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Short communication

Angstrom science: Exploring aggregates from a new viewpoint

Suojiang Zhang*, Feng Huo

Beijing Key Laboratory of Ionic Liquids Clean Process, State Key Laboratory of Multiphase Complex System, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

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Abstract

A small aggregate is composed of several or tens of molecules or ions, with at least one dimension in the range from a few to dozens of angstroms. Here, we named such aggregate system as Angstrom Aggregates (AA). AA with the specific size in angstrom meter might possess unique structure activity relationship. Unlike molecular level, nano system and the bulk, AA, an aggregate in angstrom scale is firstly proposed, its arrangement in order, electronic effect, surface interaction, confinement effect, is still unclear. However, recently, the structure and activity relationship of such aggregate in angstrom scale has attracted increasing interest in many areas, such as in ionic liquids, aqueous solution, catalytic system, and bio-system. As the physical and chemical propeties of AA strongly depends on its structure, the in situ characterization technique combined with theoretical methods should be developed to understand the exact interaction between the component of the clusters, the assembly formations, the special features, and the reaction activities. It has great scientific meaning to detect, represent and regulate the structure and function of AA precisely, facilitating in its application. A systematic and thorough research on AA in angstrom scale will promote the development of fundamental science and the progress of technology significantly.

Keywords: Angstom science; Aggregates; Aqueous system; Bio-system; Ionic liquids

1. Introduction

We lived in multi-scale world and understanding multi-scale structures in nature, life, society and engineering is a common challenge for scientists and engineers [1]. Compared to bulk or isolated ions and molecules, aggregates or clusters possess many unique physical and chemical properties due to extremely large surface-to-volume ratio and synergistic effect. The size of aggregates or clusters becomes smaller and smaller, the performance of the special features is more prominent. There are several factors driving this: the multivariate shape of molecules or ions, the complicated interactions coupled electrostatic and van der waals, different chemical activity of functional group and the steric effect of some atoms. In this communication, the structure and activity relationship of AA, including areas of ionic liquids, aqueous solutions, catalytic reactions and life science, is introduced and prospected.

2. Definition of AA

The small aggregates are composed of several or tens of molecules or ions, with at least one dimension in the range from a few to dozens of angstroms. As the size of the scale in angstrom meter and unique structure and activity relationship of aggregate molecules or ions, we named such aggregate system as Angstrom Aggregates (AA). The AA systems are different from isolated ions or molecules, because their interactions with each other, unique structure, and special activity are more complicated. As this concept focuses on the angstrom meters, which is smaller than the normal nano-systems, the quantum effects will be more prominent. The

* Corresponding author.
E-mail address: sjzhang@ipe.ac.cn (S. Zhang).

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AA systems are proposed, which makes us focus on the synergy quantum effects of multiple molecules or ions. A move toward the formation mechanism of the AA from the molecule and atom level is becoming a hotspot of vital importance in many areas, such as energy materials, green chemistry and electrochemistry. If we could accurately control the size, the structure, the chemical activity, and the polar sites of AA by understanding the complex interactions, including electrostatic, van der waals, hydrogen bond and so on, it would help us understand the nature of the AA systems and achieve breakthroughs in many application fields. The study of AA drilling into angstrom scale will greatly promote the development of fundamental science and the progress of technology.

3. Angstrom science in typical systems

3.1. Ionic systems

Recently, ionic liquids (ILs) with special characteristics have been paid extensive attentions and are pregnant with potential applications [2]. Hydrogen bond interactions might be the most important intermolecular interactions in ionic liquids. We found that hydrogen bond between the cation and anion, coupling with the strong electrostatic force, shows particular features in the geometric, energetic, electronic, and dynamic aspects, which is inherently different from that of the conventional hydrogen bond. Because the structure shows a "zig-zag" motif, in Fig. 1c, this coupling interaction is defined as the Z-bond [3]. As the existence of Z-bond, the ion-pairs in gas phase were proved by situ IR experiment and theoretical calculation [4]. In the liquid phase, the micro heterogeneity of ILs or the existence of clusters in ILs was reported experimentally and theoretically several years ago. Voth and coworkers discovered firstly that ILs can form ionic clusters by molecular dynamic simulation [5]. The clusters in liquid membrane of ILs bmimI, supporting with carbon nanotubes, were observed directly by atomic force microscope [6]. Recently, more and more aggregates or clusters in ILs have been observed and reported by molecular dynamic simulation or atomic force microscopy [7,8]. There is a typical rodlike clusters with the concentration of 0.49 mol/L IL of aqueous solution from our molecular dynamical simulation under 298 K and 1.0 atm [9] in Fig. 1a, which is about several hundred nano meters. This is a typical nanosystem, however, we still cannot obtain fully detail information about the atomic level structure and quantum effects of clusters from the in situ experiment and theoretical calculation methods so far. Especially, to elucidate the mechanism about how the aggregates effect the reaction and interact with each other is more difficult, when the systems reduced to the angstrom scale. In Fig. 1b, if ILs are confined in 5−10 Å m, the ions interact and arrange in order with the molecular sieves and have special catalytic activity. Understanding the intrinsic features of AA will greatly promote the development of the fundamental theory and the industry application of ILs.

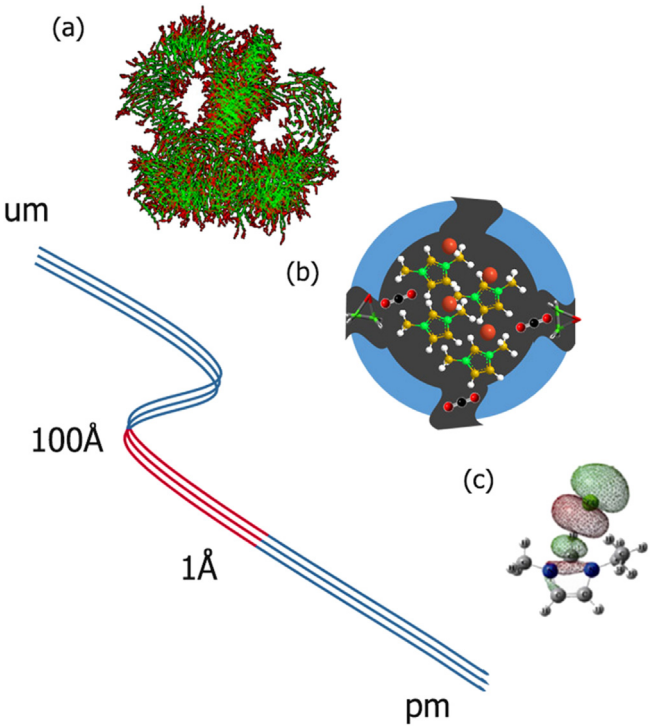

Fig. 1. (a) The ionic clusters of rodlike are performed in aqueous solution by means of molecular dynamics simulation, in several hundreds nano meters. (b) The confinement ionic aggregates were filled into pore materials. There are several pairs of ionic liquids and several molecules of reaction system, and the scale of the aggregates is in angstrom meters. (c) The ion pair of ionic liquids is isolated; the interactions of ionic liquids are calculated at the electronic level. The angstrom scale is 1−100 Å, which has unique properties distinguished than the isolated pairs or molecules, and the bigger nano systems.

3.2. Aqueous systems

Water as a ubiquitous and important solvent or media on so many aspects of human activity has been extensively researched for hundreds of years. The deceptively simple water molecule forms one of the most complex liquids and solids, numerous theoretical models of water were developed, such as three sites model (SPC), four sites model (TIP4P), five sites model (ST2) and so on [10]. The well-known result is that none of the models could describe the water as dimer, small cluster, liquid state or solid state perfectly. Debenedetti and coworkers found that a unambiguous evidence for a liquid−liquid transition in the ST2 model of water. Water can be separated to two phases of low-density liquid and high-density liquid, the stabilize interface was found in the computation [11]. There are small aggregates composed of water molecules on the liquid−liquid interface for contributing the surface energy of two different density phases in Fig. 2a. Walsh and coworkers reported that the spontaneous nucleation and growth of methane hydrate by molecular dynamics simulation [12]. The mechanism of nucleation of methane hydrates is very complex, and the formation and dynamic processes of AA systems composed by methane and water molecules is the key factor. The research on AA of water and aqueous solution by theoretical methods such as molecular simulation has

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