Clusters of Like-Charged Ions

“Like-Likes-Like”

Like charges repel but unlike charges attract. That’s what we learn in school physics when the interaction between charges and the Coulomb law are discussed. On the other hand, we find in the famous Feynman lectures that such classical expectations can be disappointed [1]. Feynman emphasized the role of intermediate counter-charges, sometimes paraphrased as “like-likes-like through an intermediate of unlikes”.

This finding was not entirely new. Langmuir discussed such attractive forces between like charges already in 1938 [2]. He suggested that the attractive interaction between large like-charged particles can be attributed to the mediation of counter-ions. Langmuir discussed the role of attractive and repulsive forces in the aggregation of like-charged micelles in various sols, gels, and protein crystals. Ise and Okubo took up the Langmuir-Feynman ideas and derived a formal theory that brought theoretical expectations and experimental findings into essential accord [3]. However, details of this counter-intuitive phenomenon remained controversial. Pollack and co-workers gave further discussion of how large-scale charge separation with intervening zones of solvating counter-ions could trigger attractive interaction. They postulated that this unique behavior might be found not only on the colloidal scale, but also possibly down to the nano and molecular levels as well [4].

Attractive forces between like charges have also been discussed for biological systems, including the polyelectrolytes DNA, F-actin, microtubules, and virus-like filaments. The understanding of like-charge attraction is therefore not only of physical interest, but also of great biological relevance. The counter-ions and the solvent molecules, in particular water, are generally expected to play an important role for the attraction between macro ions.

Water Mediates

In chemistry, the concept of ion-pair formation, including the attractive interaction between unlike-charged ions, is well accepted and plays an important role in numerous reactions such as macromolecular catalysis or biochemical hydrolysis [5].
However, the attraction between like-charged particles in solution is largely unknown or unsupported by experimental evidence. If attractive interaction is reported, it is generally found to be solvent mediated, usually by water. However, we could show recently that direct attractive interactions between ions of like charge are also possible, leading to formation of multiply charged clusters in fluid phases that lack any intervening solvent medium [6]. This phenomenon is found for so-called ionic liquids (ILs), which consist purely of small cations and anions, without the complicating features of solvating medium or macro-ion environment that characterize previously known phenomena of this type.

H-Bonds in Ionic Liquids

What led to this important discovery? For the ionic liquid [Cholinium][NTf₂] we had previously measured the intermolecular interaction between unlike-charged ions by means of far-infrared spectroscopy. Additional measurements in the mid-infrared region showed, beside the characteristic OH stretch band of cation-anion interaction, redshifted contributions suggesting OH…OH interaction between the cations themselves. Indeed, these mid-IR spectral features resembled those of ordinary alcohols in carbon tetrachloride solvent, as expected from the formation of hydrogen bonded clusters [7]. Additionally, we became aware of a recent article in Angewandte Chemie in which Weinhold and Klein postulated anti-electrostatic hydrogen bonds [8]. Their calculations indicated that attractive H-bonds between like-charged ions can lead to local minima on the potential energy surface and resultant “kinetic trapping” of spectroscopically observable H-bonded complexes, despite the fierce opposition of repulsive electrostatic forces.

So we started to do some experimental work. Because the effect was too small for the [Cholinium][NTf₂] ionic liquid, we had to consider structural variations that could lead to enhanced attractive forces between the cations. We changed two important parameters: The hydroxylated cation 1-(2-Hydroxyethyl-3-Methyl-
Imidazolium (HEMIm) was designed to make the positive charge more accessible for the counter-ion, and a weaker interacting anion [BF$_4^-$] was adopted. With this ionic liquid, we succeeded not only in obtaining further evidence for attractive interactions between like-charged ion pairs, but proof for the formation of multiply-charged clusters [6,9].

**Frequencies Correspond to Tetramers**

The calculated and observed frequencies correspond to formation of H-bonded linear trimers and cyclic tetraters. The cyclic tetramer is a showpiece that exhibits the largest red-shift in the IR spectrum. Evidently, the strong cooperativity of cyclic H-bonding is able to compensate for the increased electrostatic repulsive forces in the tetracation.

The counter-ions assist 'neutralization' of the positive imidazolium ring and allow the formation of OH···OH H-bonds between ions of like charge. A detailed analysis of the spectra and DFT calculations show that the ionic clusters have properties that are surprisingly similar to analogous neutral clusters of ethanol and propanol. In the calculations, the fourfold positively charged clusters 'survive' without the presence of counter ions. The clusters are not only beautiful, they underline the hypothesis of Weinhold and Klein that cooperative H-bonds can compensate for the repulsive forces between like-charged ions [8].

Does the formation of clusters of like-charged ions have any influence on the properties of ionic liquids? Such investigations are currently going on in our laboratories. We measure melting temperatures, densities, viscosities and conductivities of these ILs. Some preliminary indications are already available. Obviously, the ILs are only weakly inclined to crystallization. Thus, we can suppress the crystallization by formation of polyionic clusters, or promote the crystallization by choosing appropriate counter-ions. Not only the structural properties but also the dynamics of crystallization seem to be influenced by the altered cluster patterns.

More we can not say for now. Future experiments will aim at controlling the formation of these clusters by different strongly interacting counterions. Strongly interacting anions should prevent the clustering, while weakly interacting anions should promote it. Other questions will be answered soon: Do such clusters already exist in the solid phase, or are they only formed in the liquid state? What happens during the phase transition? Can we engineer specific properties that could not be achieved by simple variation of the cation and anion?
Cooperative Effects Are Critical

In our work we were not only pleased by the nice interplay between like and unlike charged ions, but that between theory and experiment. The theory has confirmed the experimental results and allows an interpretation at the molecular level. In addition, the calculations inspire further experiments with newly synthesized ionic liquids, while the experiments support the theoretical hypotheses derived from calculations.

The satisfying result of our studies is demonstration of the first experimental evidence for a direct attractive interaction between ions of the same charge which does not require large polyelectrolytes or mediating solvent molecules. The key is cooperative hydrogen bonding, which cannot be understood from simple electrostatic considerations.

Authors
Anne Knorr\(^1\), Thomas Niemann\(^1\), Peter Stange\(^1\), Frank Weinhold\(^2\), Ralf Ludwig\(^1\)

Affiliations
1 University of Rostock, Institute of Chemistry, Physical and Theoretical Chemistry, Rostock, Germany
2 University of Wisconsin-Madison, Theoretical Chemistry Institute and Department of Chemistry, Wisconsin, USA

Contact
Prof. Dr. Ralf Ludwig
University of Rostock
Institute of Chemistry
Physical and Theoretical Chemistry
Rostock, Germany
ralf.ludwig@uni-rostock.de

References


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**Contact**

*Universität Rostock*
Wismarsche Str. 43-45
18059 Rostock