UNIVERSITY OF PÉCS

Faculty of Sciences

Physical Doctoral School

The effect of kosmotropic and chaotropic ions on the thermal dependence of the distribution of water clusters of different sizes and structures

PhD Thesis

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1. Introduction

Water is the most important medium of biological, biochemical, pharmaceutical processes and pathways. It plays an extraordinarily pronounced role because it is a protic solvent: its characteristic structure emerges thanks to the hydrogen bonds that form between water molecules in condensed, liquid and solid phases. In liquid water there is a competition of weak interactions between water molecules and between water molecules and solutes. In result a dynamic equilibrium encompasses the differently sized and structured water clusters, which is dependent both on temperature and the presence of solutes.

Solutes are defined as kosmotropes or chaotropes as they are improving or destroying the order of water structure by stabilizing or disrupting water-water interactions. Ionic kosmotropes posess small size and large charge density, while ionic chaotropes are usually of larger size with low charge density.

2. Objectives

Our goal was to investigate the temperature-dependent effect of different kosmotropic and chaotropic salts on the cluster structure in liquid water. Weak interactons play an outstanding role in biological, biochemical and pharmaceutical systems – the structure of the solvent and present clusters fundamentally determines the energies of interactions between host and guest molecules in host-guest reactions during complex formation. The better understanding of the effect of the solvent and its structure on the weak interactions contributes to the design of novel pharmaceutical molecules and reactions.

3. Tools and methods used

For our measurements we used a Jobin-Yvon/Spex Fluorolog τ3 spectrofluorimeter. Dataanalysis was performed with OriginPro 8.5.1 software and Gaussian 09 was used for quantum chemical computation.

4. Novel scientific results – thesis points

I. The presence of phophate anions promotes the temperature-dependent decomposition of water clusters compared to pure water. Repeating the measurements with rising concentration of room temperature phosphoric acid solutions we determined that not the rising phosphate anion concentration due to the rising temperature is responsible for the phenomenon.

II. We determined that the rise of pH in presence of phosphate anions increases the ratio of free water molecules and three dimensional structures made up by several rings. At higher pH the presence of sodium ions contributes to the decomposition of water prisms but slows the decoposition of water rings.

III. Sulfate anions thanks to their larger surface area have larger impact on neighbouring water molecules than perchlorate ions so cyclic clusters break down more easily in the presence of the latter.

IV. Both in the presence of perchlorate and sulfate ions it has been confirmed that around potassium ions multi-layered prism clusters resist the rise in temperature and water cycles break up. In the presence of potassium ions the formation of water clusters is less entropy-driven than in the presence of sodium ions.

V. In the presence of sodium ions the multi-ring clusters break up into smaller water rings but these rings are preserved in spite of the rising temperature. The formation of water clusters is entropy-driven in their presence.

VI. While the pH of pure water decreases with rising temperature it will rise less in the presence of the chaotropic perchlorate ions and more in the presence of the kosmotropic sulfate ions. In the presence of potassium ions the change in pH is more extreme, in the presence of sodium ions it is more uniform.

9. List of publications

5.1. Publications related to the thesis

1. **Ferenc Kovács**, Sándor Kunsági-Máté:
   Change of liquid water structure under the presence of phosphate anion during changing its kosmotropic charachter to chaotopic along its deprotonation route
   Chemical Physics Letters 756 **(2020)** 137827-137831. **[IF: 2,328; Q2]**
   doi.org/10.1016/j.cplett.2020.137827

2. **Ferenc Kovács**, Hui Yan, Heng Li, Sándor Kunsági-Máté:
   Temperature-induced change of water structure in aqueous solutions of some kosmotropic and chaotropic salts
   International Journal of Molecular Sciences 22 **(2021)** 12896-12906. **[IF: 6,208; Q1/D1]**
   doi.org/10.3390/ijms222312896

5.2. Other publications

1. Dániel Filotás, Abdelilah Asserghine, Tibor Nagy, Lilla Asztalos, **Ferenc Kovács**, János Dobranszky, Livia Nagy, Géza Nagy:
   Nickel coated graphite microparticle based electrodes for carbon dioxide reduction in Monoethanolamine medium
   Electroanalysis 33:1 **(2021)** 208-215. **[IF: 3,223; Q2]**
   doi.org/10.1002/elan.202060037

2. László Kiss, **Ferenc Kovács**, Sándor Kunsági-Máté:
   Role of allyl alcohol and sodium-4-vinylbenzenesulphonate in the electrooxidation of phenol
   Chemichal Physics Letters 764 **(2021)** 138270-138274. **[IF: 2,719; Q2]**
   doi.org/10.1016/j.cplett.2020.138270

3. László Kiss, **Ferenc Kovács**, Sándor Kunsági-Máté:
   Electropolymerization of N,N'-diphenylguanidine in non-aqueous aprotic solvents and alcohols

Periodica Polytechnica - Chemical Engineering 65:1 **(2021)** 139-147. **[IF: 1,744; Q2]**
doi.org/10.3311/PPch.14959

4. László Kiss, **Ferenc Kovács**, Sándor Kunsági-Máté
Investigation of anodic behaviour of phenylethers in non-aqueous solvents on platinum and glassy carbon electrodes
Journal of the iranian chemical society 18 **(2021)** 1677-1687. **[IF: 2,271; Q3]**
doi.org/10.1007/s13738-020-02141-4

5. László Kiss, **Ferenc Kovács**, Heng Li, Sándor Kunsági-Máté:
Electrochemical polymerization of phenol on platinum and glassy carbon electrodes in mesityl oxide
Chemical Physics Letters 754 **(2020)** 137642-137648. **[IF: 2,328; Q2]**
doi.org/10.1016/j.cplett.2020.137642

6. László Kiss, Dóra Bősz, **Ferenc Kovács**, Sándor Kunsági-Máté:
Electrooxidation of phenol in alcohols and establishment of the permeability of electrodeposited films
Polymer Bulletin 76:1 **(2019)** 215-226. **[IF: 2,014; Q2]**
doi.org/10.1007/s00289-018-2372-4

7. László Kiss, Dóra Bősz, **Ferenc Kovács**, Heng Li, Géza Nagy, Sándor Kunsági-Máté:
Investigation of phenol electrooxidation in aprotic non-aqueous solvents by using cyclic and normal pulse voltammetry
Polymer Bulletin 76:11 **(2019)** 5849-5864. **[IF: 2,014; Q2]**
doi.org/10.1007/s00289-019-02678-2

8. Shaoxian Li, Priyo S. Nugraha, Xiaoqiang Su, Xieyu Chen, Quanlong Yang, Márta Unferdorben, **Ferenc Kovács**, Sándor Kunsági-Máté, Meng Liu, Xuequian Zhang, Chunmei Ouyang, Yanfeng Li, József A. Fülöp, Jiaguang Han, Weili Zhang:
Terahertz electric field modulated mode coupling in graphene-metal hybrid metamaterials
Optics Express 27:3 **(2019)** 2317-2326. **[IF: 3,669; Q1]**
doi.org/10.1364/OE.27.002317