ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 4, pp. 729–735. © Pleiades Publishing, Ltd., 2012.
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# Features of the Molecular Structure of Pyridinium Salts and Their Dissolving Power with Respect to Cellulose

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Received June 2, 2011

**Abstract**—Main geometric parameters and electronic structure of molecules of alkylpyridinium chlorides, bromides, and acetates were calculated by a quantum-chemical method. The influence of the electronic structure of molecules on their dissolving power with respect to cellulose was analyzed.

**DOI:** 10.1134/S1070363212040202

Unique properties of ionic liquids including such as thermal stability and low vapor pressure attract attention of researchers. Among the possible applications of ionic liquids, an important place belongs to processing natural raw materials based on the film-forming polysaccharides and polypeptides, like cellulose, chitosan, fibroin, and keratin [1–7]. As is well known, a large number of intra- and intermolecular hydrogen bonds stabilizes the highly ordered crystalline structure of natural polymers, causing their insolubility in water and most organic solvents. The basic requirements to the solvent systems for cellulose and other natural polymers is the presence of charges and the ability to form hydrogen bonds, and these requirements are satisfied by ionic liquids. A large number of alternative cation–anion pairs opens the way to the development of a scientific approach to the choice of solvent.

Today we know more than 1000 ionic solvents, their number is growing rapidly [8]. But only the ionic liquid with the nitrogen-based cations, mainly ammonium, pyridinium, and imidazolium, are appropriate as the solvents for cellulose. These solvents are the most studied, in particular, common trends in their dissolving power with respect to cellulose and other natural polymers were experimentally identified, and basic physical and chemical properties of the solutions were studied [9–12]. Certain efforts were made with respect to the theoretical understanding of the influence of structure of imidazolium-based ionic liquids on its dissolving power [7]. It was found that the dissolving power of imidazolium-based ionic liquids is determined by the character of electron density distribution in the molecules of these solvents consisting of cations and anions. Calculations, which agree with the experimental data, showed that the anion of the solvent interacts directly with polymer in the course of the solvation [13, 14]. Therefore, the magnitude of the effective negative charge on the electron-donor center of the anion governs the interaction energy with the polymer. The cation remaining connected with the anion creates steric hindrances to the restoration of the links between the polymer macrochains.

It is presumable that the observed pattern can be applied to other ionic liquids dissolving cellulose. The pyridinium-based ionic solvents for cellulose have been poorly studied yet. Despite the appearance already in 1934 of the first reports on the solubility of cellulose in pyridinium salts, today the total number of publications on the use of cellulose solvents based on pyridinium is small. There are data on the solubility of cellulose in some *N*-alkylpyridinium halides (Table 1). Approximately the same solubility of cellulose in *N*-benzylpyridinium and *N*-ethylpyridinium chlorides was noted [15]. In [16] a mixture of pyridinium salts with dimethyl sulfoxide in 1:2 ratio was studied with respect to the solubility of poplar biomass in this solvent, using dimethyl sulfoxide as a diluent to lower the melting temperature of the mixture. In a series of pyridinium, *N*-allylpyridinium, and *N*-butylpyridinium chlorides (that is, with increasing number of carbon atoms in the N-substituent from $C_0$ to $C_3$ and $C_4$) the solubility of the polymer decreases. The introduction of the second substituent in the ring ambiguously

**Table 1.** Solubility of cellulose in the solvent systems based on the *N*-alkylpyridinium cation[a]

| Solvent | Solubility of cellulose |
|---|---|
| [HPy]Cl | Poplar biomass 80 mg $g^{-1b}$, pine biomass 60 mg $g^{-1b}$ at 60°C [16] |
| [EPy]Cl | ~ 5% at 90–100°C [15] |
| [BPy]Cl | Poplar biomass 30 mg $g^{-1b}$ at 60°C [16] |
| [BMPy]Cl | Microcrystalline cellulose (39%), cotton (12%) at 105°C [17] |
| [APy]Cl | Poplar biomass 35 mg $g^{-1b}$ at 60°C [16]; ~ 5%, at 105–110°C [15] |
| [APy]Br | Poplar biomass 5 mg $g^{-1b}$ at 60°C [16] |
| [CmPy]Cl | Poplar biomass 70 mg $g^{-1b}$ at 60°C [16] |
| [BzPy]Cl | ~5%, at 110–115°C [15] |
| [A2MPy]Cl | 3% at 100°C [11] |

[a] Here and hereinafter: Py is pyridine, $[HPy]^+$ is pyridinium cation, $[MPy]^+$ is *N*-methylpyridinium cation, $[EPy]^+$ is *N*-ethylpyridinium cation, $[PPy]^+$ is *N*-propylpyridinium cation, $[BPy]^+$ is *N*-butylpyridinium cation, $[BMPy]^+$ is *N*-butyl-3-methylpyridinium cation, $[PtPy]^+$ is *N*-pentylpyridinium cation, $[HxPy]^+$ is *N*-hexylpyridinium cation, $[APy]^+$ is *N*-allylpyridinium cation, $[A2MPy]^+$ is *N*-allyl-2-methylpyridinium cation, $[BzPy]^+$ is *N*-benzylpyridinium cation.

[b] Dimethyl sulfoxide (1:2) added.

affects the dissolving power. Thus, the introduction of additional methyl substituent in position 2 of the *N*-allylpyridinium chloride ring decreases slightly the solvent power [11, 15], and, on the contrary, the appearance of a new methyl substituent in the 3 position of *N*-butylpyridinium chloride increases the dissolving power [16, 17].

The purpose of this study is to identify the possible relationship of the structure of ionic solvents based on pyridine on their dissolving power towards cellulose. The problem can be solved by comparing the known experimental data on the solubility of cellulose and the results of theoretical calculations reflecting the peculiarities of the geometry and electronic structure of molecules of ionic liquids.

Quantum-chemical calculations were performed using the software package Gaussian 03 (Revision B.01). The data for constructing the potential energy surface of the studied solvents were obtained as a dependence of the complexation energy $E$ of the cation–anion pair on the coordinates of the interacting nuclei, defined by the distance $R$ between the anion and atom $H^1$ of the cation (abscissa) and the torsion angle θ formed by the atoms N, $C^1$, $H^1$ of the ring and the Cl anion (ordinate). A set of no less than seventy different spatial arrangements of the cation and anion with respect to each other was obtained calculated by HF/3-21G* method. The calculation and optimization of the geometry of the alkylpyridinium cations and ion pairs formed by the cation were carried out using the method of HF/6-31G(d).

**Geometry optimization of the ionic liquid molecules**. The surface of the potential energy $E$ for the simplest *N*-methylpyridinium chloride is shown in Fig. 1. The minimum of $E$ value corresponds to the location of the anion near the atom $H^1$ (the most electron-deficient atom) of the ring and $H^6$ of the aliphatic chain (Fig. 2a). At the point of global minimum the torsion angle between atoms N, $C^1$, $H^1$, and Cl becomes 0°, since the ring of pyridine and its derivatives have a rigid and almost planar structure and the anion is located in the same plane. The energy of the complex is 0.1970 ± 0.0005 a.u., $R$ = 2.170 ± 0.005 Å. There are local minima with energy –0.1398 a.u. at $R$ = 5.8685 Å and θ = 23.3836° (Fig. 2b) and –0.13843 at $R$ = 2.7255 Å and θ = 10.8687° (Fig. 2c). The least probable relative positions of anion and cation

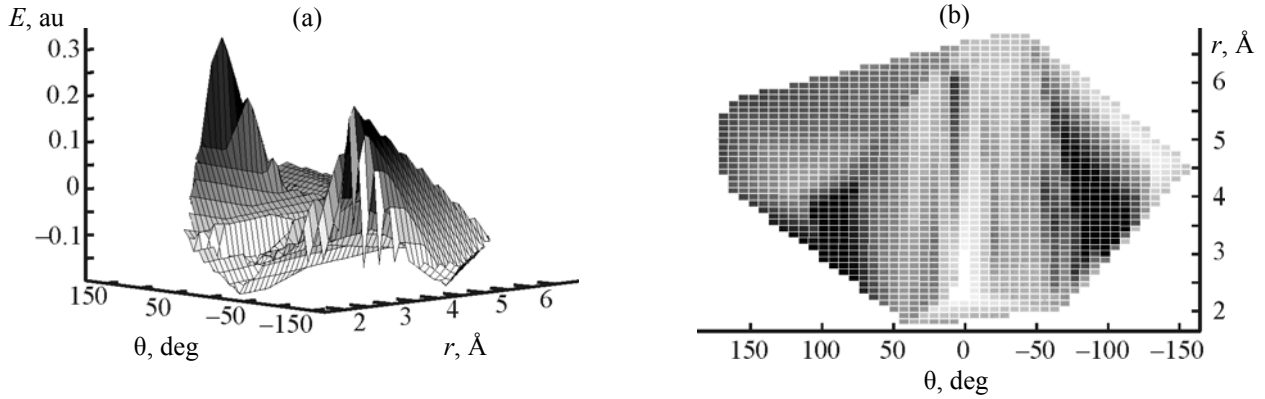


**Fig. 1.** Potential energy surface of (a) *N*-methylpyridinium chloride and (b) its profile. The tint gradient characterizes the levels of potential energy $E$: the light areas correspond to the minimum value of $E$, and dark to maximum.

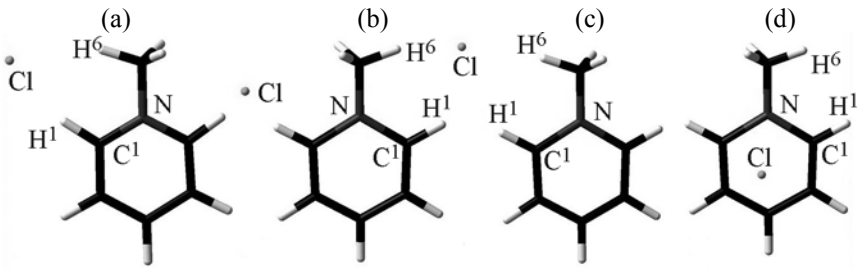


**Fig. 2.** Optimized structures of *N*-methylpyridinium chloride molecules corresponding to the minimum and maximum potential energy (see the text).

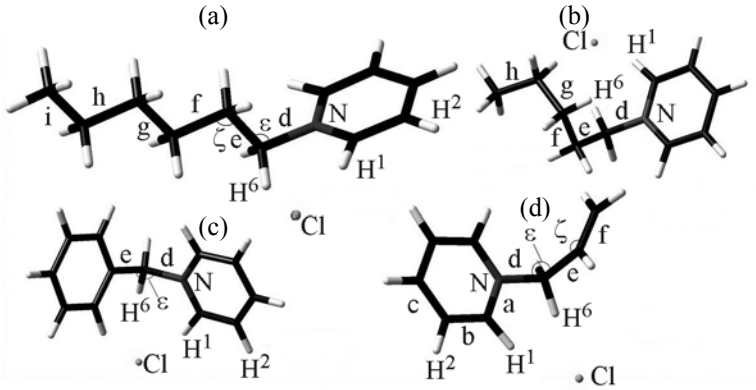


**Fig. 3.** Optimized structure of (a) *N*-hexyl- , (b) *N*-pentyl- , (c) *N*-benzyl- , and (d) *N*-allylpyridinium chlorides.

correspond to the maximum positive value of $E$ = +0.36107 a.u. at $R$ = 3.0808 Å and θ = 90.6065° (Fig. 2d). In this case the anion is located above the plane of the ring. A positive value of $E$ is due to the repulsion of the anion by the π-bonds of the pyridinium ring saturated with electron density.

**The effect of substituents on the geometry, the electron density of molecules and dissolving power of pyridinium-based ionic solvents with respect to the cellulose**. We calculated the molecules of *N*-alkylpyridinium chlorides with alkyl substituents $C_1$–$C_6$, benzyl, and disubstituted pyridine derivatives, some of them are shown in Figs. 3 and 4. According to the results of quantum-chemical calculations (Table 2), the changes in bond lengths and angles of the pyridine ring at the formation of *N*-substituted derivatives are insignificant, which characterizes the pyridinium ring as a highly rigid structure. In [18] it was also noted that the change in the geometry of various pyridine derivatives is only slight. The appreciable difference was observed only in the angles α and β of the *N*-substituted pyridinium derivatives compared with the pyridine itself.

Calculations show that the distance between the anion and the cation head group increases slightly with increasing length of the cationic substituent, but the distance between the anions and cations in the substituent is reduced. So, in a series of $C_1$–$C_6$ the distance between the chloride anion and the nearest $H^1$ atom of the ring increases (2.190 → 2.225 Å). At the extention of the chain of the alkyl substituent and its gradual "twisting" starting from $C_3$ result in stepwise approaching the anion, and the distance between the anion and the nearest atom $H^6$ of the cationic substituent is shortened (2.624 → 2.525 Å). In the $C_0$–$C_4$ series, as in the case of the imidazolium-based

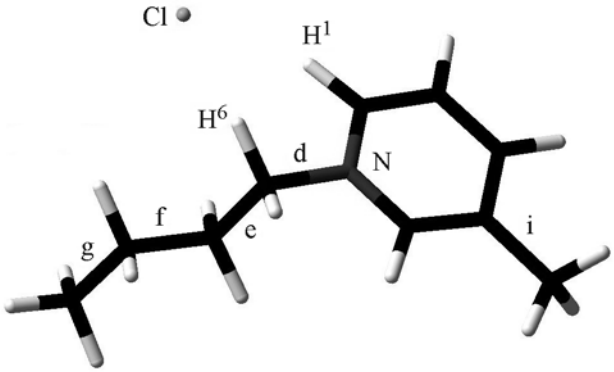


**Fig. 4.** Optimized structure of the molecule of *N*-butyl-3-methylpyridinium chloride.

**Table 2.** Geometric parameters, effective atomic charges, cation–anion interaction energy (*E,* kJ mol$^{-1}$), and dipole moments (μ, D) of the *N*-alkylpyridinium chloride models

| Parameter | Py | | [HPy]Cl | [MPy]Cl | [EPy]Cl | [PPy]Cl | [BPy]Cl | [PtPy]Cl | [HxPy]Cl | [APy]Cl | [BzPy]Cl | [BMPy]Cl | [A2MPy]Cl |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Calculated | Published [18] | | | | | | | | | | | |
| Geometry | | | | | | | | | | | | | |
| *a* | 1.321 | 1.335 | 1.325 | 1.331 | 1.333 | 1.334 | 1.334 | 1.331 | 1.333 | 1.331 | 1.331 | 1.328 | 1.340 |
| *b* | 1.385 | 1.381 | 1.377 | 1.388 | 1.386 | 1.384 | 1.384 | 1.387 | 1.385 | 1.386 | 1.386 | 1.387 | 1.378 |
| *c* | 1.384 | 1.379 | 1.387 | 1.374 | 1.376 | 1.377 | 1.377 | 1.375 | 1.377 | 1.375 | 1.375 | 1.373 | 1.377 |
| α | 117.704 | 117.670 | 122.744 | 121.34 | 121.21 | 121.19 | 121.06 | 121.06 | 121.21 | 121.28 | 121.14 | 121.42 | 121.57 |
| β | 123.607 | 122.990 | 120.268 | 119.96 | 120.08 | 120.17 | 120.20 | 120.21 | 120.11 | 120.07 | 120.19 | 119.60 | 121.09 |
| γ | 118.229 | 118.840 | 118.285 | 119.48 | 119.44 | 119.42 | 119.41 | 119.41 | 119.41 | 119.39 | 119.39 | 119.46 | 118.67 |
| δ | 118.624 | 118.650 | 120.149 | 119.46 | 119.44 | 119.41 | 119.40 | 119.39 | 119.45 | 119.48 | 119.39 | 120.51 | 119.41 |
| *d* | – | – | 1.079 | 1.486 | 1.497 | 1.497 | 1.498 | 1.498 | 1.496 | 1.501 | 1.505 | 1.495 | 1.502 |
| *e* | – | – | – | – | 1.520 | 1.525 | 1.527 | 1.528 | 1.524 | 1.500 | 1.509 | 1.524 | 1.502 |
| *f* | – | – | – | – | – | 1.528 | 1.532 | 1.535 | 1.530 | 1.319 | – | 1.530 | 1.318 |
| *g* | – | – | – | – | – | – | 1.530 | 1.535 | 1.530 | – | – | 1.528 | – |
| *h* | – | – | – | – | – | – | – | 1.529 | 1.530 | – | – | – | – |
| *i* | – | – | – | – | – | – | – | – | 1.528 | – | – | 1.509 | 1.504 |
| ε | – | – | – | – | 111.18 | 112.48 | 112.36 | 112.32 | 111.31 | 110.87 | 111.78 | 111.34 | 111.57 |
| ζ | – | – | – | – | – | 115.20 | 116.68 | 116.10 | 110.76 | 123.45 | – | 110.83 | 123.87 |
| $R_{ClH^1}$ | – | – | – | 2.190 | 2.201 | 2.203 | 2.205 | 2.221 | 2.225 | 2.221 | 2.208 | 2.231 | 2.197 |
| $R_{ClH^6}$ | – | – | 1.821 | 2.464 | 2.575 | 2.624 | 2.623 | 2.525 | 2.592 | 2.537 | 2.564 | 2.589 | 2.571 |
| Charges | | | | | | | | | | | | | |
| Cl | – | – | –0.746 | –0.852 | –0.862 | –0.864 | –0.864 | –0.852 | –0.866 | –0.866 | –0.852 | –0.868 | –0.861 |
| N | –0.515 | – | –0.685 | –0.603 | –0.604 | –0.605 | –0.605 | –0.603 | –0.611 | –0.607 | –0.602 | –0.612 | –0.671 |
| $H^1$ | 0.202 | – | 0.293 | 0.363 | 0.364 | 0.363 | 0.363 | 0.357 | 0.365 | 0.359 | 0.361 | 0.365 | 0.359 |
| $H^6$ | – | – | 0.431 | 0.325 | 0.305 | 0.304 | 0.305 | 0.317 | 0.299 | 0.314 | 0.314 | 0.299 | 0.317 |
| –*E* | – | | 436.96 | 369.92 | 367.43 | 364.03 | 362.16 | 363.13 | 365.21 | 365.15 | 866.47 | 360.42 | 358.23 |
| μ | 2.31 | 2.20 [19] | 13.58 | 12.72 | 17.60 | 18.96 | 14.54 | 15.43 | 14.61 | 16.27 | 12.26 | 15.53 | 20.94 |

ionic liquids [7], there is a tendency of gradual decrease in the interaction energy between the cation and anion; this trend correlates with the experimentally observed decrease in the dissolving power. It can be assumed that this leads to changes in the degree of ordering of the ionic liquid (density fluctuation) manifested as the appearance of polar and nonpolar domains [21], and the hydrophobic interaction between

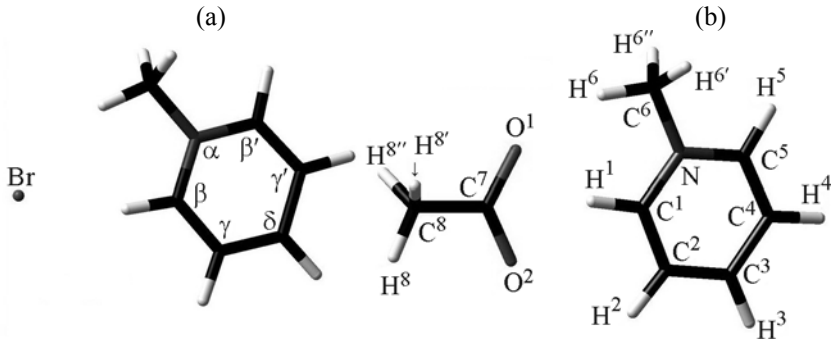


**Fig. 5.** Optimized molecular structure of (a) *N*-methylpyridinium bromide and (b) acetate.

the alkyl substituents increases. Anyway, a monotonous increase in the length of the substituent leads to a decrease in the density of the polar component.

Therefore, we can assume that the parameters of the cation–anion interaction contribute significantly to the overall dissolving power of ionic solvent, although this effect may act ambiguously and it is observed when all other conditions remain unchanged. At a significant change in the geometry of the cation (the introduction of the *N*-substituent of aromatic nature or the appearance of a second substituent), other factors begin to play an important role, primarily the magnitude of the negative charge of the anion and the charge asymmetry of the molecule. For example, adding a second substituent in the *N*-butylpyridinium chloride ring leads to an increase in the negative charge of the anion, which interacts directly with the active groups of the polymer at the solvation, thus the dissolving power of *N*-butyl-3-methylpyridinium chloride increases compared with *N*-butylpyridinium with the same anion (Table 1). It is significant that increased of asymmetric distribution of charge in the molecule and the negative charge on the nitrogen atom of the cation increase. Therefore the short-range repulsion between the cation and anion increases, and it favors the growth in the dissolving power of the ionic liquid solvent, since at the interaction with the polymer the number of unfavorable contacts between the anion and the head group of the cation decreases [21, 22].

In the case of *N*-allylpyridinium chloride, on the contrary, the introduction of a new substituent in the ring leads to a reduction of the negative charge of anion and reduced the dissolving power of *N*-allyl-2-methylpyridinium chloride in comparison with *N*-allylpyridinium chloride.

**Effect of anion on the geometry, electron density of molecules, and the dissolving power of the pyridinium-based ionic solvents**. For the analysis of the effect of changes in the cation and the anion–cation pair we examined the *N*-methylpyridinium chloride, bromide and acetate (Fig. 5). In the optimized structures of these molecules the anions are located near the $H^1$ atom of the ring characterized by a deficiency of electron density (Tables 3, 4). The same effective charge is also characteristic of the $H^5$ atom of the ring, but the charges on the atoms $H^{6'}$ and $H^{6''}$ of the side chain methyl group are smaller than on the atom $H^6$ that lies in the ring plane. Consequently, the more favorable by energy position of investigated anions is observed in the vicinity of the atoms $H^1$ and $H^6$. When optimizing the geometry of the complex the methyl group is turned so that the hydrogen atom $H^6$ is located in the plane of the ring at the side of the anion. The bond lengths of the ring in the *N*-methylpyridinium chloride and bromide are identical. The effective negative charge on the nitrogen atom of *N*-methylpyridinium chloride, bromide and acetate is almost the same. In the acetate anion, the greatest negative charge is concentrated on the $O^1$ and $O^2$ atoms.

Considering the *N*-methylpyridinium complexes with different anions one can see that both the value of the anion negative charge falls in the series of acetate > chloride > bromide (for acetate the total value of the charges on the atoms $O^1$ and $O^2$), and the positive charge on the atoms $H^1$ and $H^6$ of the pyridinium ring interacting with the anion. This is due to a decrease in the transfer of electron density at the interaction. As a result, the energy of interaction between the cation and anion decreases and the distance between the anion and cation increases in this series.

Thus, the charges on the electron donor and electron acceptor centers of molecules based on *N*-methylpyridinium decreases in the order acetate > chloride > bromide, which in practice should lead to a

**Table 3.** Bond lengths (Å); angles (deg), interaction energy $E$ (kJ mol$^{-1}$), and atomic charges in the molecules of *N*-methylpyridinium chloride and bromide

| Parameter | $[MPy]^+$ | [MPy]Cl | [MPy]Br |
|---|---|---|---|
| Geometry | | | |
| $a$ | 1.339 | 1.331 | 1.331 |
| $b$ | 1.372 | 1.387 | 1.387 |
| $c$ | 1.388 | 1.374 | 1.374 |
| α | 120.68 | 121.36 | 121.24 |
| β | 121.13 | 119.95 | 120.02 |
| β' | 121.13 | 121.27 | 121.32 |
| γ | 118.80 | 119.49 | 119.48 |
| γ' | 118.80 | 118.49 | 118.50 |
| δ | 119.46 | 119.46 | 119.43 |
| $R_{XH^1}$ | – | 2.191 | 2.348 |
| $R_{XH^6}$ | – | 2.463 | 2.580 |
| Charges | | | |
| X | – | –0.852 | –0.839 |
| N | –0.655 | –0.603 | –0.604 |
| $C^1$ | 0.163 | 0.185 | 0.174 |
| $C^2$ | –0.271 | –0.301 | –0.301 |
| $C^3$ | –0.087 | –0.097 | –0.097 |
| $C^4$ | –0.271 | –0.284 | –0.283 |
| $C^5$ | 0.163 | 0.156 | 0.165 |
| $C^6$ | –0.332 | –0.353 | –0.356 |
| $H^1$ | 0.311 | 0.363 | 0.367 |
| $H^2$ | 0.293 | 0.275 | 0.275 |
| $H^3$ | 0.296 | 0.248 | 0.258 |
| $H^4$ | 0.293 | 0.257 | 0.255 |
| $H^5$ | 0.311 | 0.255 | 0.266 |
| $H^6$ | 0.236 | 0.325 | 0.316 |
| $H^{6'}$ | 0.235 | 0.206 | 0.207 |
| $H^{6''}$ | 0.244 | 0.206 | 0.206 |
| $E$ | – | –369.92 | –372.34 |

**Table 4.** Bond lengths (Å); angles (deg), interaction energy $E$ (kJ mol$^{-1}$), and atomic charges in the molecule of *N*-methylpyridinium acetate[a]

| Parameter | Value |
|---|---|
| Geometry | |
| $a$ | 1.328 |
| $b$ | 1.389 |
| $c$ | 1.371 |
| α | 121.37 |
| β | 120.36 |
| β' | 120.91 |
| γ | 119.11 |
| γ' | 118.73 |
| δ | 119.52 |
| $R_{O^1H^1}$ | 1.981 |
| $R_{O^2H^1}$ | 2.045 |
| $\angle O^1C^7O^2$ | 125.59 (110.57) |
| $R_{C^7C^8}$ | 1.527 |
| Charges | |
| N | –0.603 |
| $C^1$ | 0.138 |
| $C^2$ | –0.301 |
| $C^3$ | –0.104 |
| $C^4$ | –0.283 |
| $C^5$ | 0.148 |
| $C^6$ | –0.362 |
| $C^7$ | 0.760 (0.723) |
| $C^8$ | –0.554 (–0.554) |
| $H^1$ | 0.442 |
| $H^2$ | 0.298 |
| $H^3$ | 0.252 |
| $H^4$ | 0.248 |
| $H^5$ | 0.258 |
| $H^6$ | 0.342 |
| $H^{6'}$ | 0.200 |
| $H^{6''}$ | 0.200 |
| $H^8$ | 0.155 (0.116) |
| $H^{8'}$ | 0.160 (0.114) |
| $H^{8''}$ | 0.155 (0.116) |
| $O^1$ | –0.789 (–0.758) |
| $O^2$ | –0.759 (–0.758) |
| $CH_3COO^-$ | –0.872 (–1.000) |
| $E$ | –418.46 |

[a] In parentheses the value for isolated acetate anion.

decrease in the energy of interaction with cellulose. Indeed, experimental data show that *N*-allylpyridinium chloride dissolves 7 times more poplar biomass than bromide (Table 1). For the ionic solvent based on imidazolium cation the same theoretical and experimental results were obtained [7]. For the solvents based on pyridinium acetate no experimental data on the dissolving capacity has been found, but it is expectable that the substituted pyridinium acetate may have a better dissolving power than the chloride and bromide.

Thus, the quantum-chemical study resulted in construction of the potential energy surface for the pyridinium-based ionic solvents and identified the most and least probable versions of mutual arrangement of anions and cations in the solvent. Calculations of the geometric parameters and electron density of

pyridinium ionic solvents with different cations and anions led to the following conclusions. With increase in the length of *N*-alkyl chain of the cation a trend occurs of removing chloride anion from the head group of the cation and approaching the cationic substituent that is becoming more "twisted" and screens the anion. The interaction energy of the cation and anion decreases, which correlates with the experimental data of reducing the dissolving power of ionic liquids with respect to cellulose with increasing length of the substituent. The greatest solvent effect show pyridinium salts with asymmetric charge distribution in the molecule and more negatively charged anion, all other conditions being the same. Comparing the solvent anions at the same cation shows that higher values of charges on the electron-donor and acceptor centers of the molecule of ionic liquid are responsible for a greater dissolving power of ionic solvent.

## ACKNOWLEDGMENTS

This study was supported by the Ministry of Education and Science of Russian Federation

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