

# Preface: Special Topic on Chemical Physics of Ionic Liquids

Cite as: J. Chem. Phys. **148**, 193501 (2018); <https://doi.org/10.1063/1.5039492>

Submitted: 08 May 2018 . Accepted: 08 May 2018 . Published Online: 17 May 2018

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## Preface: Special Topic on Chemical Physics of Ionic Liquids

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(Received 8 May 2018; accepted 8 May 2018; published online 17 May 2018)

<https://doi.org/10.1063/1.5039492>

Over the past several decades, since their reappearance in the literature, ionic liquids have progressed from being a curiosity to one of the most studied materials in physical sciences today. This tremendous attention from researchers across many fields arises from emerging applications of ionic liquids in synthesis (templated nanomaterial synthesis, biowaste processing), engineering (lubrication, damping, heat transfer), and electrochemical devices (batteries, supercapacitors), amongst others. As these applications mature, the need for detailed understanding and predictive capability becomes progressively more important. Responding to this need, a great deal of effort is now being invested in resolving molecular-scale details of structure, dynamics, and interactions in ionic liquids. This chemical physics of ionic liquids is a rich and diverse field, employing many experimental and theoretical approaches and extending its reach toward understanding a widening array of ionic materials.

Complexity of the molecular structures, dynamic relaxations, and interactions in ionic liquids provides a challenge for the techniques and theories typically applied to the liquid state. To this end, a full and clear picture emerges only with a concerted effort, involving all available tools of which many are represented in this special topic. Theoretical advances include the application of dressed ion theory to systems of high ion density for interpreting electrostatic interaction screening<sup>1</sup> and density functional theory applied to the (asymmetric) restricted primitive model electrolyte.<sup>2</sup> Experimental work here showcases a wide range of techniques such as x-ray scattering,<sup>3,4</sup> IR spectroscopy,<sup>5</sup> dielectric spectroscopy,<sup>6,7</sup> and others.<sup>8,44,45</sup> Computer simulations cover the spectrum from full quantum mechanical<sup>9</sup> to coarse-grained molecular dynamics<sup>10,11</sup> and lattice Coulomb gas<sup>12</sup> and include the development of robust force fields appropriate for ionic liquids.<sup>13</sup>

The conceptual boundaries of the field of ionic liquids have expanded in several directions in recent years, with the tools developed during the past decade to probe and understand pure ionic liquids now being applied to a range of systems that have in common a high density of ions. Many examples are featured in this special topic, including studies of ionic liquid mixtures,<sup>5</sup> poly-ionic liquids,<sup>10</sup> deep eutectic solvents,<sup>14</sup> solvate ionic liquids,<sup>15</sup> zwitterionic liquids,<sup>16</sup> and mixtures

of ionic liquids with polymers,<sup>17</sup> with salts,<sup>18,19,46</sup> or with molecular solvents.<sup>20,21,47</sup>

Papers in this special topic demonstrate the interest in ionic liquids at interfaces and in confined geometries as well as the bulk fluid. Bulk ionic liquids are investigated for both equilibrium and dynamic properties.<sup>20,22–26</sup> Interfacial properties are particularly relevant for many applications, for example, electrochemical energy storage where the nature of the electrical double layer in ionic liquids and related materials is of particular interest. To this end, papers here discuss the structure and electrochemical properties of electrode-ionic liquid interfaces,<sup>27–30</sup> the electrostatic coupling between ions near and on opposite sides of a graphene electrode,<sup>31</sup> the ionic liquids in nano-confinement,<sup>32</sup> and a method to probe ionic re-arrangements near a voltage-controlled gold electrode.<sup>33</sup>

Many fundamental studies of ionic liquids are included in the special topic, alongside several directed at particular applications. Papers of broad and general relevance investigate features such as heterogeneity in the bulk liquid,<sup>34,35</sup> speciation in protic ionic liquids and complex mixtures, solvation dynamics,<sup>36–38</sup> conductivity,<sup>23</sup> electronic structure,<sup>39,40</sup> and phase behavior.<sup>41</sup> More applied contributions aim at solving problems relevant to battery electrolytes,<sup>15,18,31</sup> protein solvation,<sup>42,48</sup> synthesis of nanomaterials,<sup>3,43</sup> and biowaste extraction.<sup>16</sup>

Overall, this special topic brings together an exciting collection of articles representing the vigorous current activity in the chemical physics of ionic liquids. Many leading experimental and theoretical groups are represented among the authors as well as young investigators recently entering the field. We are delighted to present this special topic in the Journal of Chemical Physics and hope that newcomers to the field and experienced contributors alike will find interest and inspiration from the articles collected here.

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