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Density Functional Theory Study of UO_2^{2+} Solvation in 1-Butyl-3-methylimidazolium Chloride

V. Yu. Buz'ko[a, b], G. Yu. Chuiko[b], and Kh. B. Kushkhov[c]

[a]*Laboratory of Molecular Modeling of Chemical Processes and Compounds,*
Yugtekhinform Regional Interbranch Center, ul. Mira 71, Krasnodar, 350033 Russia
[b]*Kuban State University, ul. Stavropol'skaya 149, Krasnodar, 350040 Russia*
[c]*Berbekov Kabardino-Balkarian State University, ul. Chernyshevskogo 173, Nal'chik, 360004 Russia*
e-mail: BuzkoNMR@mail.ru, hasbikushchov@yahoo.com
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Abstract—Structural characteristics and energies of $[UO_2Cl_4(BMIm)_n]^{(n-2)+}$ ($n = 1-4$) solvation complexes have been studied by the density functional theory (DFT) method in the SVWN5 local functional approximation.

Study of solvation interactions involving actinide ions and chloride-containing organic room-temperature ionic liquids (RTILs) is of interest due to the prospects for the development of new technological liquid processes of separation of a mixture of lanthanide and actinide ions [1−3], as well as for spent nuclear fuel reprocessing [4−8]. Recent practical advances in electrochemical separation of uranium from the other actinides and fission products in spent nuclear fuel reprocessing in chloride-containing RTILs [9−11] imply the necessity of further studies of specific features of the solvation behavior of actinide ions in RTILs of this type.

Solvation of the UO_2^{2+} ion in chloride-containing RTILs has been studied by X-ray crystallographic [12−14], spectrochemical [13, 15−19], and electrochemical [9, 12, 17, 19−21] methods. However, it should be noted that structural features of actinide solvation even in the most common and available RTILs have been relatively little studied.

It has been concluded from UV-visible spectroscopy and EXAFS data that, in solutions of anhydrous uranyl nitrates and perchlorates in the ionic liquid 1-butyl-3-methylimidazolium chloride (BMImCl), the high solvating ability of chloride ions accounts for the preferable formation of the $[UO_2Cl_4]^{2-}$ species with average U−O and U−Cl distances of 1.77 ± 0.01 and 2.69 ± 0.01 Å, respectively [13]. Absorption and luminescence spectroscopy data [17] have also been interpreted as evidence that $[UO_2Cl_4]^{2-}$ complex dominates in BMImCl. The $[UO_2Cl_4]^{2-}$ complex forms C−H···Cl hydrogen bonds with protons of the imidaz-

olium ring of the 1-butyl-3-methylimidazolium [17] and 1-ethyl-3-methylimidazolium [15] cations.

The diffusion coefficient of the UO_2^{2+} ion in BMImCl at 353 K calculated from experimental cyclic voltammetric measurements is 6.9×10^{-8} cm²/s [21]. This is consistent well with the diffusion coefficient of the $[UO_2Cl_4]^{2-}$ ion in the $[BuMeIm][Tf_2N]$ ionic liquid calculated at 298 K [22]; the bis(trifluoromethylsulfonyl)imide anion Tf_2N^- is believed to be weakly coordinated to the uranyl ion [13].

A noticeably lower diffusion coefficient of the UO_2^{2+} ion in BMImCl at 373 K (1.69×10^{-8} cm²/s) has been obtained in [20] from the experimental cyclic voltammetry data; the calculated diffusion activation energy of the U(VI) ion is 54 kJ/mol.

The high diffusion coefficient of the U(VI) ion in BMImCl is, in our opinion, evidence of large energies required for the breaking of several C−H···Cl hydrogen bonds involving the protons of imidazolium cations and substituting alkyl moieties and chloride anions of the primary $[UO_2Cl_4]^{2-}$ complex.

The functional possibilities of available quantumchemical program packages and computational resources allow one to successfully describe the solvation interactions involving actinides in condense media. Therefore, for studying specific features of the UO_2^{2+} ion solvation in 1-butyl-3-methylimidazolium chloride, we have applied the molecular modeling method with the use of the density functional theory (DFT) in the SVWN5 local functional approximation.
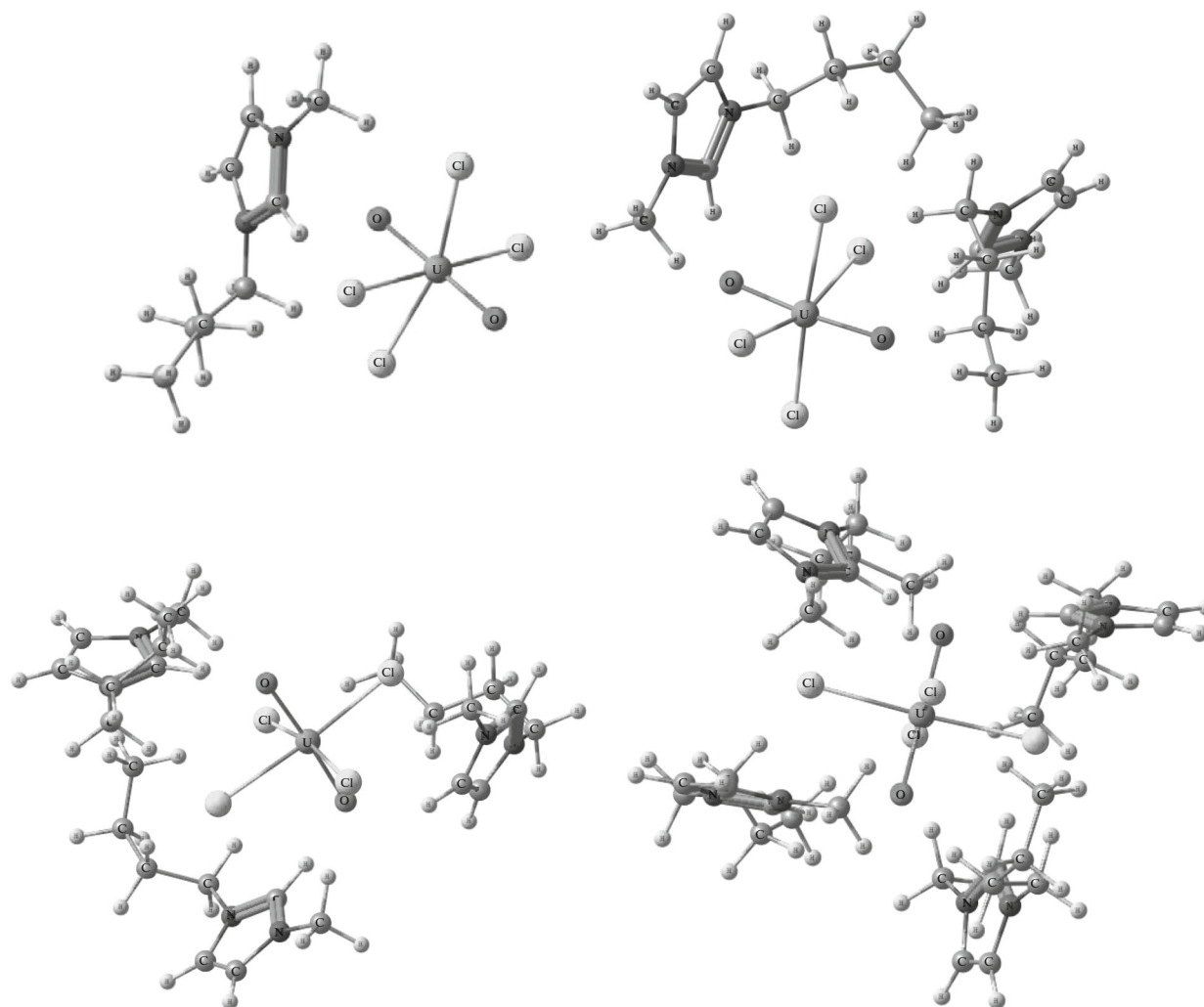
Fig. 1. Optimized structures of the $[UO_2Cl_4(BMIm)_n]^{(n-2)+}$ ($n = 1-4$) solvation complexes.

COMPUTATIONAL DETAILS

Uranyl solvation complexes in BMImCl of general formula $[UO_2Cl_4(BMIm)_n]^{(n-2)+}$ were studied by means of spin-restricted DFT calculations with the local density approximation functional SVWN5. It is worth noting that the DFT method is believed to be one of the most exact methods for calculation of structural, thermodynamic, and electronic characteristics of closed-shell metal complexes [23].

All calculations were performed with the GAUSS-IAN-03 program package [24]. Optimization of the molecular geometry of the $[UO_2Cl_4(BMIm)_n]^{(n-2)+}$ complexes was performed for the gas phase without symmetry or geometry constraints. The fact that the resulting structures corresponded to true minima on the potential energy surface was confirmed by the absence of negative values of Hessian components [25].

The choice of the $[UO_2Cl_4]^{2-}$ complex as the starting solvation structure was caused by experimental data on the structure of the U(VI) ion in dialkylimidazolium chloride ionic liquids [13, 15, 19, 21].

The calculations were performed with the use of the quasi-relativistic effective core potential LANL2DZ [26] and the corresponding double-zeta basis set for uranium and oxygen atoms [27]. The quasi-relativistic pseudopotential LANL2DZ explicitly considers one-electron scalar relativistic effects, including 78 core electrons and the outer electron configuration $6s^26p^65f^36d^17s^2$ with 12 valence electrons described as a double-zeta basis set with the contraction scheme $[10s8p2d4f] \rightarrow [3s3p2d2f]$.

As is known, to adequately calculate the structural characteristic and energies of halide complexes of triply charged actinide ions, in which the ligand molecules are strongly polarized, it is necessary to use at
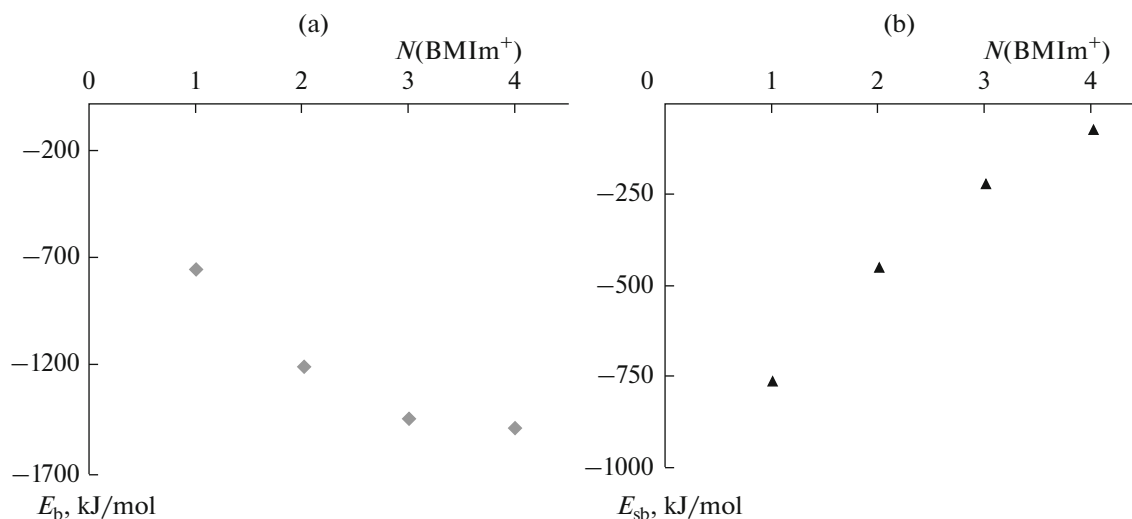
Fig. 2. (a) Binding energy in the $[UO_2Cl_4(BMIm)_n]^{(n-2)+}$ ($n = 1-4$) solvation complexes (b) successive binding energy as a function of the number of 1-butyl-3-methylimidazolium cations in the second coordination sphere.

least a valence double-zeta basis set with polarization functions on ligand atoms [28]. Therefore, we used the extended basis set MIDI! [29], being near in quality to the double-zeta basis set, in which a polarization exponent of 0.65 was used for the d orbital of the chlorine atoms.

The spin−orbit effects were not considered, since it is believed that they are small for the electron systems of heavy metal atoms with closed shells [23] and are somewhat taken into account by using the quasi-relativistic effective core potential [30, 31]. Previously, we demonstrated the applicability of the combination of the LANL2DZ effective core potential with the D95** double-zeta basis set with two polarization exponents for the p and d orbitals of chlorine atoms for the calculation of the structural characteristics of Pu(III) and Pu(IV) chloro complexes [32].

RESULTS AND DISCUSSION

Figure 1 shows the optimized structures of the $[UO_2Cl_4(BMIm)_n]^{(n-2)+}$ ($n = 1-4$) solvation complexes. As is seen, in the presence of four 1-butyl-3-methylimidazolium cations in the outer sphere of the central $[UO_2Cl_4]^{2-}$ complex, all oxygen and chlorine atoms are involved in intermolecular hydrogen bonds with BMIm$^+$ cations. The arrangement of the BMIm$^+$ cations around the metal complex core $[UO_2Cl_4]^{2-}$ is not symmetric.

The binding energy of the $[UO_2Cl_4(BMIm)_n]^{(n-2)+}$ solvation complexes ($n = 1-4$) was determined in the cluster approximation for the corresponding reaction $[UO_2Cl_4]^{2-} + nBMIm^+ \leftrightarrow [UO_2Cl_4(BMIm)_n]^{(n-2)+}$ by the equation

$$E_b = E\left([UO_2Cl_4(BMIm)_n]^{(n-2)+}\right) \\ - E\left([UO_2Cl_4]^{2-}\right) - nE(BMIm^+). \quad (1)$$

To find out the limiting number of the 1-butyl-3-methylimidazolium cations in the outer coordination sphere of the central $[UO_2Cl_4]^{2-}$ complex, the successive binding energy was calculated by the equation

$$E_{sb} = E\left([UO_2Cl_4(BMIm)_n]^{(n-2)+}\right) \\ - E\left([UO_2Cl4(BMIm)_{n-1}]^{(n-3)+}\right). \quad (2)$$

The binding energy of the $[UO_2Cl_4(BMIm)_n]^{(n-2)+}$ ($n = 1-4$) solvation complexes as a function of the number of 1-butyl-3-methylimidazolium cations in the second coordination sphere is shown in Fig. 2a. From the data on the successive binding energy (Fig. 2b), we can conclude that the energy of successive addition of imidazolium cations to the central $[UO_2Cl_4]^{2-}$ complex gradually decreases from −757 to −66 kJ/mol as the number of attached 1-butyl-3-methylimidazolium cations increases from one to four. From this tendency, we can state that in BMImCl the most favorable highest coordination number (CN) of 1-butyl-3-methylimidazolium cations in the second coordination sphere of the primary solvation complex $[UO_2Cl_4]^{2-}$ is 4. It should be noted that, according to molecular dynamic modeling data for an aqueous solution of the UO_2(Tf_2N)_2 (0.01 M) + BMImCl (0.04 mol/L) system [33], the average CN of the 1-butyl-3-methylimidazolium cations in the second coordination sphere of the $[UO_2Cl_4]^{2-}$ solvation complex is 4.3.

For the highest complex $[UO_2Cl_4(BMIm)_4]^{2+}$, the calculated binding energy is −1491 kJ/mol, which is in satisfactory agreement with the solvation energy

Calculated structural characteristics of the $[UO_2Cl_4(BMIm)_n]^{(n-2)+}$ ($n = 1–4$) solvation complexes

	$[UO_2Cl_4(BMIm)_1]^-$	$[UO_2Cl_4(BMIm)_2]^0$	$[UO_2Cl_4(BMIm)_3]^+$	$[UO_2Cl_4(BMIm)_4]^{2+}$
U(VI)−Cl, Å*	2.606 ± 0.025	2.583 ± 0.040	2.585 ± 0.019	2.579 ± 0.021
U(VI)−O, Å	1.836 ± 0.013	1.850 ± 0.003	1.844 ± 0.006	1.848 ± 0.004
U(VI)−N, Å	4.29 ± 0.02	4.73 ± 0.15	4.72 ± 0.21	4.71 ± 0.13
U(VI)−C, Å	4.94 ± 0.59	5.16 ± 0.57	5.04 ± 0.59	4.98 ± 0.51
$N_{\text{H-bonds}}$	5	10	13	18
$N((U)Cl\cdots H(C))$	4	7	10	13
$N(Cl\cdots H(CN_2))$	1	−	−	1
$N((U)O\cdots H(C))$	−	3	3	5
$N((U)O\cdots H(CN_2))$	−	2	2	3
$Cl\cdots H(C)$, Å	2.16 ± 0.10	2.41 ± 0.24	2.43 ± 0.20	2.32 ± 0.05
$Cl\cdots H(CN_2)$, Å	1.96	−	−	2.17
$O\cdots H(C)$, Å	−	2.19	2.28	2.33 ± 0.07
$O\cdots H(CN_2)$, Å		1.69 ± 0.04	1.78 ± 0.02	2.06 ± 0.13
ClHC, deg*	168 ± 6	154 ± 19	146 ± 20	164 ± 8
ClH−CN$_2$, deg	168.1	−	−	149.9
OHC, deg	−	139.3	142.2	143 ± 9
OH−CN$_2$, deg		168 ± 2	168 ± 2	142 ± 13

* The distances and angles are given with the corresponding rms deviations.

−1163 ± 21 kJ/mol of the $[UO_2Cl_4]^{2-}$ complex in the model ionic liquid BMImCl calculated by the classical molecular dynamics method [34]. It should be noted that, according classical molecular dynamics calculations, the solvation energy of the $[UO_2Cl_4]^{2-}$ complex in the 1-ethyl-3-methylimidazolium tetrachloroaluminate ionic liquid is −1222 ± 50 kJ/mol [35]; in the ionic liquid based on the 1-butyl-3-methylimidazolium cation and bis(trifluoromethylsulfonyl)imide anion, poorly coordinated to the uranyl ion, this solvation energy is −1971 ± 20 kcal/mol [13].

The structural characteristics of the $[UO_2Cl_4(BMIm)_n]^{(n-2)+}$ ($n = 1–4$) solvation complexes obtained by DFT/SWVN5 calculations are listed in the table. It follows from the table that, with an increase in the number of 1-butyl-3-methylimidazolium cations attached to the central $[UO_2Cl_4]^{2-}$ complex, the number of intermolecular hydrogen bonds (U)O···H(C) involving the uranyl oxygen atoms and 1-butyl-3-methylimidazolium protons continuously increases, while the number of (U)Cl···H(C) hydrogen bonds increases linearly by three for each successively added BMIm$^+$ cation.

For the highest $[UO_2Cl_4(BMIm)_4]^{2+}$ complex, the averaged U−O distance is 1.848 ± 0.004 Å, the OUO angle in the uranyl cation is 177.1°, and the average U−Cl distance is 2.579 ± 0.021 Å. X-ray crystallographic study [14] has shown that, in the crystalline mixed-ligand 1-ethyl-3-methylimidazolium trichloronitra-touranylate $[C_2MIm]_2[UO_2Cl_3(NO_3)]$, the average U−O distance is 1.779 ± 0.003 Å, the OUO angle in the uranyl cation is 175.2°, and the average U−Cl distance is 2.680 ± 0.009 Å. The above data [14] allow us to suggest that the C−H···Cl hydrogen bond involving an imidazolium proton and a chloride anion of the primary $[UO_2Cl_4]^{2-}$ solvation complex is responsible for the elongation of the U−Cl$_1$ distance by 0.015 Å as compared to the U−Cl$_2$ distance disturbed by the C−H···Cl hydrogen bond between the methyl group of 1-ethyl-3-methylimidazolium and the chloride anion of the $[UO_2Cl_4]^{2-}$ complex.

In the highest solvation complex $[UO_2Cl_4(BMIm)_4]^{2+}$, there are observed 13 C−H···Cl hydrogen bonds involving alkyl protons of 1-butyl-3-methylimidazolium cations and chloride ions of the primary solvation complex $[UO_2Cl_4]^{2-}$. The average C−H···Cl hydrogen bond is 2.32 ± 0.05 Å, and the average CHCl angle is 164° ± 8°. It is worth noting that the vast majority of the terminal methyl protons in the solvation complexes under consideration are involved in C−H···Cl(U) hydrogen bonds.

Let us mention for comparison that, according to X-ray crystallographic analysis of crystalline tetramethylammonium tetrachlorouranylate $[Me_4N]_2[UO_2Cl_4]$, the U−O distance is 1.766 ± 0.004 Å, and the average U−Cl distance is 2.66 ± 0.02 Å [36]. There are observed, on average, eight C−H···Cl hydrogen bonds per $[UO_2Cl_4]^{2-}$ structural unit surrounded by four

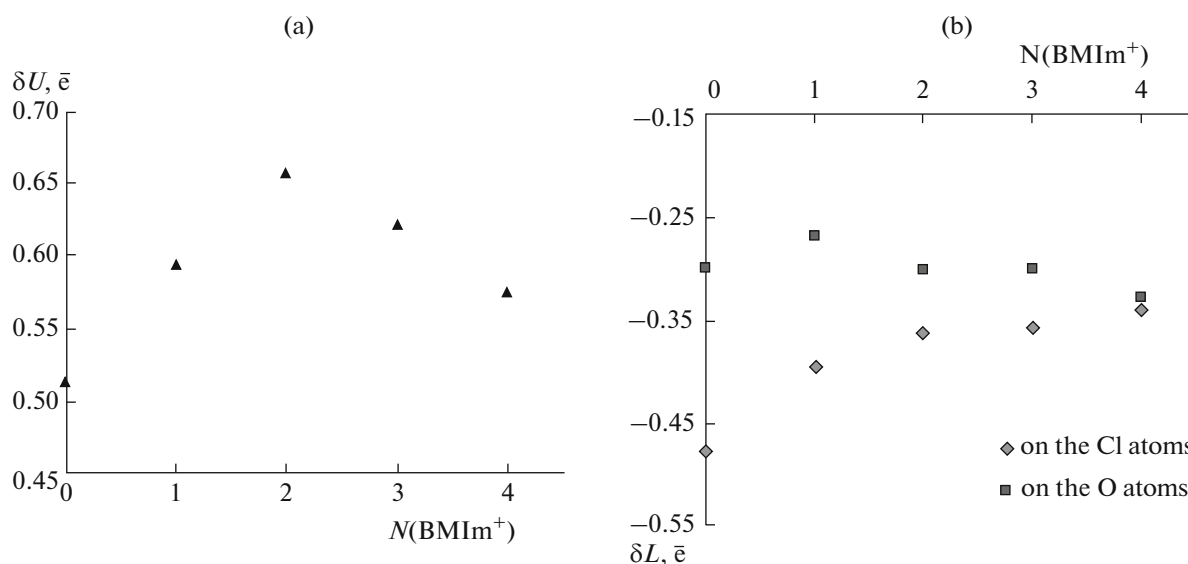**Fig. 3.** Calculated Mulliken charges on the (a) uranium and (b) oxygen and chlorine atoms in the $[UO_2Cl_4(BMIm)_n]^{(n-2)+}$ ($n = 1-4$) solvation complexes.

tetramethylammonium cations between methyl protons of the cation and chloride ions of the primary solvation complex $[UO_2Cl_4]^{2-}$. The averaged (C)H···Cl distance is 2.94 ± 0.04 Å at the average CHCl angle of $133° \pm 3°$ [36].

For the highest solvation complex $[UO_2Cl_4(BMIm)_4]^{2+}$, there are also observed three C−H···O(U) hydrogen bonds involving H-group protons of the 1-butyl-3-methylimidazolium cation and the oxygen atoms of the primary solvation complex $[UO_2Cl_4]^{2-}$. The average H···O distance for the C−H···O hydrogen bond is 2.06 ± 0.13 Å at the average CHO angle of $142° \pm 13°$. In addition, the $[UO_2Cl_4(BMIm)_4]^{2-}$ solvation complex has two C−H···O(U) hydrogen bonds between methylene protons of the butyl substituent of the 1-butyl-3-methylimidazolium cation and the oxygen atoms of the primary solvation complex $[UO_2Cl_4]^{2-}$ with the average H···O distance of 2.33 ± 0.07 Å and the average CHO angle of $143° \pm 9°$. The average length of the (U)O···H(C) intermolecular hydrogen bonds increases linearly with an increase in the total number of the observed intermolecular hydrogen bonds of the (U)O···H(C) and (U)Cl···H(C) types. We can conclude that the successive introduction of 1-butyl-3-methylimidazolium cations into the second coordination sphere of the primary solvation complex $[UO_2Cl_4]^{2-}$ leads to a gradual weakening of the (U)O···H(C) intermolecular hydrogen bonds because of electron−electron and steric interactions between bulky 1-butyl-3-methylimidazolium cations in the resulting $[UO_2Cl_4(BMIm)_n]^{(n-2)+}$ solvation complexes.

It is also worth noting that, in the $[Me_4N]_2[UO_2Cl_4]$ compound, there are observed four hydrogen bonds

between the $[UO_2Cl_4]^{2-}$ structural unit and its four surrounding tetramethylammonium cations, which involve methyl protons of the cations and lone electron pairs of the uranyl oxygen atoms. The average (C)H···O distance is 2.65 ± 0.04 Å, and the average CHO angle is $142° \pm 3°$ [36]. Comparison of these values with our data allows us to conclude that it is precisely the polarized "acidic" proton in the 1-butyl-3-methylimidazolium cation that is responsible for noticeably shorter (C)H···O bonds in the $\{[UO_2Cl_4][BMIm]_4\}^{2+}$ complex as compared with the $\{[UO_2Cl_4][Me_4N]_4\}^{2+}$ complex. This conclusion is consistent with the data in [17] that the involvement of aromatic protons of the 1-butyl-3-methylimidazolium cation in strong (U)Cl···H(C) hydrogen bonds leads to the more stable solvation structure of the uranyl ion in BMImCl as compared with its solvation in tetraalkylammonium chlorides.

The calculated Mulliken charges on the uranium, oxygen, and chlorine atoms in the solvation complexes $[UO_2Cl_4(BMIm)_n]^{(n-2)+}$ ($n = 0-4$) are shown in Fig. 3.

Analysis of the Mulliken charge on the uranium atom indicates that the initial increase in the positive charge on the central ion is due to the redistribution of electron density on the oxygen and chloride anions because of their involvement in hydrogen bonds with C−H groups of 1-butyl-3-methylimidazolium. As the total charge of the $[UO_2Cl_4(BMIm)_n]^{(n-2)+}$ complex becomes positive, the Mulliken charge on the uranium atom starts decreasing, which correlates well with the same decrease in the average length of the Cl···H−C hydrogen bond in the complex. It can be assumed that the high degree of charge transfer from the chloride anions to the hydrogen atoms in numerous Cl···H−C bonds leads to a decrease in the degree of iconicity of

the U−Cl bonds in the central $[UO_2Cl_4]^{2-}$ complex. We have arrived at the conclusion that the coordination of the 1-butyl-3-methylimidazolium cations to the primary metal complex $[UO_2Cl_4]^{2-}$ leads to the appearance of a significant energy contribution owing to the formation of numerous (U)Cl···H−C and (U)O···H−C hydrogen bonds and, simultaneously, decreases the ionicity of the U−Cl bonds and the stabilization energy of the central metal complex $[UO_2Cl_4]^{2-}$.

Analysis of charges on the chloride ions in the first coordination sphere shows that formation of a large number of U−Cl···H(C) hydrogen bonds with a high degree of covalence leads to a decrease in the degree of polarization of the U−Cl bonds. Nevertheless, the formation of U−O···H(C) hydrogen bonds in the highest solvation complexes $[UO_2Cl_4(BMIm)_n]^{(n-2)+}$ leads to a small increase in the negative charge on the uranyl oxygen atoms.

According to our quantum-chemical calculations, it is precisely the formation of numerous (U)Cl···H−C and (U)O···H−C hydrogen bonds upon solvation of uranyl ions in the BMImCl ionic liquid that is responsible for the low experimentally observed [20, 21] diffusion coefficients of the uranyl ion on the order of 10^{-8}− 10^{-7} cm^2/s as compared with molecular solvents [21]. Formation of numerous intermolecular hydrogen bonds in the highest solvation complexes $[UO_2Cl_4(BMIm)_n]^{(n-2)+}$ also accounts for the high U(VI) diffusion activation energy in BMImCl (54 kJ/mol) [20]. This is caused by the high energies required for the rupture of several (U)Cl···H−C and/or (U)O···H−C hydrogen bonds in the highest solvation complex $[UO_2Cl_4(BMIm)_4]^{2+}$ for the diffusion motion of the primary $[UO_2Cl_4]^{2-}$ complex.

Thus, DFT/SVWN5 calculations of the $[UO_2Cl_4(BMIm)_n]^{(n-2)+}$ ($n = 1-4$) solvation complexes allow us to conclude that solvation of the UO_2^{2+} ion in the 1-butyl-3-methylimidazolium chloride ionic liquid is dominated by C−H···Cl hydrogen bonds between imidazolium and alkyl protons and the chloride ions of the primary $[UO_2Cl_4]^{2-}$ complex.

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