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Effect of Structure of Ionic Liquids on Their Dissolving Power Toward Natural Polymers

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Abstract—Experimental and calculated data on the effect of anion and cation structure on the dissolving power of ionic liquids based on imidazole toward the natural polymers cellulose, fibroin and keratin are presented.

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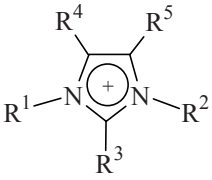
In the recent years attention grew toward ionic liquids application in various areas of science and technology, owing to specific properties of these solutions of organic salts. Ionic liquid are used in organic synthesis and biocatalysis and as solvents for the natural polymers including polysaccharides and polypeptides [1–5]. With the ionic liquids commonly based on imidazole can be prepared solutions of cellulose, fibrin and keratin with high enough concentration that is prospective for creation on this basis of recycling technology for processing the side products of natural polymers to convert them into fibers and films. Nowadays, industry produces ionic liquids based on imidazol with various anions (Cl^-, Br^-, I^-, SCN^-, CH_3COO^-, BF_4^-, PF_6^- and others) and with the cations of general formula:



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According to [1], for the dissolving cellulose can be used ionic liquids with the cations **A** where R^1 and R^2 are alkyl groups with the chain C_1–C_6, R^3 = H or CH_3, $R^4 = R^5$ = H.

A survey of the published data on the solubility of natural polymers in various ionic liquids shows that dissolving power of an ionic liquid depends on the structure of the solvent anion and cation. However, this topic remains poorly studied. There is no information concerning targeted attempts to explain the difference in dissolving power from the viewpoint of features of chemical and electronic structure of the molecules of ionic solvents. Therefore this investigation is aimed at the study of the effect of the ionic solvent molecular structure on its dissolving power toward natural polymers. Such problem can be solved by coupling experimental and theoretical methods of investigation. Quantum-chemical calculation allows considering the interconnection between experimental observations and calculated molecular parameters.

For the study of solubility we used samples of natural polymers: wood cellulose sulfate with polymerization number 495, content of α-cellulose 95.8 %; silk fibroin *Bombyx mori* washed up from contaminants; common serum albumin (molecular mass *MM* = 40000), dextarn (*MM* = 65000), crab chitosan (*MM* = 35000), cellulose acetobutyrate (*MM* = 30000), and potato starch (*MM* = 40000). We also used synthetic polymers such as polyvinyl alcohol (*MM* = 30000), polyvinylpyrrolidone (*MM* = 35000), plymethylmethacrylate (*MM* = 40000), poly-*L*-lactic acid (*MM* = 45000), poly-3-hydroxybutyric acid (*MM* = 35000), polyethylene (*MM* = 60000), polypropylene (*MM* = 100000), polyamide-6 (*MM* = 30000), polyamide-12 (*MM* = 30000), polyethyleneterephthalate (*MM* = 30000), and polycaprolactam (*MM* = 25000).

The solubility was studied with the ionic liquids 1-ethyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium chloride, 1-hexyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium acetate, all chemicals of "chemically pure" grade from BASF. The

experiments on solubility were carried out under controlled temperature at stirring, each next weighted portion of polymer was added after dissolution of the preceding one. The solubility was monitored with a microscope in polarized beam, at zoom up to ×250.

The quantum-chemical calculations were carried out by restricted Hartree–Fock method with 6-31G* basis. Interaction of solvent with cellulose was modeled with cellobiose as a model.

Effect of the anion nature on the dissolving power of ionic liquid. At one and same cation, the dissolving power of ionic liquid varies considerably depending on the anion, as can be seen from the data in Table 1. For example, 1-butyl-3-methylimidazolium chloride dissolves twice amount of cellulose compared to the bromide or thiocyanate. Silk fibroin is well soluble in 1-butyl-3-methylimidazolium chloride, but replacement of chloride anion by Br^-, I^-, or BF_4^- the solubility power of the ionic liquid falls or completely disappears. Comparison of the data in Table 1 on the solubility of wool keratin also leads to conclusion that the solvent containing chloride anion has higher solubility power than respective bromide, and with the anions BF_4^- or PF_6^- this ionic liquid does not dissolves keratin. Eventually, 1-butyl-3-methylimidazolium chloride shows the higher dissolving power compared to the ionic liquids with the same cation but with other anions listed in Table 1.

The experiments show that in the series of ionic liquids those containing acetate anion play a specific role. We carried out a comparative study of dissolving power of 1-butyl-3-methylimidazolium chloride and acetate toward a series of natural and synthetic polymers. Table 2 lists values of maximal concentration of solutions of the studied polymers achieved at the temperature of dissolving 85°C.

Table 1. Maximal concentration of polymers in ionic liquids at 100°C

Anion	Polymer		
	cellulose	Fibroin	Keratin (at 130°C)
Cl^-	10	13.2 [3]	11 [5]
Br^-	4	0.7 [3]	2 [5]
SCN^-	3.5		
I^-		0.2 [3]	
BF_4^-	0	0	0
PF_6^-	0	0	0

It can be seen that the studied ionic liquids are more appropriate for dissolving natural polymers rather than synthetic ones. Among the synthetic polymers a high concentration could be achieved with the hydrophilic polyvinyl alcohol. Acetate substitution for the chloride anion increases dissolving power of the liquid both toward polysaccharides (cellulose, dextran) and polypeptides (fibroin, albumin).

The order of decrease in the solubility power of the liquids based on 1-butyl-3-methylimidazolium as a dependence on the nature of anion is as follows: $CH_3COO^- > Cl^- >> Br^- \cong SCN^-$. The best solvents in this series are acetate and chloride.

To explain the effect of the anion structure on the dissolving power of ionic liquids we attracted the results of quantum-chemical calculations. The methods of quantum chemistry allow revealing the basic parameters of molecules and solvate complexes. Now is accepted that the ionic liquids do not form derivatives with cellulose but transfer the polymer to the solution according to the mechanism of "direct" dissolution. Therefore the energetic characteristics of solvate complex formation can be used for explanation of the difference in the dissolving power of compounds.

In Figs. 1a and 1b are depicted optimized structures of 1-butyl-3-methylimidazolium chloride and acetate.

In the solvent molecules the effective positive charge (a numerical characteristics of electron density

Table 2. Maximal concentration (wt %) of natural polymers in solutions in the ionic liquids with 1-butyl-3-methylimidazolium cation at 90°C

Polymer	Ionic liquid anion	
	Cl^-	CH_3COO^-
Natural polymers[a]		
Cellulose	5	10
Dextran	15	20
Fibroin	10	25
Albumin	10	20
Synthetic polymers[b]		
Polyvinyl alcohol	10	20
Polyvinylpyrrolidone	–	1

[a] Insoluble natural polymers: chitozan, cellulose acetobutyrate, starch. [b] Insoluble synthetic polymers: polymethylmethacrylate, polylactic acid, polyhydroxybutyric acid, polyethylene, polypropylene, polyamide-6, polyamide-12, polyethyleneterephthalate, polycaprolactam, polyethyleneglycol.

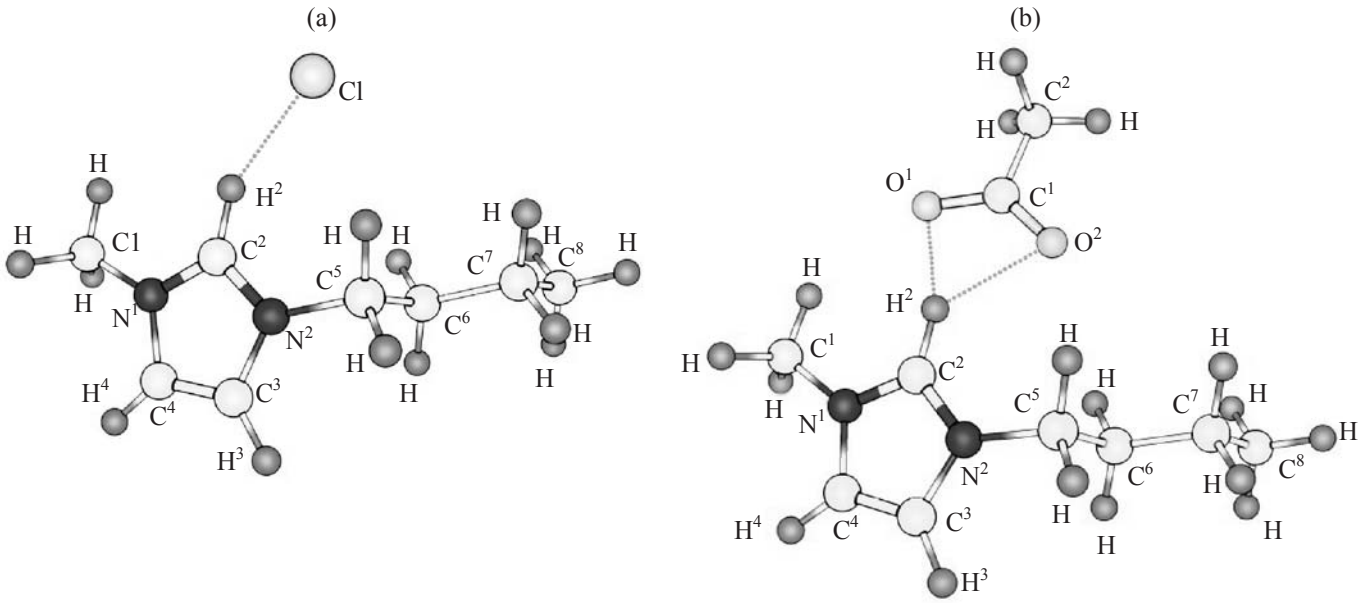

Fig. 1. Optimized structural formulas of 1-butyl-3-methylimidazolium molecules: (a) chloride, (b) acetate.

deficiency) is located mainly on the hydrogen atoms H^2, H^3 and H^4 of the imidazolium ring. The higher positive charge bears atom H^2 of both the molecules regardless the anion, but with the acetate anion the positive charge on the H^2 atom is higher than in the case of chloride anion (Table 3).

The negative effective charge (the value characterizing electron density excess) is located on the anion. In the acetate anion it is concentrated on the oxygen atoms O^1 and O^2, the total negative charge is higher that that on the chloride anion.

In the case of imidazolium cations containing two alkyl radicals, to the most stable system corresponds location of anion near the atom H^2, as seen in Fig. 1. Chloride anion forms with this atom a hydrogen bond, while acetate anion forms simultaneously two hydrogen bonds, the bond lengths (the cation–anion distances) are given in Table 3. The anion–cation interaction energy is 72 kcal mol^{-1} in the case of chloride and 85 kcal mol^{-1} in 1-butyl-3-methylimidazolium acetate.

Thus, by comparison of two solvents differ by anions we succeeded to elucidate that on the electron-donor and electron-acceptor centers of 1-butyl-3-methylimidazolium acetate molecule are localized higher by value charges than in the molecule of 1-butyl-3-methylimidazolium chloride. This results in higher by value energy of the interaction between the cation and anion of the acetate-containing solvent.

Optimization of potential energy of solvate complex formed by celloboise and a molecule of ionic liquid show the interaction scheme as depicted in Fig. 2. More detailed scheme of the optimized structure of the celloboise–1-butyl-3-methylimidazolium chloride was given by us in [9].

Table 3. Principal molecular parameters of 1-butyl-3-methylimidazolium chloride and acetate

Parameter	Atoms	Anion	
		Cl^-	CH_3COO^-
Effective charges at the cation atoms, e	H^2	+0.36	+0.44
	H^3	+0.26	+0.25
	H^4	+0.26	+0.25
Effective charges at the cation atoms, e	Cl	–0.86	
	O^1		–0.79
	O^2		–0.77
Cation–anion distance, Å	$H^2\cdots Cl$	2.148	
	$H^2\cdots O^1$		1.878
	$H^2\cdots O^2$		2.145
Cation–anion interaction energy, kcal mol^{-1}		–72	–85
Ionic liquid–cellulose interaction energy, kcal mol^{-1}		–24	–(28–31)

Table 4. Maximal polymer concentration (wt %) in solutions with R^1,R^2,R^3-alkylimidazolium chloride at different R^1 and R^3 ($R^2 = CH_3$) at 100°C

R_1	R_2	R_3	Polymer		
			fibroin	fructose	saccharose
C_2H_5	–	CH_3	23.3 [3]		
C_4H_9	–	CH_3	13.2 [3]	56 [6]	18 [6]
C_6H_{13}	–	CH_3	4.0		
C_4H_9	CH_3	CH_3	8.3 [3]	40 [6]	14 [6]

The anion of the solvent form hydrogen bonds with the hydroxyl groups protons in the neighboring celloboise centers keeping simultaneously a strong bond with the cation which does not interact directly with cellobiose due to steric hindrances. Calculated energy values of the solvate complex formation are –24 kcal mol^{-1} for the chloride and up to –31 kcal mol^{-1} for 1-butyl-3-methylimidazolium acetate.

Thus, the higher dissolving power of 1-butyl-3-methylimidazolium acetate as compared with the chloride is explainable by the higher value of interaction energy of the former with the polymer active groups which is caused by the higher value of the charge on the anion atoms interacting with the cellulose hydroxy groups.

Effect of the cation structure on the dissolving power of ionic liquid. The structure of the cation shows not less effect on the dissolving power of ionic liquid than the nature of anion. Analyzing the experimental data listed in Table 4 we conclude that the value of maximally achieved concentration of a natural polymer in the solution in a great extent depends on the length and the number of alkyl groups in the imidazolium cation.

Solubility of fibroin in 1-ethyl-3-methylimidazolium chloride at 100°C practically is twice over that in 1-butyl-3-methylimidazolium chloride, and approximately 6-fold higher than in 1-hexyl-3-methylimidazolium chloride (23, 13, and 4 wt %, respectively). It can be concluded that increase in the length of alkyl group in the imidazolium cation ring decreases dissolving power of respective ionic liquid. The same occurs at the attaching third alkyl group to the ring. Solubility of fibroin in 1-butyl-2,3-dimethylimidazolium chloride is approximately one fourth of that in 1-butyl-3-methylimidazolium chloride. This regulaity is seen also at the dissolving fructose or saccharose. Hence, increase in hydrophobicity of ionic liquid due to increase in length or in the number of alkyl groups in the cation leads to decrease in the solubility in them of the hydrophilic natural polymers.

The results of quantum-chemical calculations of the perameters of solvent molecules containing chloride anion and various imidazolium cations are listed in Table 5.

Noteworthy that in the 1-butyl-2,3-dimethylimidazolium cation the group R^3 occupies the position of H^2, therefore the chloride anion is located on the opposite side near the hydrogen atom H^3 (Fig. 3).

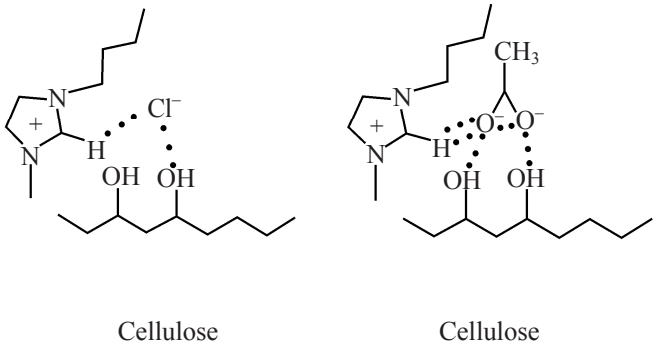

Fig. 2. Scheme of interaction with cellulose of 1-butyl-3-methylimidazolium chloride (left) and acetate (right).

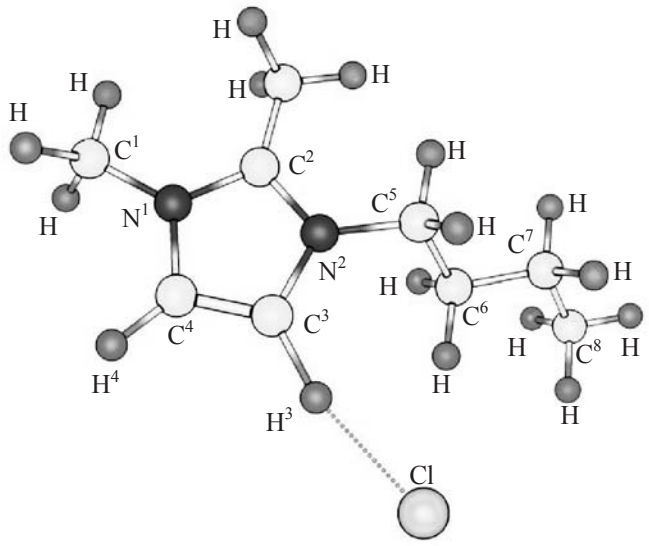

Fig. 3. Optimized structural formula of 1-butyl-2,3-dimethylimidazolium chloride.

Table 5. Bond lengths, atomic charges and energies of cation– anion bonding in the molecules of R^1,R^2,R^3-alkylimidazolium chlorides with various R^1 and R^3 ($R^2 = CH_3$)

Characteristic of ionic liquid molecule	$R^3 = H$					$R^3 = CH_3$
	$R^1 = CH_3$	$R^1 = C_2H_5$	$R^1 = C_3H_7$	$R^1 = C_4H_9$	$R^1 = C_7H_{15}$	CH_3
H-bond length between cation and anion, $Cl\cdots H^2$, Å	2.05	2.128	2.142	2.148	2.149	
H-bond length between cation and anion, $Cl\cdots H^3$, Å						2.340
Bond length $C^2\cdots H^2$, Å	1.095	1.088	1.087	1.087	1.087	
Bond length $C^3\cdots H^3$, Å						1.077
Bond angle $Cl\cdots H^2C^2$, deg	179.7	157	156.3	155.2	155.3	
Atomic charge H^2 in the cation[a], e	+0.2329	+0.2189		+0.2258		
Energy of interaction anion–cation[b], kJ mol^{-1}	–392.95	–378.07	–373.35	–370.14		

[a] Calculation by Monte-Carlo MD method in AMBER force field [7]. [b] Calculation by B3LYP/6-31+G* method [8].

Increase in the length of alkyl group R^1 or attaching third alkyl group R^3 to the imidazolium cation ring leads to decrease in the value of positive effective charge on the hydrogen atom H^2 (H^3) to which the solvent anion is directly attached. Therefore the distance between the anion and cation grows and energy of their interaction falls. It can be assumed that it is this fact causes a decrease in the dissolving power of the ionic liquid, because other parameters, the negative charge of the chloride anion and interaction energy of the solvent with the cellulose fragment remain practically intact at the change of the cation structure.

As seen from the above scheme of interaction of cellulose fragment with solvent, the anion forms hydrogen bonds with the proton-donor centers of the polymer links, while bulky cation in the vicinity hindrances sterically a reconstruction of hydrogen bonds between the polymer chains destroyed due to solvation. Therefore strong interaction between the anion and cation explains indirectly the effect of the latter on the dissolving power of ionic liquid.

Resuming the carried out investigation we can conclude the following. Dissolving power of an ionic liquid based on imidazole is defined by the character of distribution of electron density in the solvent molecules which in turn is defined by structure of the cation and anion. The anion of ionic liquid plays major role forming hydrogen bonds with the protons of the polymer active groups. Energy of anion interaction with the polymer depends on the value of negative charge on its electron-donor centers. Cation hindrances sterically a reconstruction of hydrogen bonds between the polymeric chains. The cation–anion bonding strength in the solvent molecules depends on the effective positive charge on the cation electron-acceptor centers. Increase in the length and number of alkyl groups attached to the imidazolium cation leads to decrease in the energy of interaction between the cation and anion due to decrease in the positive charge on the hydrogen atoms of imidazolium ring.

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