

THESES OF DOCTORAL (Ph.D.) DISSERTATION

**Colloidal stability in the presence of ionic liquids:
Tuning interactions in particle dispersions**

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Szeged

2024

1. Introduction and objectives

Ionic liquids (ILs) are usually defined as compounds consisting entirely of ions with melting points below 100 °C – sometimes even liquid at ambient conditions – and therefore have several advantageous properties, including a wide electrochemical window, high chemical and thermal stability, and low vapour pressure. Due to the latter property, they are considered “green” solvents or media. These remarkable properties, combined with their tuneability based on the nature of their ionic constituents, make ILs extremely interesting for a variety of applications. Since the use of nano- and colloidal particles dispersed in ILs is a dynamically developing field, especially in synthesis, catalysis, and various electrochemical applications, it is of particular interest to study the interactions of the IL components with the dispersed particles in these systems. The interfacial structure or layering of the constituent ions plays an important role in the colloidal stability of IL-containing dispersions, which has a major influence on the success of the application.

It is well known that particle aggregation processes in aqueous dispersions are governed by a balance between attractive (van der Waals, magnetic dipolar) and repulsive (electrostatic, steric) forces. These interactions are well-described by classical theories, such as the DLVO theory (named after Boris Derjaguin, Lev Landau, Evert Verwey, and Theodoor Overbeek). However, evaluating the role of electrostatic forces becomes difficult when the solvent itself consists only of ions, as is the case with ILs. The existence of stable dispersions observed in ILs contradicts the DLVO theory, as it predicts the existence of unstable dispersions at high electrolyte concentrations. This contradiction arises from the strong ionic character of ILs, which effectively screens the classical long-range repulsive interparticle forces. Consequently, understanding the interactions between the constituents of ILs and the dispersed particles is crucial to broadening the range of applications of IL-containing dispersions.

Although the physicochemical characterisation of ILs in their bulk phase is well advanced, the study of their interfacial properties is a relatively new endeavour. During the dispersion of (nano)particles in ILs, the interfacial self-assembly of the IL constituents and the subsequent solvation of the particle surfaces significantly affect the colloidal stability of these dispersions. Nevertheless, the understanding of the colloidal phenomena and the relevant physicochemical parameters in these media is still very limited. Our primary goal was therefore to map the charge and aggregation relations of the model latex particles in the presence of ILs. Particular emphasis was placed on exploring the influence of various factors, including water and salt content, to understand how these parameters affect colloidal stability.

Furthermore, ion specificity strongly influences the stability of IL-containing dispersions, which often hinders the applicability of colloidal systems. The IL cations and anions can be arranged in series based on their adsorption affinity to a given surface and their effects on the surface charge, similar to the Hofmeister series of ions originally constructed for protein destabilisation by simple salts. The second objective was therefore to investigate the affinity of IL constituents to surfaces of polymeric latex particles with the same sign of charge, but different surface functionalities. This issue can be adequately addressed in aqueous IL solutions by investigating the fundamental charging and aggregation processes while systematically changing the structure of the ILs.

Additionally, benefiting from the above properties, ILs have proven to be an alternative to conventional molecular solvents for the exfoliation of layered materials. They offer the unique ability to facilitate both one-step delamination in a liquid phase and subsequent stabilisation of the resulting 2D nanosheets in dispersions. While spontaneous exfoliation is unlikely, mixing and sonication of layered particles in suitable ILs can be used to overcome interlayer forces and produce unilamellar- or few-layer nanosheets. Hence, the third objective revolves around the study of interactions between IL constituents and layered materials — namely layered double hydroxides (LDH) — in both aqueous and pure IL medium. First, the effect of IL cations and anions on the charging and aggregation characteristics in aqueous IL dispersions was investigated. These findings serve as a valuable resource for selecting the most suitable ILs based on their structural and physicochemical properties for a given application, thereby optimising the choice of solvent.

Subsequently, two ILs were selected as delamination media based on previous information and the observed affinity of the IL constituents to the LDH surface. These ILs had already been extensively studied and it was expected that their favourable interfacial properties as well as their moderate viscosity would be beneficial in delamination processes. Thus, the fourth objective was to prove the concept of delamination of LDHs by ILs under ambient conditions, which would be an excellent way to prepare 2D double hydroxide nanosheet dispersions in one step using non-volatile “green” solvents.

2. Experimental

Among the particles investigated spherical amidine (AL) and sulphate (SL) functionalised polystyrene-based latex particles were commercially available, while layered double hydroxides (LDH) were prepared by coprecipitation. To tune the surface characteristics of SL, a saturated polyimidazolium (IP-2) polymer layer was adsorbed on the oppositely charged particle surface. The IP-2 polymer was obtained in collaboration with Prof. Paul J. Dyson (EPF Lausanne, Switzerland).

The size and charge of the particles and composites were measured by dynamic light scattering (DLS) and electrophoretic light scattering (ELS), respectively. The same techniques were used to fine-tune the loading of the individual components during surface functionalisation and to evaluate the colloidal stability under different experimental conditions. Aggregation processes in the particle dispersions were assessed by following the change in particle size over time, while the charging features were quantified using electrophoretic mobility or zeta potential and subsequently calculated charge density values. Commercial ILs (Figure 1) and their aqueous solutions were characterised by measuring the viscosity and refractive index of the IL solutions, which were crucial inputs for the light scattering measurements.

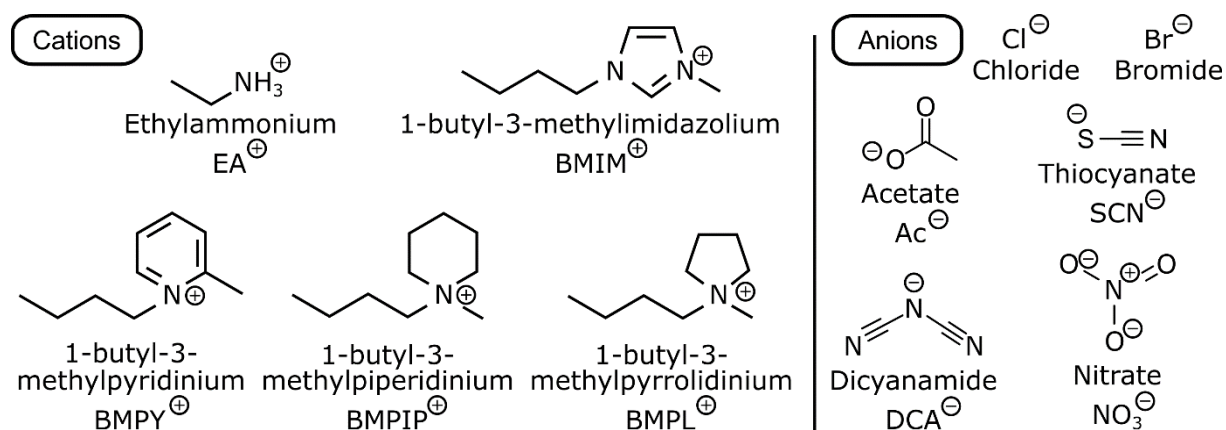


Figure 1. Constituent cations and anions of the investigated ILs.

The structure of the particles was investigated by powder X-ray diffractometry (XRD), small-angle X-ray scattering (SAXS), and small- and wide-angle X-ray scattering (SWAXS), while the size and morphological features were studied by atomic force microscopy (AFM) and transmission electron microscopy (TEM). The SAXS and SWAXS measurements were performed in collaboration with the group of Prof. Matija Tomšič (University of Ljubljana, Slovenia).

3. New scientific results

T1. Three main aggregation regimes were identified in latex dispersions as the IL-to-water ratio varied, where (1) DLVO-type forces dominate aggregation in diluted IL samples, then (2) aggregation is slowed down at higher IL concentrations due to increased viscosity, while (3) in pure ILs, particle stability arises from the repulsive oscillatory forces caused by the assembled IL layers on the particle surfaces [2].

Aggregation of both bare sulphate latex (SL) and IP-2 polymer-coated sulphate latex particles (SL-IP-2) in aqueous ethylammonium nitrate (EAN) is primarily governed by DLVO-type electrostatic interactions. In this regime, the aggregation rate increased sharply with IL content until it reached a plateau value (Figure 2), which was determined by the diffusion rate of the particles. By further increasing the IL concentration, the diffusion of the particles is limited by the increased viscosity of the medium, which leads to a slight increase in stability (viscous stabilisation). In pure IL – when only a small amount of water was present – highly stable dispersions could be observed, which contradicts many theories describing colloidal stability that predict rapid particle aggregation at high ionic contents.

In pure EAN, no particle movement could be detected when an electric field was applied during electrophoretic light scattering measurements. This observation indicates that the stabilising mechanism in these systems is not electrostatic in nature, as is the case in dilute IL solutions. Instead, the dispersions are stable due to repulsive oscillatory forces resulting from the layer-by-layer assembly of the IL constituents on the particle surfaces (solvation stabilisation). These results shed light on the origin of the main interparticle forces responsible for the colloidal stability of the particles both in pure ILs and in their aqueous solutions.

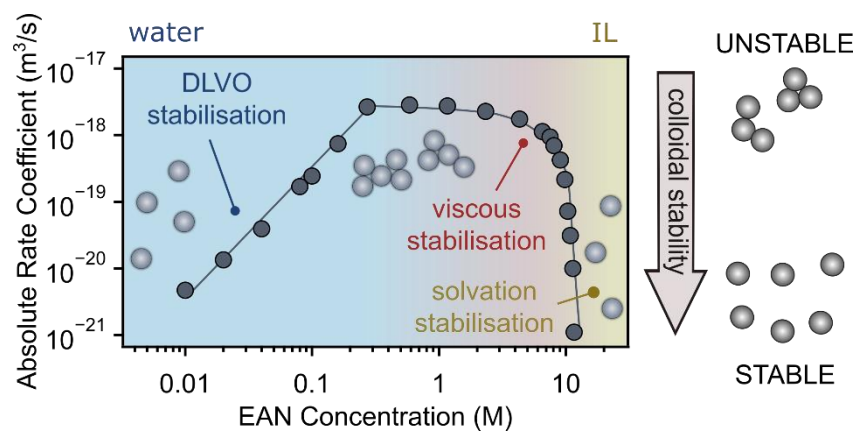


Figure 2. EAN concentration-dependent aggregation regimes in the case of SL particles.

T2. The presence of inorganic salt in IL-containing latex dispersions alters the interfacial assembly of the IL ions and thus affects the colloidal stability. The extent of the effect depends on the nature of the added ions (size, hydrophobicity, and affinity to the particle surface) and the surface properties of the particles [2].

The effect of the addition of inorganic salt (sodium nitrate) on the aggregation processes was investigated in SL-EAN dispersions over wide concentrations. In this way, it was possible to assess the effect of sodium ions – since nitrate ions were already present in the mixtures as a component of the investigated IL – on particle aggregation. For the negatively charged SL particles, a significant stabilisation was observed in the intermediate EAN concentration range, which is attributed to the accumulation of sodium ions at the interface. Moreover, this stabilisation was more pronounced with an increasing amount of added salt. In contrast, the presence of salt did not affect the colloidal stability of the positively charged SL-IP-2 particles. The effect of the added ions is therefore mainly determined by their charge, size, affinity to the surface, and the surface characteristics of the tested particles.

T3. The ion-specific effect strongly influences the charging and aggregation features of latex particles in dispersions with dilute aqueous IL medium, but this effect can be masked by functionalising the particle surface with a polyimidazolium (IP-2) polymer. However, the aggregation processes can be described by the DLVO theory [4].

The surface charges and colloidal stability of polymeric latex particles were investigated in the presence of aqueous IL solutions containing various anions and BMIM⁺ cations. It was shown that the charging and aggregation features of positively charged amidine latex (AL) particles were sensitive to the type of anion present, as the ion-specific adsorption led to a different alteration in surface charge density, such that the critical coagulation concentration (CCC) values followed the Cl⁻ > Br⁻ > NO₃⁻ > Ac⁻ order. This tendency is consistent with the indirect Hofmeister series of anions for positively charged hydrophobic surfaces. While ion-specific adsorption is responsible for the different destabilising effects, the mechanism of particle aggregation can be well described assuming the attractive and repulsive forces included in the DLVO theory. However, these ion-specific interactions could be masked by functionalising the negatively charged SL surface with positively charged IP-2 polymer, whereupon the anions affected the colloidal stability to the same extent, i.e., the CCC of the SL-IP-2 particles were the same regardless of the IL composition.

T4. The aggregation processes of LDH particles in aqueous IL dispersions are driven by DLVO-type forces, but the specific adsorption of IL components to the particle surface significantly affects the strength of the electrostatic interactions between the particles and thus the colloidal stability. Inspired by the Hofmeister series, the IL anions and cations have been arranged based on their ability to destabilise LDH dispersions [3].

By systematically changing the composition of ILs, the effect of IL anions and cations on colloidal stability in LDH dispersions was investigated, which allowed the IL constituents to be arranged based on their adsorption affinity to the LDH surface, similar to the Hofmeister series of inorganic ions. The CCC values obtained were strongly dependent on the chemical composition of both the counterions ($\text{Cl}^- > \text{Br}^- > \text{DCA}^- > \text{SCN}^- > \text{NO}_3^-$) and the coions ($\text{BMIM}^+ > \text{BMPIP}^+ > \text{BMPL}^+ > \text{BMPY}^+$). The aggregation processes were governed by DLVO-type forces, while the IL compounds altered the surface charge of LDH to different extents due to their distinct adsorption affinities, resulting in different CCC values. The magnitude of the variation observed in CCC was much more significant for counterions compared to coions, as their adsorption on the surface of the oppositely charged particle is electrostatically favoured, resulting in a more significant change in surface charge. Further valuable information was obtained by comparing the CCCs determined in the presence of IL-forming anions with inorganic salt-forming ones. The CCCs for Cl^- , NO_3^- , and SCN^- anions showed significant differences when BMIM^+ or K^+ cations were present in the system, a phenomenon that emphasises the importance of ion pair formation observed for ILs.

T5. The concept of delamination of LDH particles by ILs (EAN, BMIMSCN) under ambient conditions proved to be an excellent way to prepare single- and few-layer double hydroxide nanosheet dispersions in a single step [1].

It has been demonstrated that it is possible to delaminate LDH particles in IL medium (EAN, BMIMSCN) under ambient conditions in a single step. The process was assisted by ultrasonication and mixing, respectively, to produce single- and few-layer double hydroxide nanosheets. The disruption of the layered structure in the ILs was confirmed by the disappearance of diffraction peaks observed for LDH and its aqueous dispersion. The process led to a significant reduction in both the thickness and lateral dimensions of the nanosheets, indicating simultaneous delamination and disaggregation of LDH in ILs. The obtained 2D double hydroxide nanosheet–IL samples were stable for months without the addition of stabilising agents.

4. Applications

This dissertation aimed to investigate the basic colloidal phenomena observed in IL-containing dispersions, and the primary use of the findings is expected in the development of IL-based and IL-containing dispersions. The interfacial assembly of IL components and the solvation of particle surfaces are decisive factors that affect the colloidal stability and thus the applicability of these dispersions. By understanding the ion specificity and the effects of water and inorganic salts on the interparticle forces, the stability of particle-IL systems could be tuned. Based on the present findings, the stability regimes in a given system could be qualitatively predicted if the physicochemical properties of the particles and ILs used and the parameters affecting stability are known. This is particularly important when these dispersions are designed for specific applications, such as the development of composite materials, heterogeneous catalysis, or heat transfer fluids.

Another important aspect is that ion specificity often hinders the application of complex IL media in dispersions. Therefore, the ability to mask interfacial ion-specific effects could be beneficial to ensure the stability of colloidal systems with complex ionic environments, for example in battery development and catalysis.

Delamination of layered materials in suspension is the most practical way to produce large amounts of single-layer graphene-like nanosheets. In solvent-induced delamination, the lamellar particles are dispersed in a suitable – often organic – solvent and delamination takes place after ion exchange in the presence of an additional compound (e.g., a polymer or surfactant) that can stabilise the resulting dispersion. The main challenge in this field today is to replace the prevailing organic solvents with a “greener” alternative. Therefore, the concept of delamination of layered materials, such as LDH, with ILs under ambient conditions offers a more environmentally friendly and efficient method of producing nanosheets. This has profound implications for material synthesis and opens the doors for scalable production of 2D materials for applications in electronics, sensing, and advanced coatings.

5. Scientific publications

Hungarian Scientific Bibliography (MTMT) identifier: 10074020

Papers related to the theses

- Dóra Takács**, Gábor Varga, Edit Csapó, Andrej Jamnik, Matija Tomšič, István Szilágyi
Delamination of layered double hydroxide in ionic liquids under ambient conditions
JOURNAL OF PHYSICAL CHEMISTRY LETTERS 13 (2022) 11850.
DOI: 10.1021/acs.jpcclett.2c03275 SJR indicator: Q1
Independent citation: 3 Impact factor: 5.7
- Dóra Takács**, Matija Tomšič, István Szilágyi
Effect of water and salt on the colloidal stability of latex particles in ionic liquid solutions
COLLOIDS AND INTERFACES 6 (2022) 2.
DOI: 10.3390/colloids6010002 SJR indicator: Q2
Independent citation: 5 Impact factor: 2.4
- Dóra Takács**, Bojana Katana, Adél Szerlauth, Dániel Sebők, Matija Tomšič, István Szilágyi
Influence of adsorption of ionic liquid constituents on the stability of layered double hydroxide colloids
SOFT MATTER 17 (2021) 9116.
DOI: 10.1039/D1SM01074C SJR indicator: Q1
Independent citation: 5 Impact factor: 4.0
- Bojana Katana, **Dóra Takács**, Felix Daniel Bobbink, Paul J. Dyson, Nizar B. Alsharif, Matija Tomšič, István Szilágyi (*shared first authorship*)
Masking specific effects of ionic liquid constituents at the solid–liquid interface by surface functionalization
PHYSICAL CHEMISTRY CHEMICAL PHYSICS 22 (2020) 24764.
DOI: 10.1039/D0CP02805C SJR indicator: Q1
Independent citation: 7 Impact factor: 3.7

Papers not related to the theses

- Dóra Takács**, Maja Adžić, Nejra Omerović, Milan Vraneš, Jaroslav Katona, Marko Pavlović
Electrolyte-induced aggregation of zein protein nanoparticles in aqueous dispersions
JOURNAL OF COLLOID AND INTERFACE SCIENCE 656 (2024) 457.
DOI: 10.1016/j.jcis.2023.11.123 SJR indicator: Q1
Independent citation: 1 Impact factor (2022): 9.9
- Dóra Takács**, Tamás Szabó, Andrej Jamnik, Matija Tomšič, István Szilágyi
Colloidal interactions of microplastic particles with anionic clays in electrolyte solutions
LANGMUIR 39 (2023) 12835.
DOI: 10.1021/acs.langmuir.3c01700 SJR indicator: Q1
Independent citation: 3 Impact factor (2022): 3.9

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3. Zsófia Vargáné Árok, Szilárd Sáringer, **Dóra Takács**, Coline Bretz, Ádám Juhász, István Szilágyi
Effect of salinity on solution properties of a partially hydrolyzed polyacrylamide
JOURNAL OF MOLECULAR LIQUIDS 384 (2023) 122192.
DOI: 10.1016/j.molliq.2023.122192 SJR indicator: Q1
Independent citation: 2 Impact factor (2022): 6.0

 4. Bojana Katana, Kata Panna Kókai, Szilárd Sáringer, Adél Szerlauth, **Dóra Takács**, István Szilágyi
The influence of solvents and colloidal particles on the efficiency of molecular antioxidants
ANTIOXIDANTS 12 (2023) 99.
DOI: 10.3390/antiox12010099 SJR indicator: Q1
Independent citation: 3 Impact factor (2022): 7.0

 5. **Dóra Takács**, Tamás Péter, Zsófia Vargáné Árok, Bojana Katana, Snežana Papović, Slobodan Gadzuric, Milan Vraneš, István Szilágyi
Structure–stability relationship in aqueous colloids of latex particles and gemini surfactants
JOURNAL OF PHYSICAL CHEMISTRY B 126 (2022) 9095.
DOI: 10.1021/acs.jpcc.2c06259 SJR indicator: Q1
Independent citation: 2 Impact factor: 3.3

 6. Nizar B. Alsharif, Gergely F. Samu, Szilárd Sáringer, Adél Szerlauth, **Dóra Takács**, Viktória Hornok, Imre Dékány, István Szilágyi
Antioxidant colloids via heteroaggregation of cerium oxide nanoparticles and latex beads
COLLOIDS AND SURFACES B: BIOINTERFACES 216 (2022) 112531.
DOI: 10.1016/j.colsurfb.2022.112531 SJR indicator: Q1
Independent citation: 7 Impact factor: 5.8

 7. Adél Szerlauth, Edina Balog, **Dóra Takács**, Szilárd Sáringer, Gábor Varga, Gábor Schuszter, István Szilágyi
Self-assembly of delaminated layered double hydroxide nanosheets for the recovery of lamellar structure
COLLOIDS AND INTERFACES SCIENCE COMMUNICATION 46 (2022) 100564.
DOI: 10.1016/j.colcom.2021.100564 SJR indicator: Q1
Independent citation: 5 Impact factor: 4.5

 8. Bojana Katana, **Dóra Takács**, Adél Szerlauth, Szilárd Sáringer, Gábor Varga, Andrej Jamnik, Felix D. Bobbink, Paul J. Dyson, István Szilágyi
Aggregation of halloysite nanotubes in the presence of multivalent ions and ionic liquids
LANGMUIR 37 (2021) 11869.
DOI: 10.1021/acs.langmuir.1c01949 SJR indicator: Q1
Independent citation: 7 Impact factor: 4.3
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9. Nizar B. Alsharif, Katalin Bere, Szilárd Sáringer, Gergely F. Samu, **Dóra Takács**, Viktória Hornok, István Szilágyi
Design of hybrid biocatalysts by controlled heteroaggregation of manganese oxide and sulfate latex particles to combat reactive oxygen species
 JOURNAL OF MATERIALS CHEMISTRY B 9 (2021) 4929.
 DOI: 10.1039/D1TB00505G SJR indicator: Q1
 Independent citation: 4 Impact factor: 7.6
10. Tímea Hegedűs, **Dóra Takács**, Livia Vásárhelyi, István Szilágyi, Kónya Zoltán
Specific ion effect on aggregation and charging properties of boron nitride nanospheres
 LANGMUIR 37 (2021) 2466.
 DOI: 10.1021/acs.langmuir.0c03533 SJR indicator: Q1
 Independent citation: 13 Impact factor: 4.3
11. Bojana Katana, **Dóra Takács**, Edit Csapó, Tamás Szabó, Andrej Jamnik, István Szilágyi
Ion specific effects on the stability of halloysite nanotube colloids—inorganic salts versus ionic liquids
 JOURNAL OF PHYSICAL CHEMISTRY B 124 (2020) 9757.
 DOI: 10.1021/acs.jpcc.0c07885 SJR indicator: Q1
 Independent citation: 19 Impact factor: 3.0
12. **Dóra Takács**, Gábor Schuszter, Dániel Sebők, Ákos Kukovecz, Dezső Horváth, Ágota Tóth
Magnetic-field-manipulated growth of flow-driven precipitate membrane tubes
 CHEMISTRY – A EUROPEAN JOURNAL 25 (2019) 14826.
 DOI: 10.1002/chem.201902830 SJR indicator: Q1
 Independent citation: 7 Impact factor: 4.9

Scientometric data

Peer-reviewed publications: 16	In relation to the theses: 4
Cumulative impact factor: 80.3	In relation to the theses: 15.8
Independent citations: 93	In relation to the theses: 20

Oral and poster presentations related to the theses

- Dóra Takács**, István Szilágyi (oral presentation)
Influencing the colloidal interactions in ionic liquid-based dispersions by altering the water and salt content
 96th ACS Colloid and Surface Science Symposium
 10–13 July 2022, Golden, Colorado, USA
 - Dóra Takács**, Bojana Katana, István Szilágyi (oral presentation)
Effect of ionic liquid constituents on the stability of layered double hydroxide dispersions
 18th European Student Colloid Conference
 26–30 June 2022, Szeged, Hungary
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3. **Dóra Takács**, István Szilágyi (oral presentation)
Tuning the aggregation of latex particles in ionic liquids by changing the water and salt content
28th EUCHEM Conference on Molten Salts and Ionic Liquids
5–10 June 2022, Patras, Greece
 4. **Dóra Takács**, Bojana Katana, István Szilágyi (oral presentation)
Effect of ionic liquid constituents on the stability of nanoclay colloids
33rd Australian Colloid and Surface Science Student Conference
31 January–2 February 2022, online
 5. **Dóra Takács**, István Szilágyi (oral presentation)
Tuning colloidal interactions in ionic liquid-water mixtures
35th Conference of the European Colloid and Interface Society
5–10 September 2021, online
 6. **Dóra Takács**, Bojana Katana, Felix D. Bobbink, Paul J. Dyson, István Szilágyi (poster)
Masking specific effects of ionic liquid constituents at the solid-liquid interface by surface functionalization
Geneva Colloids 2021
8–9 April 2021, online
 7. **Dóra Takács**, Bojana Katana, István Szilágyi (oral presentation)
Tuning particle stability in aqueous solutions of ionic liquids
XLIII. Chemistry Lectures
27–29 October 2020, online

Oral and poster presentations not related to the theses

1. **Dóra Takács**, István Szilágyi (oral presentation)
Heteroaggregation of microplastics with anionic clays in an aquatic environment
38th International Conference on Solution Chemistry
9–14 July 2023, Belgrade, Serbia
2. **Dóra Takács**, Ágota Tóth (oral presentation)
Mágneses tér hatása a paramágneses csapadékmintázatokra
XXXIV. National Student Chemistry Conference
21–23 March 2019, Budapest, Hungary
3. **Dóra Takács**, Gábor Schuszter, Dezső Horváth, Ágota Tóth (oral presentation)
Mágneses tér hatása a paramágneses csapadékmintázatokra
XLI. Chemistry Lectures
15–17 October 2018, Szeged, Hungary