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Ionic liquids: Liquid structure☆

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ABSTRACT

The objective of this paper is the elaboration of liquid structure model for ionic liquids (IL) with cation:anion ratio 1:1. Described model consists of ionic and alkyl domains. The ionic domain is neutral. It has octupole structure: 4 cations and 4 anions are distributed in cube vertexes. The alkyl domains are formed by alkyl chains of cations. Elaborated model explains properties of IL: low melting points, hygroscopicity (including hydrophobic IL), and viscosity.

1. Introduction

For nearly two dozens of years ionic liquids (ILs) attract the quickly growing attention due to outstanding properties: negligible vapor pressure, excellent thermal stability, wide interval of hydrophilic–hydrophobic balance, good dissolution properties with many organic and inorganic compounds including polymers or cellulose, and low flammability. Ionic liquids are expected as superior environmentally friendly solvents for chemical synthesis, homogeneous catalysis, biocatalysis, separation technologies, nanomaterial preparations, templates for production of porous solids, hydraulic fluids, and lubricants [1]. In addition, the high ionic conductivity and wide electrochemical windows make ILs excellent candidates for electrolytes avoiding corrosion or leakage. Unique collection of IL properties promises wide range of applications of ILs in electrochemical technologies as solvent-free electrolytes in various devices and processes, such as rechargeable lithium batteries, fuel cells, chemical sensors, electrochemical capacitors, dye-sensitized solar cells, and the electrodeposition [2,3].

In the opinion of many researchers, investigations of ILs would be more fruitful if the principles of structure formation for ILs were known. Some results of the IL structure investigations were published during last decade, but regular investigations of IL liquid structures started since 2005 after development of empirical potentials for molecular dynamics (MD) simulations, which are appropriate to ionic interactions in ILs [4].

Structural heterogeneity of ILs is suspected. It is believed [5] that structural heterogeneity underlies all the aspects of chemical physics of ILs, including solvation, dynamics, and transport; understanding the role of the anion–cation interactions in modulation of side-chain aggregation and control of the nature of nonpolar domains has important applications in industrial separation chemistry including gas separation and carbon dioxide capture, and in IL-based catalytic systems.

X-ray, synchrotron beam and neutron diffractions [6–8] are used for IL liquid structure determination, apart from MD and NMR [9,10]. Interpretation of diffraction patterns for liquid ILs is restricted without MD because the radial distribution functions of ILs have 3–4 wide maxima, which contain information on IL structure, and arbitrary interpretation is practically unavoidable without MD. MD is used in this hot topic both separately and in combination with diffraction: radial distribution function is calculated by MD and the best coincidence of calculated curve with experimental one is used for structure interpretation.

Some ideas about IL liquid structures were developed in the theory of electrolyte solutions. The basis of the contemporary pseudolattice theory of ionic solutions was founded by Lowell W. Bahe [11], who interpreted quantitatively thermodynamic properties of concentrated solutions of electrolytes on the basis of statistical arrangement of ions in the bulk. This arrangement was set by Madelung constant specific for NaCl and CaF_2 crystals if cation:anion ratio in electrolytes were1:1 or 1:2, respectively. It was found that the Bahe's approach is applicable for 1:1 electrolyte solutions up to 4 M concentrations and 1:2 electrolyte solutions up to 3 M concentrations, but not for higher concentrations.

Varela et al. [12] generalized Bahe's approach taking the van der Waals interactions into consideration. The resulting theory is capable of describing the thermodynamic and transport properties of highly concentrated solutions in a satisfactory manner.

At last it was demonstrated [13,14] that the Bahe–Varela formalism is applicable to ILs: the calculated thermodynamic properties coincide with experimental ones quite well.

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Table 1
Positions of maxima in radial distribution functions for imidazolium ILs.

IL	Cat–an, Å	An–an, Å	Cat–cat, Å	Cat–an, an–an, cat–cat, Å	Reference
1	2	3	4	5	6
C_2mim NTf_2	6	9	9	15	[23]
$C_nC_n$im NTf_2 symmetr. $n=2–5$	4.7	7.3–8.1	7.3–8.1	12.1	[24]
$C_nC_n$im NTf_2 asymmetr. $n=2–5$	4.7	7.1–7.4	7.1–7.4	11.4	[24]
CH_3Py NTf_2	5.0		8	15–17	[25]
C_1mim NTf_2	5.0		7.0	13	[26]
C_2mimBF_4	5.5	8.5	8.5	13	[27]

So IL liquid structure with the cation:anion ratio 1:1 should be like NaCl in some extent. The goal of this paper is the development of the qualitative liquid structure model for 1:1 ILs.

2. Model description

Now there are two concept views on IL liquid structures: some researchers [15–19] consider nanoscale structural heterogeneities formed by alkyl chains as real ones, but others [20–22] insist that structural heterogeneities result from incorrect interpretation of experimental data.

IL structure model development depends on a choice of one or other afore-mentioned concepts. That is why the arguments in favor of one or another concept should be found first of all. The attention should be brought to the fact that nonpolar aliphatic hydrocarbons do not solve in ILs, which all are polar without exception; so alkyls (being components of cations and anions of ILs and distributed in IL volume) have to aggregate in accordance with colloidal chemistry rules. The alkyl aggregation should involve organization of ions in some sort of domains due to interconnection of alkyls and ions, and any ionic domain should be preferably neutral, because electrolytes do not dissociate in contact with nonpolar hydrocarbon media. So the choice of domain concept for IL liquid structure looks more productive.

The experimental data are presented in Table 1 for some imidazolium ILs with cation:anion ratio 1:1.

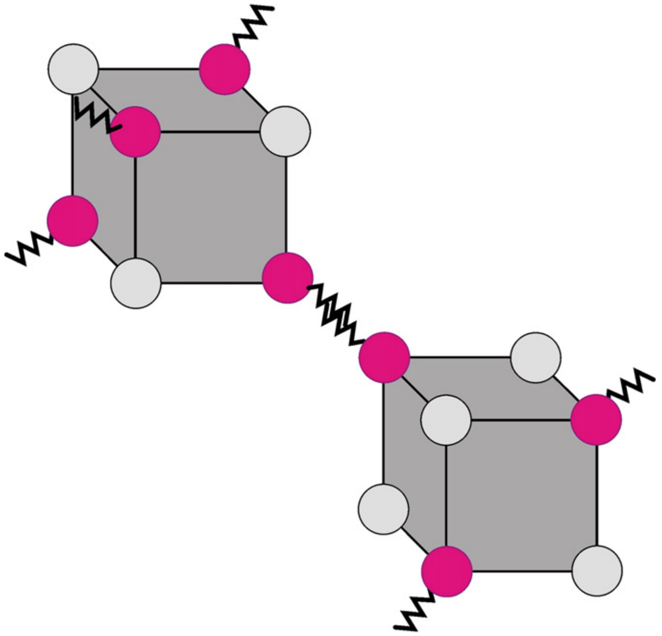

Fig. 1. Octupoles in imidazolium ILs. Cations are red, anions are blank, zigzags are alkyls.

Table 2
Positions of maxima in radial distribution functions for tetraalkylammonium(phosphonium) ILs.

IL	Cat–an, Å	An–an, Å	Cat–cat, Å	Cat–an, an–an, cat–cat, Å	Reference
1	2	3	4	5	6
$(C_6)_3PC_{14}Cl$	4.1	8	7	10.5	[28]
R_3NCH_3 NTf_2, $R=C_4,C_6,C_8$	4.6	8.0		10–15	[29]
C_4C_1Pyr NTf_2	6	10	10	15	[30]
C_3C_1Pyr NTf_2	6	10	10	16	[31]
$(C_1)_3NR$ NTf_2, $R=C_8–C_{16}$	~5	~8	~8	~15	[32]

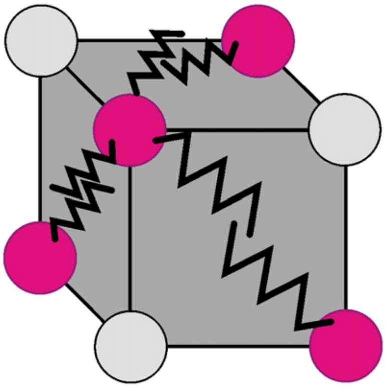

Fig. 2. Octupole in tetraalkylammonium(phosphonium) ILs. Cations are red, anions are blank, zigzags are alkyls.

Anion–anion (column 3) and cation–cation (column 4) distances for one and the same IL are equal and approximately √2 times longer than cation–anion distance (column 2). This fact is a hint on a formation of octupole: cations and anions are distributed in vertexes of cube, cation–anion distances (column 2) are edges of cube and distances in columns 3 and 4 (Table 1) are diagonals of the cube faces. The data in column 5 indicate the distances between nearest

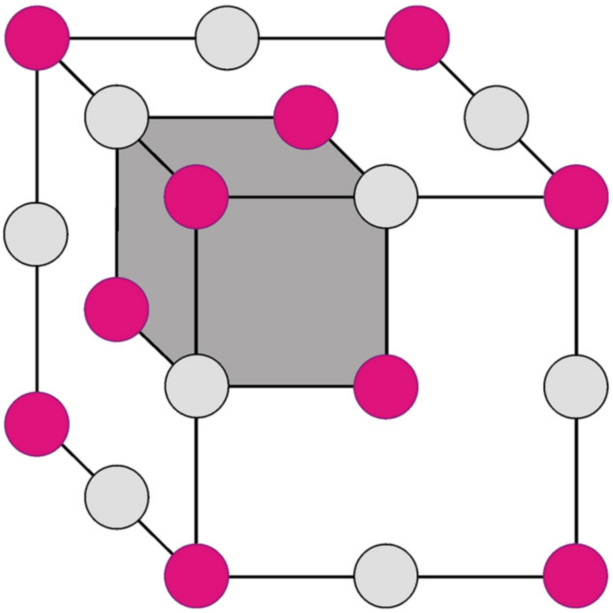

Fig. 3. Partition of NaCl structure type to octupoles. Sodium ions are red, chloride anions are blank.