: Amsterdam, The Netherlands, 2005.
4. K. Kaupmees, I. Kaljurand, I. Leito. *J. Phys. Chem. A* **2010**, *114*, 11788–11793.

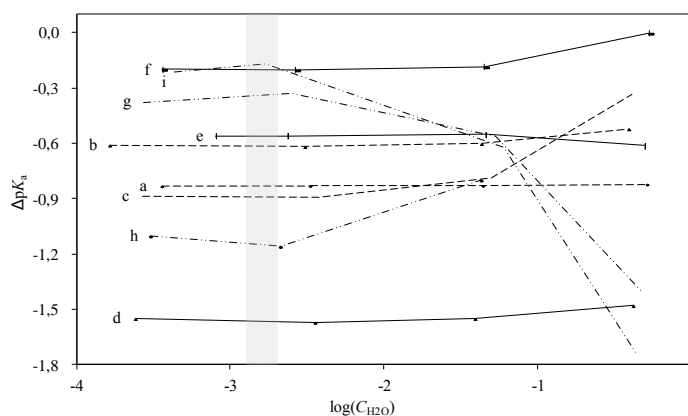


Fig.1. Influence of water content (expressed as logarithm of molar concentration) on the relative acidities (ΔpK_a) of acid pairs.