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The Relationship of the Energy of Interaction of Alkali Metal Cations with an Aprotic Solvent Molecule with Quantum Topological Electron Density Characteristics

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Abstract—The optimal geometry and wave functions of the complexes $[M(Solv)]^+$ (M = Li, Na, K; Solv is an aprotic solvent molecule) were calculated and the topological characteristics of the electron density distribution at the $(3,-1)$ critical points (CP) of ion−molecule bonds were analyzed by the density functional theory in the B3LYP/6-31+G(d, p) approximation. The parametric dependences for the energy of ion−molecule bonds in terms of the local kinetic and potential electron energy densities at the bond CTs were proposed.

The solvated complexes of metal salts are formed in all industrial processes that utilize metal compounds in aqueous and non-aqueous solutions. In aprotic solvents, the interaction between the solvent and the solute results in more efficient solvation of cations. The molecules of these solvents contain negatively charged oxygen or nitrogen atoms with lone electron pairs, which are able to coordinate and thus stabilize a metal cation. The general formula of the simple solvated complexes is $[M(Solv)_n]^+$, where M is the metal cation, Solv is a solvent molecule, and n is the coordination number [1]. The major contribution to the formation energy of the solvated complexes is made by nonvalence interactions between the metal cation and the negatively charged oxygen or nitrogen atom of the aprotic solvent molecule. The electron density distribution characteristics derived from topological analysis using the quantum atoms-in-molecules theory (QTAIM) can not only be used to describe the nature of chemical bonds, but also underlie the development of approaches to estimation of the bond energy [2]. The energy of non-valence interactions (E_{int}, a.u.) is usually determined by the Espinosa−Molins−Lecomte formula [3, 4]:

$$E_{int} = 0.5\nu(\mathbf{r}), \qquad (1)$$

where $\nu(\mathbf{r})$, a.u. is the potential energy density at the critical point (CP) designated as $(3,-1)$.

This formula proved to be well applicable in the case of "weak" and "medium" hydrogen bonds such as OH···O, CH···O and NH···O. In the case of "strong" H-bonds, the energies are overestimated. A linear type of dependence (1) with a different pro-

portionality factor is also retained for H-bonds in which fluorine acts as the electron density donor [5]. The diversified types of H-bonds cannot be described satisfactorily by a common linear relation [6]. The applicability of relation (1) to estimation of the $M^+···Solv$ energy requires verification and, if necessary, correction of the equations.

The purpose of this study is to analyze the electron density characteristics in the $[M(Solv)]^+$ complexes (M = Li, Na, K; Solv is nitromethane (NM), nitrobenzene (NB), benzonitrile (BN), acetonitrile (AN), 1,4-dioxane (DO), propylene carbonate (PC), acetone (AC), diethyl ether (DE), tetrahydrofuran (THF), tributyl phosphate (TBP), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), triethylamine (TEA), hexamethylphosphoramide (HMPA), ethylene carbonate (EC), and dimethyl carbonate (DMC), differing in the Gutmann donor number (*DN*), and their relationship with the interaction energy between the cation and the solvent molecule.

CALCULATION PROCEDURE

The DFT calculations in the B3LYP/6-31+G(d,p) approximation for the optimal geometry of the solvated complexes were carried out using the GAUSSIAN 09 program package [7]. The stationary point location in the geometry optimization was verified by checking that all of the calculated vibrational frequencies are real. The molecular graphs of the complexes were calculated and the electron density distribution functions ($\rho(\mathbf{r})$) were analyzed in the framework of the QTAIM method [2] using the AIMAll program package [8].
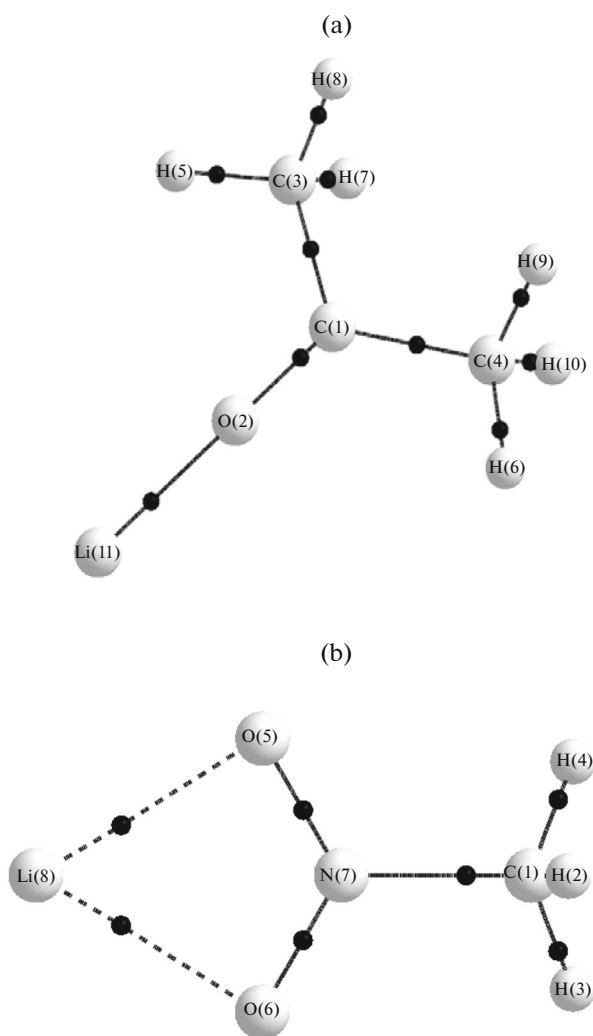
(a)

(b)

Fig. 1. Molecular graph for the complexes (a) $[Li(AC)]^+$ and (b) $[Li(NM)]^+$.

RESULTS AND DISCUSSION

The views of the intermolecular specific interactions have now been formed [2]. A necessary condition for the presence of a bond between any two atoms is the existence of an electron density extremum at the CT with the signature $(3,-1)$. Quantum topological analysis has recognized the bond lines and the critical points of the $M^+\cdots Solv$ bonds for non-covalent interatomic contacts (Fig. 1). At the bond CPs, $\rho(\mathbf{r})$, electron density Laplacian ($\Delta\rho(\mathbf{r})$), and the kinetic ($g(\mathbf{r})$), potential ($v(\mathbf{r})$), and electronic $h_e(\mathbf{r})$ electron energy densities have been determined; these values quantitatively reflect the character of interatomic interactions (Table 1). The values $\Delta\rho(\mathbf{r}) > 0$, $h_e(\mathbf{r}) > 0$, and $|\lambda_1/\lambda_3| < 1$ (λ_i are the eigen values of the Hessian matrix) indicate that the $M^+\cdots Solv$ contact can be considered as a closed-shell interaction. For classification of the types of bonds, an important factor is the ratio of the kinetic energy to the electronic charge $g(\mathbf{r})/\rho(\mathbf{r})$. From the ratio of measurement units of $g(\mathbf{r})$ and $\rho(\mathbf{r})$, it follows that it represents a measure of the local kinetic energy per electron. For covalent bonds, this value is less than $0.3-0.4$, while for bonds between closed-shell atoms, it can increase to unity or more [2]. It can be seen from Table 1 that in the series of solvents differing in the *DN* values in the range of $2.7-39.8$, the $g(\mathbf{r})/\rho(\mathbf{r})$ ratio for the $Li^+\cdots Solv$ bonds varies from 1.3 to 1.85. It is noteworthy that starting from *DN* of approximately 15.1 and higher, the $g(\mathbf{r})/\rho(\mathbf{r})$ ratio varies slightly. This indicates that the local kinetic energy per electron has reached saturation. The $g(\mathbf{r})/\rho(\mathbf{r})$ ratio depends on the polarizing ability of the cation and increases in the series $K^+ < Na^+ < Li^+$ in the $1.43-1.61$ range. The electron density is concentrated in atom basins and is very low in the interatomic space (low $|\lambda_1/\lambda_3|$ ratios far below unity varying in the $0.13-0.17$ range). The $Li^+\cdots Solv$ contact is dynamically highly stable for a number of solvents (BN, AN, TBP, DMF, DMSO, TEA, HMPA, EC, and DMC), as indicated by the ellipticity values ($\varepsilon = \lambda_1/\lambda_2 - 1$) varying in the $0.0-0.05$ range. In this case, the $Li^+\cdots Solv$ bond has a cylindrical symmetry, because at the $(3,-1)$ CT, $\lambda_1 \approx \lambda_2$, and hence the contribution of the π-component of the bond is nearly absent.

The interaction energy (E_{int}) between the cation and the solvent molecule was calculated as the energy difference (ΔE) between the complex and the components. The basis set superposition error (BSSE) does not exceed 1% and virtually does not affect the stabilization energies of the complexes. The E_{int} and $v(\mathbf{r})$, $g(\mathbf{r})$ values calculated for 47 complexes are described by the linear equations

$$E_{int} = -0.0193 + 1.0528v(\mathbf{r})$$
$$\text{(correlation coefficient } R = 0.905\text{),} \tag{2}$$

$$E_{int} = -(0.0209 + 0.7926g(\mathbf{r})) \ (R = 0.908). \tag{3}$$

The parameters in equations (2) and (3) were determined for the case where E_{int}, $v(\mathbf{r})$, and $g(\mathbf{r})$ are expressed in atomic energy units. The considerable difference between the proportionality factors in equations (1) and (2) implies that the Espinosa–Molins–Lecomte formula is inapplicable to estimation of the $M^+\cdots Solv$ interaction energies. In order to take into account the nature of atomic interactions expressed as the balance of the $v(\mathbf{r})$ and $g(\mathbf{r})$ densities and their contribution to E_{int}, a multiple linear regression was constructed, with the regression equation having the form

$$E_{int} = -0.0204 + 0.3797v(\mathbf{r}) - 0.5071g(\mathbf{r})$$
$$(R = 0.9956 \pm 0.0013), \tag{4}$$

with the confidential interval $\alpha = 0.01$ and the mean absolute deviation of 0.0049 a.u.

Table 1. Characteristics of the electron density distribution at the CT (3,−1) of $M^+{\cdots}Solv^*$ bonds

Bond	DN	d, Å	$\rho(\mathbf{r})$, $e\,a_0^{-3}$	$-\nu(\mathbf{r})$, a.u.	$g(\mathbf{r})$, a.u.	$h_e(\mathbf{r})$, a.u.	$\Delta\rho(\mathbf{r})$, $e\,a_0^{-5}$	$-\Delta E$, a.u.	ε
Li···O (NM)	2.7	2.070	0.0209	0.0214	0.0272	0.0058	0.1317	0.0598	0.17
		2.076	0.0211	0.0217	0.0275	0.0058	0.1335		0.17
Na···O (NM)		2.421	0.0168	0.0168	0.0205	0.0037	0.0951	0.0454	0.06
		2.413	0.0171	0.0165	0.0201	0.0036	0.0972		0.05
K···O (NM)		2.855	0.0132	0.0105	0.0120	0.0015	0.0543	0.0329	0.04
		2.855	0.0132	0.0105	0.0121	0.0015	0.0544		0.04
Li···O (NB)	4.4	1.998	0.0257	0.0279	0.0353	0.0075	0.1713	0.0763	0.1
		1.995	0.0259	0.0282	0.0357	0.0076	0.1732		0.09
Na···O (NB)		2.350	0.02	0.0201	0.0249	0.1185	0.1185	0.0575	0.03
		2.350	0.02	0.0201	0.0249	0.1187	0.1187		0.03
K···O(NB)		2.783	0.0155	0.0128	0.0145	0.0017	0.0647	0.0416	0.02
		2.784	0.0155	0.0128	0.0145	0.0017	0.0647		0.02
Li···O (BN)	11.9	1.879	0.0369	0.0424	0.0544	0.012	0.2660	0.0757	0.01
Na···N (BN)		2.236	0.0272	0.0274	0.0364	0.0090	0.1816	0.0569	0.01
K···N (BN)		2.668	0.0204	0.0160	0.0196	0.0036	0.0929	0.0408	0.01
Li···N (AN)	14.1	1.90	0.0346	0.0385	0.0503	0.0117	0.2479	0.0696	0.0
Na···N (AN)		2.256	0.0258	0.0254	0.0340	0.0086	0.1703	0.0524	0.0
K···N (AN)		2.692	0.0193	0.0148	0.0183	0.0035	0.0872	0.0375	0.0
Li···O (DO)	14.8	1.802	0.0412	0.0527	0.0671	0.0144	0.3261	0.0596	0.11
Na···O (DO)		2.182	0.0288	0.0315	0.0403	0.0088	0.1963	0.0406	0.13
K···O (DO)		2,614	0,0216	0,0194	0,0218	0,0024	0,0968	0,0263	0,16
Li···O (PC)	15.1	1.742	0.0424	0.0584	0.0773	0.0189	0.3852	0.0741	0.15
Na···O (PC)		2.109	0.0301	0.0347	0.0472	0.0125	0.2388	0.0609	0.04
K···O (PC)		2.505	0.0235	0.0219	0.0270	0.0051	0.1283	0.0454	0.05
Li···O (EC)	16.4	1.746	0.0418	0.0571	0.0759	0.0188	0.3787	0.0785	0.04
Na···O (EC)		2.114	0.0296	0.0341	0.0464	0.0123	0.2348	0.0590	0.04
K···O (EC)		2.515	0.0231	0.0213	0.0263	0.0050	0.1253	0.0439	0.05
Li···O (AC)	17.0	1.755	0.0412	0.0558	0.0743	0.0185	0.3707	0.0733	0.08
Na···O (AC)		2.124	0.0291	0.0332	0.0451	0.0119	0.2282	0.0536	0.09
K···O (AC)		2.530	0.0225	0.0206	0.0254	0.0047	0.1204	0.0387	0.11
Li···O (DE)	19.2	1.806	0.0411	0.0522	0.0663	0.0141	0.3214	0.0683	0.17
Na···O (DE)		2.178	0.0292	0.0320	0.0408	0.0087	0.1987	0.0478	0.13
K···O (DE)		2.620	0.0213	0.0190	0.0214	0.0024	0.0949	0.0311	0.16
Li···O (THF)	20.0	1.797	0.0420	0.0542	0.0686	0.0145	0.3326	0.0690	0.10
Na···O (THF)		2.171	0.0298	0.0329	0.0420	0.0092	0.2048	0.0488	0.12
K···O (THF)		2.60	0.0225	0.0202	0.0227	0.0025	0.1010	0.0335	0.14
Li···O (TBP)	23.7	1.723	0.0476	0.0679	0.0863	0.0184	0.4187	0.0995	0.01
Na···O (TBP)		2.091	0.0334	0.0394	0.0521	0.0127	0.2593	0.0746	0.01
K···O (TBP)		2.477	0.0268	0.0255	0.0302	0.0047	0.1397	0.0557	0.01
Li···O (DMF)	26.6	1.730	0.0452	0.0638	0.0828	0.0190	0.4073	0.0864	0.03

Table 1. (Contd.)

Bond	DN	d, Å	$\rho(\mathbf{r})$, $e\,a_0^{-3}$	$-\nu(\mathbf{r})$, a.u.	$g(\mathbf{r})$, a.u.	$h_e(\mathbf{r})$, a.u.	$\Delta\rho(\mathbf{r})$, $e\,a_0^{-5}$	$-\Delta E$, a.u.	ε
Na···O (DMF)		2.101	0.0317	0.0371	0.0496	0.0125	0.2487	0.0638	0.03
K···O (DMF)		2.491	0.0250	0.0236	0.0286	0.0049	0.1342	0.0468	0.05
Li···O (DMSO)	29.8	1.722	0.0452	0.0647	0.0833	0.0189	0.4081	0.0909	0.0
Na···O (DMSO)		2.086	0.0319	0.0382	0.0509	0.0127	0.2543	0.0678	0.01
K···O (DMSO)		2.467	0.0256	0.0249	0.0301	0.0052	0.1411	0.0506	0.01
Li···N (TEA)	31.0	1.956	0.0383	0.0415	0.0488	0.0073	0.2242	0.0724	0.0
Na···N (TEA)		2.327	0.0278	0.0264	0.0322	0.0057	0.1516	0.0508	0.0
K···N (TEA)		2.824	0.0190	0.0143	0.0155	0.0012	0.0667	0.0298	0.0
Li···O (HMPA)	39.8	1.705	0.050	0.0735	0.0924	0.0189	0.4449	0.1020	0.0
Na···O(HMPA)		2.078	0.0344	0.0413	0.0544	0.0131	0.2700	0.0757	0.0
K···O (HMPA)		2.458	0.0277	0.0269	0.0319	0.0050	0.1479	0.0556	0.0
Li···O (DMC)		1.742	0.0426	0.0589	0.0776	0.0187	0.3857	0.0684	0.04
Na···O (DMC)		2.118	0.0295	0.0339	0.0459	0.0120	0.2316	0.0482	0.04
K···O (DMC)		2.526	0.0226	0.0209	0.0256	0.0047	0.1211	0.0330	0.05

*a_0 is the Bohr radius; $h_e(\mathbf{r}) = \nu(\mathbf{r}) + g(\mathbf{r})$.

The revealed correlations are important for studying the energy characteristics of the stable configurations of solvated complexes with a mixed solvent containing two or more sorts of solvent molecules in the coordination sphere. Furthermore, they can be used to investigate the mutual effects of the ligands in the complexes at the quantitative level and to elucidate the role of weak intermolecular interactions in the formation of molecular and crystal structures of complexes. The correlations we established are applicable to detailed investigation of energy characteristics of ion–molecule bonds in the electrolyte systems based on solid polymeric electrolytes, which can also be treated as solutions of salts from the physicochemical standpoint, with the polymer functioning as the solvent [9]. Polymers usually contain the same electron-donating groups as common aprotic solvents used in liquid lithium-conducting electrolytes.

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