



Historical perspective

Ionic liquids for nano- and microstructures preparation. Part 1: Properties and multifunctional role



Justyna Łuczak^{a,*}, Marta Paszkiewicz^b, Anna Krukowska^b, Anna Malankowska^a, Adriana Zaleska-Medynska^a

^a Faculty of Chemistry, Department of Chemical Technology, Gdansk University of Technology, G. Narutowicza 11/12, Gdansk 80-233, Poland

^b Faculty of Chemistry, Department of Environmental Technology, University of Gdansk, Wita Stwosza 63, Gdansk 80-308, Poland

ARTICLE INFO

Available online 18 August 2015

Keywords:

Ionic liquids
Nanoparticle interaction
Nanomaterial synthesis
Microstructure preparation

ABSTRACT

Ionic liquids (ILs) are a broad group of organic salts of varying structure and properties, used in energy conversion and storage, chemical analysis, separation processes, as well as in the preparation of particles in nano- and microscale. In material engineering, ionic liquids are applied to synthesize mainly metal nanoparticles and 3D semiconductor microparticles. They could generally serve as a structuring agent or as a reaction medium (solvent). This review deals with the recent progress in general understanding of the ILs role in particle growth and stabilization and the application of ionic liquids for nano- and microparticles synthesis. The first part of the paper is focused on the interactions between ionic liquids and growing particles. The stabilization of growing particles by steric hindrance, electrostatic interaction, solvation forces, viscous stabilization, and ability of ILs to serve as a soft template is detailed discussed. For the first time, the miscellaneous role of the ILs in nano- and microparticle preparation composed of metals as well as semiconductors is collected, and the formation mechanisms are graphically presented and discussed based on their structure and selected properties. The second part of the paper gives a comprehensive overview of recent experimental studies dealing with the applications of ionic liquids for preparation of metal and semiconductor-based nano- and microparticles. A wide spectrum of preparation routes using ionic liquids are presented, including precipitation, sol-gel technique, hydrothermal method, nanocasting, and microwave or ultrasound-mediated methods.

© 2015 Elsevier B.V. All rights reserved.

Contents

1. Introduction	14
2. Structure, composition, and properties of ionic liquids	14
3. Ionic interactions and nanostructural organization in ionic liquids	16
4. The role of ionic liquids in nano- and microstructures preparation	17
4.1. Ionic liquid protective layer formation	20
4.1.1. Electrostatic stabilization by anion	20
4.1.2. Parallel coordination by the cation	20
4.1.3. Ionic liquid ion pair stabilization	20
4.1.4. Steric stabilization	21
4.1.5. Stabilization by solvation forces	21
4.2. Viscous stabilization	21
4.3. Stabilization by intermediates or by-products	22
4.4. The role of the impurities	22
4.5. Stabilization by ligands—functionalization of the ionic liquid	23
4.6. Ionic liquids as source of F ⁻ anions generated <i>in situ</i>	23
4.7. Ionic liquid micellar systems	24
4.8. Ionic liquid as reducing agents	24
4.9. Ionic liquid as “all in one” media	24

* Corresponding author. Tel.: +48 58 347 13 65.

E-mail address: justyna.luczak@pg.gda.pl (J. Łuczak).

4.10. Microemulsion systems based on the ionic liquids	25
5. Conclusions and outlook	25
Acknowledgments	26
References	26

1. Introduction

The great interest in the synthesis, physicochemical properties, and applications of ionic liquids (ILs) is based on their unique and highly customizable properties. Ionic liquids are a group of salts composed only of ions and have a melting point below 100 °C [1]. The low vapor pressure and high polarity of these compounds have attracted a lot of attention, being utilized in a variety of applications. Considering a great practical relevance of ILs, there is already rich literature on different aspects of ionic liquids. The negligible vapor pressure and thermal stability make ILs valuable solvents in the separation processes such as CO₂ capture [2], ionic liquid-based membranes [3], chromatographic and electrophoretic separation [4,5], liquid-liquid extraction [6], and liquid-solid state extraction [7] techniques. Suitable cation–anion coupling accompanied by high electrochemical stability, non-flammability, and ionic conductivity provides materials for energy applications by means of electrolytes for variety of batteries [8], membranes in fuel cells [9], or biomass dissolution and hydrolysis for biofuel production [10,11]. A few recent reviews were also focused on the use of IL in organic and inorganic synthesis [12], catalysis [13], and biocatalysis [14]. Several earlier reviews deal also with the ability of ILs to adsorb onto a metal surface and produce a protective film thereby working as lubricants [15] or surface active agents [16]. The applications of ionic liquids confined in nano-pores, including experimental studies dealing with changes in the physicochemical properties of ionic liquids, such as thermal phase transition, stability, dynamical behavior, optical properties, etc., as well as recent theoretical studies highlighting the layering and structural heterogeneity of ionic liquids confined in nano-pores were discussed in detail in a review paper by Singh et al. [17]. Ionic liquids were also proposed as a novel alternative absorbent combined with refrigerant such as water, ammonia, alcohols, and hydrofluorocarbons and used as working pairs for an absorption refrigeration cycle, heat pump, and absorption power cycle. Imidazolium IL working pairs were described regarding the status of evaluation and selection methods, thermophysical property measurement, and modeling, as well as their future prospect assessments by Zheng et al. [18]. Several reviews also deal with selected properties of ILs, including transport properties [19], wetting behavior [20], particles self-assembly at IL-based interfaces [21], and toxicity and environmental fate [22].

According to their structure and structure-dependent properties, ionic liquids seem to be a useful and promising group of compounds in synthesis of metal and semiconductor nano- and microparticles. However, the following questions are still arising: What properties of ILs are crucial in the particle preparation? What are structural descriptors of ILs influencing size and shape of the particles? What role can ILs play in the nano- and microparticle preparation? What is possible mode of action of ILs in the reaction mixture? How do IL mediate the chemical reactions involving ILs?

These aspects are crucial to select ILs and method of IL-assisted preparation method and understand ILs effect. In this regard in this review, we will summarize, describe, and schematically present the numerous ways that ionic liquids could interact with growing nano- and microparticles during their preparation routes and how these interactions affect the size and shape of finally formed solid particles. The possible roles of ILs in solid particle preparation are analyzed and discussed based on their structure and selected properties. Thus, in the next sections of this review, the structure and selected properties of ionic liquids are summarized taking into account solvents most often used in experimental and modeling studies, followed by a discussion of the types of

interaction between ILs and growing particles and the synthesis of the multiple role that ionic liquids can play during preparation route.

2. Structure, composition, and properties of ionic liquids

According to the literature data, ionic liquids are divided into two main groups: aprotic and protic ILs [1]. The aprotic ionic liquids, more popularly used and also known as “conventional” or “classical” ILs, are usually built of large, organic cations and smaller anions. Organic cations contain a positively charged nitrogen, phosphorus, or sulfur atom, e.g., derivatives of imidazolium, ammonium, pyridinium, sulfonium, phosphonium, and others, as shown in Table 1. Anions that form ionic liquids may be either inorganic or organic ions having a diffuse or protected negative charge. Commonly used inorganic anions are halides [Cl], [Br], hexafluorophosphate [PF₆], tetrafluoroborate [BF₄], and bis(trifluoromethanesulfonyl)imide [Tf₂N], and typical organic anions are alkylsulfate [ASO₄], alkylsulfonate [ASO₃], p-toluenesulfonate [Tos], trifluoroacetate [CF₃COO], etc. [23]. Protic ionic liquids are generally prepared through proton transfer from a Brønsted acid to a Brønsted base [1]. Selected cations and anions—ionic liquid components, together with their structures and abbreviations, are presented in Table 1.

There is also an interest in task-specific ionic liquids, the compounds in which both cation and anion may be functionalized (e.g., fluorinated, chiral, and metal containing) being often designed for given applications [24]. It is worth mentioning, that various abbreviations for ionic liquid cations are commonly used in literature. For example, a 1-butyl-3-methylimidazolium cation can be abbreviated as follows [BMIM], [bmim], [C₄MIM], [C₄mim], and [IM14], etc. In this paper, for most of the ionic liquids, we use acronyms of the [BMIM] type—that is, short, easily understood, and gives an indication of what chemical groups are present in the ionic liquid structure. For ammonium, sulfonium, and phosphonium salts, giving butyltrimethylammonium salt as an example, the acronym [N₄₁₁₁] is used.

Ionic liquids have attracted much attention in the nano- and micro-sized material's preparation due to their valuable properties such as negligible vapor pressure, wide liquid range, good dissolving ability, high thermal stability, excellent microwave absorbing ability, electric conductivity, wide electrochemical window, non-flammability, etc. Additionally, the ability to modify the cation structure and anion selection and, as a consequence, to alter their physicochemical properties provides new media for solvation processes.

A variety of ILs were already investigated for nanostructures preparation with respect to the cation type (imidazolium [25,26], ammonium [27,28], pyridinium [29,30], and phosphonium [31,32]), the chain length of the alkyl substituent in the heterocyclic cation (C₂–C₁₈) [33], and the structure of the anion ([Cl], [Br], [BF₄], [PF₆], [Tf₂N]) [34, 35]. It was revealed that their useful properties can be applied in the effective preparation of nanomaterials and microstructures with controlled physical and structural properties, i.e., specific surface area, density of crystalline defects, particle size, and shape.

Physicochemical properties of ILs relevant for nano- and microparticle preparation could be divided into the following groups:

- A. Melting and decomposition temperatures—low melting points are related to the difficulty of crystalline structure formation that results from the large, asymmetrical shape, and flexible ions with delocalized charge that constitute ILs. Unlike common organic fluids, the liquid range of the ILs may be as large as 200–300 °C. The thermal stability of ionic liquids is determined

Download English Version:

<https://daneshyari.com/en/article/590600>

Download Persian Version:

<https://daneshyari.com/article/590600>

[Daneshyari.com](https://daneshyari.com)