11-2012

Ion Man

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Repository Citation
Hoffmann, Markus M., "Ion Man" (2012). Chemistry Faculty Publications. 7.
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As a starting point, could you provide an outline of your current research project, what led to the study and its chief aims and objectives?

Our research concerns ionic liquids, which are salts that are liquid below 100 °C. We wondered if cations and anions are perhaps so strongly associated that a mixture of two ionic liquids, with the same cation but different anion, would produce two sets of Nuclear Magnetic Resonance (NMR) spectral features. That test was negative, but then we thought, maybe when dissolved in a nonpolar organic solvent that will favour ion pairing, we might observe two sets of peaks, and we did. However, further tests revealed that only one of the two ionic liquids alone caused the two sets and we could assign the sets to represent an equilibrium between freely dissociated ions and paired ions. This was the beginning of a broader ongoing study of binary systems of ionic liquids and solvents of low polarity, where we attempt to better understand the speciation and dynamics of the present equilibrium species.

How is your research being conducted? What methods are you using and why?

We carry out physicochemical measurements, mainly NMR spectroscopy, which besides its usual use of qualitative identification of chemical compounds can also provide access to understanding intermolecular interactions and dynamics. Our physicochemical measurements such as measurements of self-diffusion, viscosity, and surface tension are generally of standard nature. We are measuring these quantities as a function of composition and temperature, and from the combined dataset we can learn a lot about the behaviour of the binary system. Because the techniques are standard they are much more amenable to working with undergraduate students who are true beginners in the laboratory as well as to integrating the instruments in the physical chemistry laboratory curriculum.

Could you describe your major findings thus far? How are they influencing the project?

The most recent, and in my opinion most unexpected finding so far, has actually come from studying a binary system of a particular ionic liquid in chloroform that does not show two NMR resonance sets.

Initially, we were only interested in checking that ion pairing is indeed still present, and the absence of the second NMR resonance set is due to fast ion exchange. However, we found that the average size of all present ionic liquid species first increases with concentration, as one would expect since larger concentration favours the formation of ion pairs and eventually aggregates, but then undergoes a maximum at quite a low concentration, which is completely unexpected because the aggregate size should increase and not decrease with ionic liquid concentration.

To explain this phenomenon, that to the best of our knowledge has not been documented before, we currently hypothesise that mass transport changes from ion pairs and aggregates moving through the solution by themselves to a hopping mechanism of ion pairs from one aggregate to the next. This is only an initial hypothesis that needs to be carefully scrutinised with much more research, which thus has changed the direction of our project.

Have you experienced any challenges during your study? How were they overcome?

We faced the particular challenge of having to relocate our laboratory twice within one and a half years due to a complete renovation of our building, with partial funding from the National Science Foundation for the renovation of all research laboratory space. With careful planning and a lot of ‘elbow grease’ we were still able to do research between the moves.

What are the expected implications of your research? What applications will it have to industry?

Chemists frequently use solvents for carrying out chemical synthesis, separations and many other applications. As a consequence, they are constantly dealing with multi-component systems. The first conceived applications of ionic liquids include their use as electrolyte for electrochemistry as well as in batteries and fuel cells and as novel reaction media that would be inherently safer and environmentally benign because of their low volatility.

In the meantime, the number and diversity of applications using ionic liquids has increased dramatically, and in some of these novel applications the ionic liquids are not the major but a minor component (solute) of the system, such as in separation applications, as a cosolvent for chemical reactions and in the analysis of surface pore morphologies of specialised materials.
IONIC LIQUIDS’ ARE salts that are liquid below 100 °C. Ionic liquids have recently been the subject of increasing interest in science and industry because they have the potential to replace traditional organic solvents that are volatile and hazardous. Very little is known about salts dissolved in organic solvents of low polarity because ordinary, inorganic salts are typically not soluble in such solvents. However, ionic liquids that are combinations of an organic cation and an inorganic anion are in many cases completely soluble in such solvents. Therefore, studies of salts in solvents of low polarity have only become possible and indeed necessary with the advent of ionic liquids. Understanding the speciation and equilibria of such salts in solvents of low polarity is a necessary prerequisite for developing theories that can quantitatively describe these solutions.

PRINCIPAL CHEMICAL EQUILIBRIA OF IONS IN SOLUTION

When a salt is dissolved into a solvent, it may completely dissociate into cations (ions bearing a positive charge) and anions (ions bearing a negative charge). Depending on the nature of the salt and solvent, as well as conditions such as concentration and temperature, the salt may not completely dissociate but still dissolve as short-lived individual cation-anion units, called ion pairs. Ion pairs can be further distinguished between a contact ion pair, where the cation and anion are in direct contact, and a solvent separated ion pair where the cation and anion are close together but still separated by a layer of solvent. Additionally, the cations and anions may aggregate to varying degrees: two ion pairs may form an ion quadrupole or four ion pairs an ion octupole. These aggregates are not necessarily charge balanced. They could be combinations of two cations and three anions, four cations and three anions and so on. Small ion sizes, low solvent polarity, lower temperatures and larger concentrations move the equilibria from freely dissociated ions, to ion pairs, to ion aggregation and ultimately to the formation of a solid phase, or in the case of ionic liquids another liquid phase when the salt becomes non-soluble.

DESCRIBING ION PAIRING AND AGGREGATION BEHAVIOUR

Researchers at The College at Brockport, State University of New York are currently investigating the ion pairing and aggregation behaviour of ionic liquids dissolved in low polarity solvents. Funded by the National Science Foundation (NSF) and led by Professor Markus Hoffmann, the team is specifically focusing on ionic liquids containing the bis(trifluoromethanesulfonyl)amide anion, which have unusually long ion pairing lifetimes in these low polarity solvents.

Ionic education

Undergraduates from The College at Brockport, State University of New York team with high school students from local schools to conduct investigations into ion pairing and aggregation of ionic liquids.

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Hoffmann’s research employs nuclear magnetic resonance (NMR) methods, specifically diffusion ordered spectroscopy, to measure self-diffusion coefficients, in addition to classical viscometric, conductivity and tensiometric measurements. The group is also synthesising ionic liquids and is carrying out calorimetric studies in collaboration with Dr Annegret Stark who is currently at the Institute for Industrial Chemistry at the University of Leipzig in Germany.

EDUCATING THE NEXT GENERATION OF SCIENTISTS

The research group includes a number of undergraduate students, and Hoffmann is passionate about his role as an educator. As The College at Brockport is a principally undergraduate institution, all of the students in Hoffmann’s team are undergraduates. Hoffmann believes that sometimes, because they are beginners, undergraduate students ask excellent questions that raise new thoughts and ideas. For example, it was an undergraduate student who suggested trying to detect two resonance sets in NMR spectroscopy for a mixture of ionic liquids with the same cation but a different anion; an idea from which the current project stems. As part of the collaboration with Stark, every year an undergraduate student from Hoffmann’s team travels to Germany to work in her laboratory synthesising ionic liquids, which is her main expertise. This is a very exciting opportunity for the student, who experiences much more than laboratory research.

Working with undergraduate students, who are not only beginners but are usually present for one or two academic years, requires a significant investment of time in training and close supervision, which is what Hoffmann enjoys the most: “It is actually amazing to see how much progress the students make in the short time of just a few months,” he enthuses. “That is why undergraduate research is so important, not only to prepare students for their future careers but also to spark inspiration in the next generation of scientists.” Indeed, about 80 per cent of the undergraduate students who have conducted research under Hoffmann’s guidance have continued their education at the graduate level after obtaining their bachelor’s degree.

Hoffmann is also reaching out to high school students, particularly those from underrepresented groups, and he has mentored several through the American Chemical Society’s Project SEED programme which offers opportunities for talented, economically-disadvantaged high school students to experience what it is like to be a chemist. Part of his approach is to pair up high school students with undergraduate students, which is successful because the undergraduate student learns even more when forced to explain specific aspects more frequently to the high school student.

FUTURE DIRECTIONS

Interest in ionic liquids as a medium for chemical synthesis, chemical separations, and other special applications has risen dramatically over the last decade, and ultimately, Hoffmann’s research will contribute to the fundamental understanding of ionic liquids, and in particular the connection between their intermolecular, and inter ionic interactions and their observed bulk behaviour.

Hoffmann is increasingly thankful for having received NSF support for his research because it has not only allowed significant progress to be made on the project, but has also supported the training of undergraduate students and improved the infrastructure for research and teaching through enabling the purchase of a number of equipment acquisitions that are now also used in the physical chemistry laboratory curriculum at The College at Brockport. He is now applying for a renewal of his NSF grant, and plans to direct his future research on ionic liquids in the exploration of an apparent breakdown of the Stokes Einstein equation (Einstein’s equation for the diffusion coefficient of a ‘Stokes’ particle undergoing Brownian Motion in a quiescent fluid at uniform temperature) in fairly dilute ionic liquid solutions in organic solvents of low polarity. He also plans on a pilot project with a high school teacher, to promote talented high school students and to explore the feasibility of incorporating experiments with ionic liquids into the high school laboratory curriculum.