Proc. Estonian Acad. Sci. Chem., 40, N 2, 118—121
https://doi.org/10.3176/chem.1991.2.06

УДК 539.196.3

Peeter BURK and Mati KARELSON**

SELF-CONSISTENT REACTION FIELD OF AN IONIC ATMOSPHERE

Self-consistent reaction field method was modified in order to take into account the interaction of a solute molecule with ionic atmosphere, formed around it in ionic solution.

1. Introduction

Quantum-chemical calculations refer traditionally to isolated molecules. However, most of the chemically interesting processes occur in condensed media (liquids, solutions). Several methods have been applied too, the problem needs more thorough experimental and theoretical e. g. "supermolecule" approach [1, 2, 3], self-consistent reaction field (SCRF) approach [4, 5, 6], etc. [7, 8].

In the present work the SCRF method was modified by taking into account the interaction of the neutral or charged molecule with the ionic atmosphere created around it in electrolyte solution.

2. Theory

According to the model developed by us, the quantum-chemical Mulliken's partial charges located on the atomic nuclei create around themselves the respective ionic atmosphere. The latter can be represented as the excess space-charge density $\Gamma(r)$ around a point-charge q (Mulliken's partial charge) as follows [9]:

$$\Gamma(r) = -\frac{A\sigma^2\varepsilon}{4\pi} \cdot \frac{e^{-\sigma r}}{r}, \tag{1}$$

where

$$A = \frac{q}{\varepsilon}, \tag{2}$$

$$\sigma = \frac{2\sqrt{\pi}}{I}, \tag{3}$$

ε is the macroscopic dielectric constant of the solvent, r is the distance from the point-charge and I is the average distance between the nearest-neighbour ions at the absolutely uniform distribution of them in the solution (in atomic units). The ionic atmospheres created by all the partial charges in the solute molecule will interact with each other and nuclei and electrons in the molecule according to the electrostatic principle of superposition. Correspondingly, the following sum must be added to the total energy of the molecule in the ionic solution:

* Tartu Ülikooli füüsika-keemia teaduskonna keemia osakond (Department of Chemistry, Tartu University). 202400 Tartu, Jakobi 2, Estonia.

$$E_i = E_{cre} + E_{int} + E_{atm} + dE_{el}, \quad (4)$$

where

$$E_{cre} = \frac{\sigma}{2\varepsilon} \sum_{i=1}^{N} q_i^2, \quad (5)$$

$$E_{int} = \sum_{i<j}^{N}\sum^{N} \frac{q_i z_j [\exp(-R_{ij}\sigma) - 1]}{\varepsilon R_{ij}} - \frac{\sigma}{\varepsilon} \sum_{i=1}^{N} q_i z_i, \quad (6)$$

$$E_{atm} = \sum_{i<j}^{N}\sum^{N} \frac{q_i q_j [1 - \exp(-R_{ij}\sigma)]}{2\varepsilon R_{ij}}. \quad (7)$$

In those formulae E_{cre} denotes the energy of the creation of ionic atmosphere [9], E_{int} is the energy of interaction between ionic atmospheres and atomic nuclei [9] and E_{atm} is the energy of interaction between ionic atmospheres themselves [10]. The fourth term dE_{el}, which corresponds to the change of electronic energy of the solute molecule by the interaction between its electrons and ionic atmospheres is not calculated directly according to the classical model, but added to the electronic Hamiltonian, which can then be represented as

$$\hat{H} = \hat{H}_0 + \sum_{i}^{N} \frac{-A_i \exp[(-R_i\sigma) - 1]}{R_i}, \quad (8)$$

where $\hat{H}_0$ is standard SCRF electronic Hamiltonian for a molecule, dissolved in the polarizable medium [4, 5], and the sum is taken over all the electrons in the molecule.

3. Applications

The MOPAC program package [11] was used in the modified form which accounts for the reaction field effects in dense media [12]. The Hamiltonian matrix elements H_{ij} on atomic basis were modified in accordance to formula (8):

$$H_{ij} = H^0_{ij} + \sum_{l=1}^{N} \int \Phi_i \left| -A \frac{\exp(-R_k\sigma) - 1}{R_k} \right| \Phi_j \, d\tau, \quad (9)$$

where H^0_{ij} is the standard Hamiltonian matrix element and Φ_i and Φ_j denote the atomic orbitals. The integrals were calculated by using Mulliken's approximation [13] (i. e. the distances R_k between the electrons and the centres of ionic atmosphere were replaced by their average values) as follows

$$\int \Phi_i \left| -A \frac{\exp(-R_k\sigma) - 1}{R_k} \right| \Phi_j \, d\tau = -A_k \frac{\exp(-R_k\sigma) - 1}{R_k} S_{ij}, \quad (10)$$

where S_{ij} is the overlap integral between orbitals Φ_i and Φ_j.

The calculations were carried out by using semiempirical AM1 parametrization [14] on neutral methanol molecule (radius of the cavity for SCRF $a_0 = 2.02$ Å), anion of acetic acid ($a_0 = 2.10$ Å), cation of methylammonium ($a_0 = 2.55$ Å) and zwitterionic form of glycine ($a_0 = 2.34$ Å) in water ($\varepsilon = 78$) varying the concentration of 1 : 1 electrolyte in solution from 1 μM to 1 M. In all cases the geometry of molecules was fully optimized. The results of calculations are presented in Tables 1—4.

Table 1

Results of the calculation of methanol

Concentration of ions, M	Heat of formation, kcal/mol	Difference from SCRF energy, kcal/mol
0.000001	—59.627	0.0
0.00001	—59.627	0.0
0.0001	—59.426	0.001
0.001	—59.625	0.002
0.01	—59.623	0.004
0.1	—59.621	0.006
1.0	—59.620	0.007

Table 2

Results of the calculation of the acetic acid anion

Concentration of ions, M	Heat of formation, kcal/mol	Difference from SCRF energy, kcal/mol
0.000001	—205.557	0.005
0.00001	—205.564	0.012
0.0001	—205.577	0.025
0.001	—205.606	0.054
0.01	—205.667	0.115
0.1	—205.798	0.246
1.0	—206.077	0.525

Table 3

Results of the calculation of the ethylammonium cation

Concentration of ions, M	Heat of formation, kcal/mol	Difference from SCRF energy, kcal/mol
0.000001	69.313	0.004
0.00001	69.307	0.010
0.0001	69.295	0.022
0.001	69.270	0.047
0.01	69.218	0.099
0.1	69.118	0.199
1.0	68.941	0.376

Table 4

Results of the calculation of the glycine zwitterion

Concentration of ions, M	Heat of formation, kcal/mol	Difference from SCRF energy, kcal/mol
0.000001	—183.602	0.001
0.00001	—183.608	0.007
0.0001	—183.413	0.012
0.001	—183.627	0.026
0.01	—183.652	0.051
0.1	—183.724	0.103
1.0	—183.799	0.197

It can be seen that in the case of neutral molecule the difference between ordinary SCRF and self-consistent ionic field (SCIF) energies is not significant, but in the case of anion, cation and zwitterion it is considerable at medium and higher concentrations of ions in the solution. However, the dependence of the SCRF energies of anion and cation is substantially different from the very low concentrations of ions in solution (cf. Tables 1 and 2). It is well-known that the individual energies of ions in electrolyte solution can be experimentally determined only on the basis of some extrathermodynamic assumptions [15]. Our approach gives these energies to multiatomic ions without any of these assumptions and allows therefore the study of the specific interactions of these ions with the ionic atmosphere.

The geometries of the ions studied in the present work are insensitive to the change of the ionic atmosphere. However, this may be different for systems characterized by direct polar resonance in their structure. As observed by us earlier [16], ordinary reaction field effects may be large on the geometrical parameters (bond lengths, bond angles and conformational angles) of these molecular species. The results of the corresponding systematic investigation will be published elsewhere.

REFERENCES

1. *Bonaccorsi, R., Ohio, C., Tomasi, J.* The effect of solvent on electronic transitions and other properties of molecular solutes. — Curr. Asp. Quant. Chem., 1981, **21**, 407—413.
2. *Gresh, N., Claverie, P., Pullman, A.* Intermolecular interactions: reproduction of the results of *ab initio* supermolecule computations by an additive procedure. — Int. J. Quant. Chem. Symp., 1979, **13**, 243—259.

3. *Otto, P.* Investigation of the interaction between molecules at medium distances: III. SCF LCAO MO supermolecule, perturbational and MCF calculations for two and three interacting molecules. — Chem. Phys., 1978. **33**, 407—414.
4. *Karelson, M.* Modified semiempirical approach to the quantum chemical calculations of molecules. — Organic Reactivity, 1980, **17**, 357—365.
5. *Tapia, O., Goscinski, O.* Self-consistent reaction field theory of solvent effects. — Mol. Phys., 1975, **29**, 1653—1675.
6. *Constanciel, R., Tapia, O.* On the theory of solvent effects. The virtual charge model to represent the solvent polarization. — Theoret. Chim. Acta, 1978, **48**, 75—83.
7. *Hoshi, H., Sakurai, M., Inone, Y., Chujo, R.* Medium effects on the molecular electronic structure. I. The formation of a theory for the estimation of a molecular electronic structure surrounded by an anisotropic media. — J. Chem. Phys., 1987, **87**, 1107—1115.
8. *Drummond, M. L. J.* A supertensor formalism for solute-continuum solvent interactions with an arbitrarily shaped cavity. I. Theory and implementation. — J. Chem. Phys., 1988, **88**, 5014—5027.
9. *Karelson, M.* Ion distribution in electrolyte solutions. — Organic Reactivity, 1985, **22**, 361—372.
10. *Karelson, M.* The primary salt effect on the dissociation of dicarbocylic acids. — Organic Reactivity, 1985, **23**, 338—352.
11. *Stewart, J. J. P.* MOPAC Program Package. QCPE, 1983.
12. *Tamm, T., Karelson, M.* Quantum-chemical investigation of the reaction field effects on the polar resonance in disubstituted ethylenes. — Organic Reactivity, 1989, **26**, 211—230.
13. *Dewar, M. J. S.* The Molecular Orbital Theory of Organic Chemistry. McGraw-Hill, New York, 1969, 110—114.
14. *Dewar, M. J. S., Zoebisch, E. G., Healy, E. F., Stewart, J. J. P.* AM1: a new general purpose quantum mechanical molecular model. — J. Amer. Chem. Soc., 1985, **107**, 3902—3909.
15. *Robinson, R. A., Stokes, R. H.* Electrolyte Solutions. Butterworths, London, 1969.
16. *Karelson, M. M., Katritzky, A. R., Szafran, M., Zerner, M. C.* A theoretical treatment of solvent effects on the tautomeric equilibria of five-membered rings with two heteroatoms. — J. Chem. Soc. Perkin Trans. 2, 1990, 195—201.

Presented by V. Palm

Received
Jan. 29, 1991

Peeter BURK, Mati KARELSON

IOONSE ATMOSFÄÄRI KOOSKÕLALINE REAKTSIOONIVÄLI

Kooskõlalise reaktsioonivälja meetodit modifitseeriti nii, et see arvestaks ka lahustunud aine molekuli interaktsiooni elektrolüüdi lahuses molekuli ümber moodustuva ioonatmosfääriga.

Пеетер БУРК, Мати КАРЕЛСОН

САМОСОГЛАСОВАННОЕ РЕАКЦИОННОЕ ПОЛЕ ИОННОЙ АТМОСФЕРЫ

Метод самосогласованного реакционного поля модифицирован для учета взаимодействия между молекулой растворенного вещества и ионной атмосферой, которая образуется вокруг него в растворе электролита.