DELAMINATION OF LAYERED MATERIALS AND STRUCTURE-DYNAMICS RELATIONSHIP IN GREEN SOLVENTS

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cooperative research project
between

UNIVERSITY OF SZEGED, HUNGARY
&
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MOTIVATION

The main goal of this bilateral Hungarian-Slovenian project was to design stable dispersions of 2D nanosheets in ionic liquids (ILs) for development of hybrid nanocomposites. Within this bilateral cooperation, a joint project (N1-0139) was running in parallel on the Slovenian side (ARRS). Given the landmark development around the graphene-like materials, this topic attracts widespread contemporary interest. Besides, ILs represent a new type of solvents owing to their unique physicochemical properties making them promising candidates to replace hazardous organic solvents. Therefore, the novelty of the project is twofold, (i) design of 2D and composite materials as well as (ii) application of ILs as medium in particle dispersions. The challenges were addressed by combination of experimental and theoretical approaches in preparation of lamellar particles, studying their interaction with ILs and formation of complex structures. The cooperation between the Hungarian and Slovenian partner was beneficial during the project since they well-complemented each other in terms of expertise and infrastructure.

MAIN ACHIEVEMENTS

Design of lamellar nanomaterials

One of the most important parts of the research was to obtain lamellar materials, as sources of 2D nanosheets in delamination processes. Beside layered double hydroxides (LDHs) and titanate oxides (LTOs) included in the original research plan, other lamellar compounds such as boron nitride nanospheres (BNNS) and halloysite nanotubes (HNTs) were obtained. The main criteria of these compounds were the high purity, narrow particle size distribution and good dispersibility in liquid phases.

As primary potential source of 2D nanosheets, LDHs were synthesized by different techniques. A novel synthetic method was developed, in which mesoporous LDH was prepared by applying a sacrificial surfactant template (DOI: 10.1016/j.jcis.2020.08.118). Due to the highly porous structure, the obtained material was a promising candidate in delamination processes, since the ILs and other solvent constituents diffused more effortless into the interlamellar space and hence, the interfacial assembly led to delamination into unilamellar nanosheets. Besides, intercalated LDHs and their surface modified derivatives were prepared by co-precipitation methods (DOIs: 10.1039/d0sm01531h and 10.1039/D0DT04186F). It was found that treatment of the LDH particles with organic solvents gives rise to an increased specific surface area, which was highly beneficial in the further delamination studies.

The LTOs were prepared by calcination of titania in the presence of carbonate salts at high temperature. Single phase LTO of excellent purity and crystallinity was obtained. To improve the surface properties such as the density of functional groups, an acidic post treatment was applied. Both LDH and LTO materials were characterized by X-ray diffraction (XRD) and light scattering techniques to confirm the formation and to explore their size and morphology.

Invited review papers on 2D materials have been published (DOIs: 10.3390/cryst10030148 and 10.1016/j.addr.2022.114590) by the Hungarian group, in which focus was made also on the synthesis of 2D structures to identify possible substrate particle systems for delamination. Accordingly, this opportunity was used to look through the related literature data to find the most promising synthetic routes for LDHs, LTOs and other lamellar materials to be applied as possible targets in the present research. One of the later ones is layered boron-nitride nanomaterials, which are of graphene-like structures and thus, attracted significant attention, since they are potential source of unilamellar 2D nanosheets. The BNNS particles were synthesized by a continuously operated chemical vapor deposition process resulting in high purity materials of narrow size distribution (DOI: 10.1021/acs.langmuir.0c03533).

Finally, commercially available halloysite nanotubes (HNTs) of layered structure were also acquired. These naturally occurring clay materials are sustainable sources of inorganic 2D nanosheets, while a key issue was to improve their dispersibility in liquids. This challenge was addressed by alkaline treatment of the raw materials leading to enrichment of the surface functional groups and to subsequent stabilization of the HNT particles in dispersions (DOI: 10.1021/acs.jpcb.0c07885).

Dispersion characteristics in the presence of simple salts and ILs

To achieve effective solvent-induced delamination, the colloidal stability of the particle dispersions must be controlled. This requires the thorough investigation and understanding of the major interparticle forces. This issue was pursued with the above particles in the presence of inorganic salts and ILs. Surface charge and rate of aggregation were the most important parameters, which were systematically determined under different experimental conditions to assess the stability of the particle dispersions.

First, the influence of IL anions and cations on the charging and aggregation properties of LDH particles were comprehensively studied with light scattering techniques (DOI: 10.1039/D1SM01074C). The interfacial assembly of IL constituents was probed, as this phenomenon most likely plays a crucial role in the stability and delamination tendency of LDH particles in ionic media. Specific adsorption of IL constituents was observed. Although the origin of the interparticle forces was very similar in all systems regardless of the ILs present, the ion specific effects were found to be important for the adsorption of the IL ions on the surfaces. This observation shed light on the fact that ILs interact specifically with the particles. Accordingly, the charging and aggregation properties were predominantly determined by the composition of the ILs, as they can modify the surface charge to different extents due to the different adsorption affinity of the IL constituents (Figure 1). The obtained information provided useful insights to explain delamination mechanisms with LDHs.

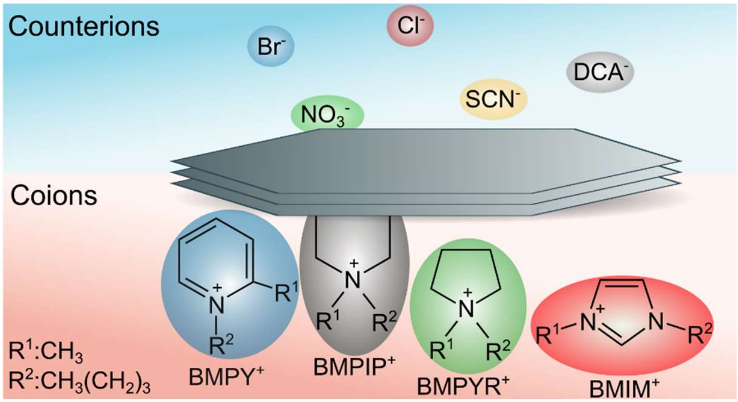

Figure 1. Illustration of affinity of IL constituents to the surface of LDH particles. The nitrate and BMPIP$^+$ IL composing ions adsorbed the strongest among the counter and coions, respectively. The alkyl chain length (R^1 and R^2) of the IL cations was the same in all systems.

Moreover, the interfacial properties of some salts and ILs were assessed using HNT particles, (DOIs: 10.1021/acs.jpcb.0c07885 and 10.1021/acs.langmuir.1c01949). These cationic clays were used to study surface assembly of IL constituents through following the charging and aggregation processes in dispersions. IL solutions containing cations of different alkyl chains were applied to probe the effect of IL hydrophobicity on the adsorption processes. For bare HNT, it was found that the strength of adsorption increased with the hydrophobicity, while for polymer-functionalized particles, no specific interaction was observed between the salt or IL constituent cations and the particle surface, i.e., ion specific effects were masked by the polymer layer. Given the growing interest in clay materials dispersed in electrolyte or IL solutions, these results bring important quantitative information about the interfacial properties and subsequently, help to design fine particle dispersions in ILs.

Although spherical polymeric latex particles cannot be transformed into 2D nanosheets, they possess smooth and homogeneous surfaces and served as excellent substrates to explore interfacial and interparticle interactions with light scattering techniques. The aim of these studies was to investigate the affinity of the IL constituents to the surface, which is a key parameter in liquid delamination processes. This information is essential for choosing the most appropriate IL constituents for such a purpose. The most important and novel results were that (i) ion specific adsorption can be tuned by appropriate surface modification, for instance, significant adsorption of IL constituent could be prevented by surface coating with an IL polymer (DOI: 10.1039/d0cp02805c); (ii) addition of inert salts or water had remarkable effect on the stability of particles dispersed in ILs through the disruption of the self-assembled IL layers on the surface (DOI: 10.3390/colloids6010002) and (iii) application of Gemini (containing 2 head groups and 2 alkyl chains) ILs led to strong surface adsorption, which may reverse the charge of the particles (DOI: 10.1021/acs.jpcb.2c06259). Schematic illustration of interfacial IL assembly in the presence of added inert salts or surface-active polymers are presented in Figure 2.

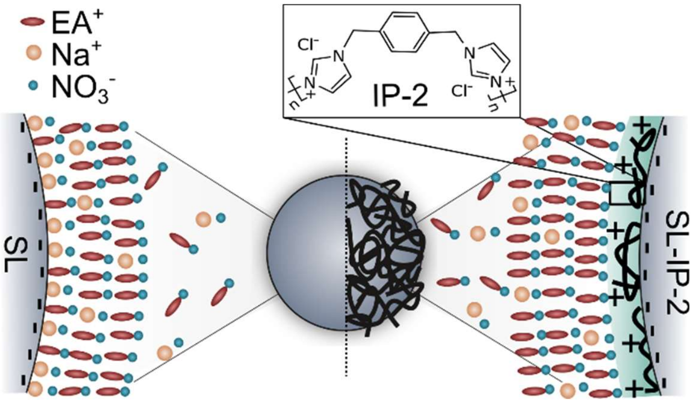

Figure 2. Structure of solid-liquid interface in case of negatively (left) and positively (right) charged surfaces immersed in EAN solutions in the presence of added sodium ions. The positive charge was formed upon functionalization of the latex particles with the IP-2 IL polymer (structure is shown in the inset).

Besides, investigation of the colloidal stability of BNNS suspensions in different ionic media was performed. The influence of various mono- and multivalent cations as well as anions on the charging and aggregation properties of the negatively charged particles was studied over a wide range of salt concentrations (DOI: 10.1021/acs.langmuir.0c03533) and in the presence of polymers to improve the dispersibility of the particles (DOI: 10.1021/acs.langmuir.1c00656). For monovalent ions, similar trends were determined in the stability and charging of the particles irrespective of the salt composition, i.e., no ion specific effects were observed. Once multivalent counterions were involved, the critical coagulation concentrations decreased with the valence. However, the destabilization ability of the coions was much weaker. The predominant interparticle forces were identified as electrical double-layer repulsion and van der Waals attraction. These findings offered useful information to design processable BNNS dispersions for further studies.

In the above investigations, aggregation regimes were important parameters to describe the colloidal stability of the samples. Therefore, a method was developed to calculate critical coagulation concentration values of particles from their surface charge data without directly measuring the evolution of their hydrodynamic size in time-resolved experiments (DOI: 10.3390/colloids4020020). This novel technique saved enormous amount of time during the dispersion stability assessments of particle-IL systems.

Structural aspects in solutions of surface-active agents

A combined theoretical and experimental study on the hydration phenomena of relatively large functional molecules in green solvents and in their aqueous mixtures was performed, i.e., the nonionic surfactant Brij 35 in alcohols and in aqueous alcohol-rich ternary systems (DOI: 10.1016/j.jcis.2021.02.113). The significance of this study to this project and beyond was twofold. Firstly, this first application of ‘complemented-system approach’ to the surfactant system proved that such a combined approach is readily available for studies in the colloidal domain and will promote the use of this powerful methodology, based on experimental and calculated small- and wide-angle X-ray scattering (SWAXS) data, in studies on colloidal systems. In parallel, the combined methodology of molecular dynamics (MD) and the ‘complemented-system approach’ has been adapted for the studies of systems with larger molecules, which was also important for its applications in ILs. Secondly, it showed how detailed the preferential solvation, hydration, interaction, structural and dynamic features at intra- and inter-molecular levels in organic and mixed solvents can be determined by this methodology, if only the molecular models used prove to be realistic enough. The latter was simultaneously verified by comparing the calculated and experimental SWAXS results. The solvation and hydration properties are of paramount importance in ensuring the colloidal stability of particle dispersions due to their effect on the interparticle forces.

In addition, SWAXS measurements were performed on ethylammonium nitrate (EAN) and propylammonium nitrate (PAN), which are the model protic ILs chosen to be studied by computer simulations and later tested as the possible delamination medium in our investigations. Unfortunately, only a few available molecular models could be found for these two ILs in the literature, which was even stronger motivation to study them from this aspect. However, the first structural tests from MD simulations in solution reflected some problems of the molecular models applied in reproducing the structural situation, as revealed by the experimental SWAXS data. Therefore, a more advanced polarizable molecular models of EAN and PAN was used in MD simulations. In parallel, the workflow for simulations and calculations of the dynamic properties of ILs (e.g., self-diffusion, conductivity and ionicity) was successfully adapted, while density, refractive index and dynamic viscosity measurements of various IL samples were carried out. The latter two parameters were necessary to know to analyse data from light scattering measurements.

Delamination of layered compounds and restacking into complex structures

Liquid phase delamination of layered materials into single- or few-layer nanosheets leads to stable nanoscale dispersions of 2D materials. One of the main goals of the project was to obtain such a low dimensional system of high surface area. This goal was achieved by dispersing LDHs into room temperature ILs, as discussed below. Besides, to understand the principal mechanism of restacking of 2D materials into more complex structures was also investigated to obtain composite materials.

The delamination of LDH particles, prepared by the sacrificial template method, was eventually studied in two ILs - EAN and 1-butyl-3-methylimidazolium thiocyanate (BMIMSCN) (Figure 3 and DOI: 10.1021/acs.jpclett.2c03275).

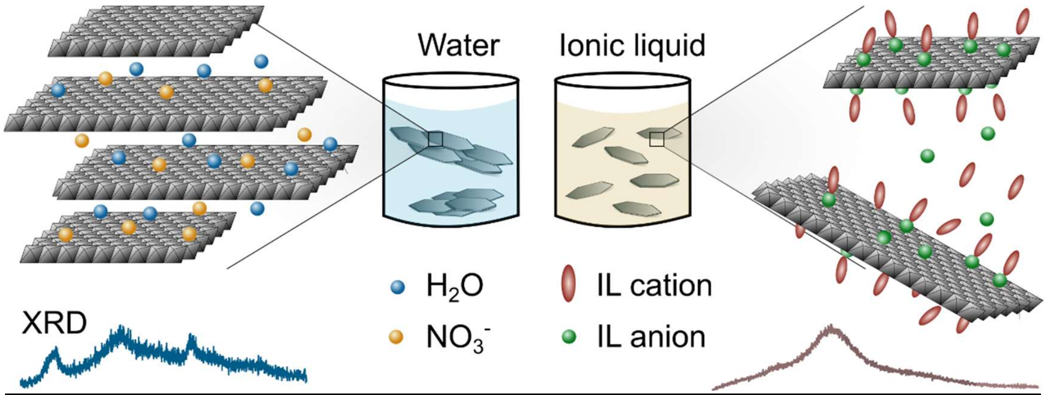

Figure 3. Scheme of the IL-induced delamination process showing the layered structure of LDH (left) and the unilamellar double hydroxide nanosheets (right). The delamination is initiated by the replacement of interlayer nitrate and water molecules by the IL constituents. Typical XRD patterns measured for the lamellar and delaminated double hydroxides are also shown.

These ILs were selected, since EAN is one of the most investigated and less costly IL, while $BMIM^+$ cations showed advantageous features at solid-liquid interfaces. The as-prepared lamellar structure of LDH disappeared upon dispersing it in ILs due to spontaneous delamination into 2D nanosheets confirmed by X-ray scattering and diffraction techniques and further evaluated by height profile assessment of the nanoparticles by atomic force microscopy. The results showed that both the thickness and lateral size of the dispersed particles decreased in the IL-based samples indicating that cleavage of the LDH materials takes place in addition to delamination. The possible mechanism is that self-assembly of the IL constituents at the LDH surface led to formation of well-defined cation-anion layers leading to the development of repulsive oscillatory surface forces. Such forces overcome attractive interactions and thus, delamination of LDH into unilamellar double hydroxide nanosheets occurred. The findings prove the concept of spontaneous (or with minimal external energy investment) delamination of layered materials by ILs - an excellent way to prepare 2D LDH nanosheet dispersions in one step using non-volatile green solvents.

The aggregation mechanism of double hydroxide nanosheets to form more complex nanostructures has been revealed at the first time (DOI: 10.1016/j.colcom.2021.100564). The nanosheets underwent ordered restacking upon salt-induced aggregation within short time intervals followed by the formation of house-of-cards-type aggregated clusters over longer periods. More precisely, at low electrolyte concentrations and during short period of times, 2D double hydroxides stacked together in plate-plate orientation giving rise to the recovery of the conventional LDH nanostructure. Once the lamellar structure was built up, the LDH particles aggregated, and house-of-cards structures formed. The initial restacking periods were shorter with increasing the salt concentration and disappeared at high ionic strengths. The results of morphological studies by microscopy techniques were in good agreement with the findings obtained in dispersions.

To obtain hybrid nanocomposites, LDH and latex particles were aggregated in the presence of ILs. Comprehensive scattering studies revealed that latexes form stable dispersions (DOI: 10.3390/colloids6010002), while LDH delaminates into 2D nanosheets in pure EAN (DOI: 10.1021/acs.jpclett.2c03275). The heteroaggregation in the sphere-plate (latex-nanosheet) geometry resulted in various composite structures depending on the experimental conditions, e.g., on the particle concentration, IL dose and amount of added salt. In this way, composite materials can be obtained, while their structure can be tuned since interactions between the particles is driven by the interfacial IL layers. These results give important insights into IL-induced aggregation and subsequent formation of various composite materials, which can be used for energy, catalysis, and environmental applications.

GENERAL REMARKS

International and national cooperation

The research was carried out in collaboration with the Slovenian partners (Matija Tomšič, Andrej Jamnik and Jure Cerar at the University of Ljubljana, N1-0139 ARRS project) in terms of scientific discussions, sample preparations and use of infrastructure. In addition, IL polymer samples were received from Paul J. Dyson (EPFL, Switzerland), while atomic force microscopy measurements were carried out in collaboration with the laboratory of Edit Csapó (University of Szeged). Data analysis and method development were accomplished with the help of Gregor Trefalt (University of Geneva, Switzerland) for rapid determination of critical coagulation concentrations in dispersions. The BNNS particles were prepared in cooperation with the research group of Zoltán Kónya (University of Szeged). The above joint research activities led to common publications with these scientists.

Dissemination of the results

The findings of the research were released in the form of scientific publications, conference presentations and social media communications. Regarding articles, 17 have been already published. The sum impact factor of these papers is 88.3, which reflect that the results were released in high impact journals of prestigious publishers (e.g., American Chemical Society, Royal Society of Chemistry or Elsevier). One of the principal investigators (Istvan Szilagyi or Matija Tomšič) was always corresponding author of these papers. The project participants presented the findings on various conferences in the form of oral and poster presentations, as listed below. The highly ranked meetings included the Conference of the European Colloid & Interface Society, EUCHEM Conference on Molten Salts & Ionic Liquids and ACS Colloid & Surface Science Symposium, while the younger team members gave oral presentations at student conferences such as the Australian Colloid & Surface Science Student Conference, European Student Colloid Conference, and the Szeged Chemistry Lectures. The most interesting results were also disseminated on Twitter and LinkedIn; these social media platforms are regularly being used by the project members.

Selected conference participations, at which the results of the project were presented by the team members either from the Hungarian or the Slovenian side.

D. Takács, M. Tomšič, G. Varga, E. Csapó, A. Jamnik, I. Szilagyi: Dispersions of delaminated double hydroxides in ionic liquids, Poster presentation, 36th Conference of the European Colloid and Interface Society, (4-9 September 2022), Crete, Greece (in-person)

B. Katana, D. Takács, I. Szilagyi: Effect of ionic liquid constituents on the stability of halloysite nanotube dispersions, Oral presentation, 28th EUCHEM Conference on Molten Salts and Ionic Liquids, (5-10 June 2022), Patras, Greece (in-person)

B. Katana, D. Takács, I. Szilagyi: Halloysite nanotube colloids – Ion specific effects and enzyme immobilization, Oral presentation, 18th European Student Colloid Conference, (26-30 June 2022), Szeged, Hungary (in-person)

D. Takács, B. Katana, I. Szilagyi: Effect of ionic liquid constituents on the stability of nanoclay colloids, Oral presentation, 33rd Australian Colloid and Surface Science Student Conference, (31 January-2 February 2022) (online)

D. Takács, I. Szilagyi: Tuning colloidal interactions in ionic liquid-water mixtures, Oral presentation, 35th Conference of the European Colloid and Interface Society, (5-10 September 2021) (online)

J. Cerar, A. Jamnik, I. Szilagyi, M. Tomšič: Performance of different molecular models in characterizing the structure and dynamics of ethylammonium nitrate. Poster presentation, 35th Conference of the European Colloid and Interface Society, (5-10 September 2021) (online)

J. Cerar, A. Jamnik, I. Szilagyi, M. Tomšič: Solvation of Brij35 in alcohol and alcohol/water systems : structure and dynamics. Poster presentation, 35th Conference of the European Colloid and Interface Society, (5-10 September 2021) (online)

D. Takács, B. Katana, I. Szilagyi: Specific effects of ionic liquid constituents on the stability of particle dispersions, Oral presentation, 95th ACS Colloid and Surface Science Symposium, (14-16 June 2021) (online)

D. Takács, B. Katana, F. D. Bobbink, P. J. Dyson, I. Szilagyi: Masking specific effects of ionic liquid constituents at the solid-liquid interface by surface functionalization, Poster presentation, Geneva Colloids 2021, (8-9 April 2021) (online)

D. Takács, B. Katana, I. Szilagyi: Tuning particle stability in aqueous solutions of ionic liquids, Oral presentation, XLIII. Szeged Chemistry Lectures, (27-29 October 2020) (online)

The influence of CoVid19 pandemic on the project performance

Although the CoVid19 World epidemic and the related travel restrictions in Hungary and Slovenia somewhat hindered the smooth performance of the project especially in years 1 and 2, the main scientific goals were successfully achieved, as discussed above. The pandemic situation prevented some personal visits and especially the exchange of young project participants from both the Hungarian and Slovenian sides, but the samples to be studied were successfully and regularly exchanged by post. In addition, many of the research meetings must have been held online (Zoom and Skype platforms), which was originally planned to be organized in-person.