Ionic liquids with dimethyl phosphate anion–Promising materials in science and technology.

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Ionic liquids (IL) have found different applications in chemistry and other branches of technique during the last quarter of century [1,2]. Combination of various cations and anions provides the possibility to adjust structures of ILs to intended applications in the very best way in contrast to traditional organic solvents (molecular liquids) that should be used without variations of their properties. Ammonium, phosphonium and different heterocyclic cations together with halide, sulfate, sulfonate, dimethyl phosphate (DMP) and other anions present a huge variety of IL. Salts with DMP anion (IL-DMP) form a small but highly promising group in the family of IL [3]. These materials are used in different branches of science and industry, the most popular their application being dissolution of biopolymers (mainly cellulose) from different biological resources (wood, sugarcane, etc.) [4-9]. Less attention is payed to extraction processes of other substances with IL-DMP (for example, polyterpenes from wood bark [10] or dimethyl disulfide from model oil through extractive desulfurization [11]), dissolution of chitin [12] or dissolution of proteins, such as keratin [13] or gelatin [14]. Surprisingly, some enzymes are stable and active in IL-DMP media [15], and they sometimes have even improved activity and stability compared to water solutions [16].

Chemical and thermal stability of IL-DMP are higher than other IL. They may be used at temperatures up to 350°C and can withstand a prolonged treatment with even strong acids or bases. IL-DMP do not cause corrosion of metallic parts of equipment that is essential for their industrial applications. Therefore IL-DMP are successfully used in different branches of science and technology: as lubricants in machineries at high-temperatures [8], as solvents in gas chromatography [17], for modification of membranes (for example, polyethersulfone membranes [18]), as electrolytes for batteries [19], as separation agents [20], and many others.

IL-DMP are successfully also used as solvents in organic synthesis – the production of glycerol carbonate from glycerol [21], the conversion of glucose to 5-(hydroxymethyl)furfural [22], polyamidation reactions of some amino acids [23] and some other transformations of organic compounds.

The main preparation method of IL-DMP is the treatment of tertiary amines or nitrogen heterocycles with trimethyl phosphate – alkylation reaction of tertiary amines with the reagent [3,24]. Only some years ago a new method has appeared – the metathesis (exchange) of chloride ion for DMP anion in the most popular and quite frequently commercially available IL containing chloride anion. In fact, the mentioned synthesis is the alkylation reaction of chloride ion, the evaluated gaseous chloromethane diverting the reaction equilibrium to right [25]. The method noticeably extends the possibility to diversify the nomenclature of IL-DMP.

Different analytical methods are used for characterization of IL-DMP, their selection being determined mainly by the planned utilization. ^{1}H NMR spectroscopy is the main method for the evaluation of their structures nowadays (qualitative analysis). The correspondence of the chemical shifts and the integral intensities of resonance signals in cations and anions of IL-DMP sometimes serve also for quantitative analysis, especially in cases of chloride ion metathesis into DMP anion where integral intensities of the resonance signals of methyl group protons of the anion should fully correspond to those of the cation. LC/MS also is widely used both for qualitative and quantitative analysis of IL-DMP. A specific method for quantitative analysis of IL-DMP has been developed in our laboratory lately [24]. It is a simple titration of IL-DMP with perchloric acid in the medium of glacial acetic acid. Titration curves have pronounced equivalence points, and the method is useful both for laboratory and industrial applications. Other analytical methods (thermogravimetry, determination of viscosity, etc.) are used only when needed for the application of IL-DMP.

The use of IL-DMP as the solvent (reaction medium) is their main application area in our laboratory, mainly for condensation reactions, including syntheses of heterocyclic compounds [24-27]. IL-DMP solubilizes almost every organic and inorganic substance, including most of catalysts. Homogeneous media and high resistance towards acids, bases and elevated temperature allow performing different chemical reactions in IL-DMP. Quite frequently the same IL-DMP serves both as the solvent and the catalyst, especially for different condensation reactions, the DMP anion providing the necessary basicity. Apart from it, IL-DMP can be reused for several times in many condensation reactions and syntheses of heterocycles without any purification if the product is extracted from the reaction mixture by a solvent [25-27]. Such a possibility makes IL-DMP economically promising in technological processes.

Two fields of application of IL-DMP have started in our laboratory recently – the treatment of clays with IL-DMP for the preparation of specific sorbents and the modification of membranes with IL-DMP for electric batteries. Both routes are developing successfully at present.

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