Theoretical Investigations of Metal Ion Complexes with Polymer Ligands Based on Glycidyl Ethers of 3,5,7,3',4'-Pentahydroxyflavone

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Abstract - The paper has been devoted to the quantum-chemical prediction formation of polymer complexes based on glycidyl ethers of quercetin with some metal ions. Based on the calculated quantum chemical calculations with semi-empirical PM3 method, the heats of formation and the geometric parameters of the chelate complexes were predicted.

Keywords – polymer, quercetin, complex, structure, metal

1. Introduction

In recent decades, polymeric materials have been widely used in various applications [1, 2]. This is especially true in the field of environmental protection [3], where polymer materials can be used as luminescent chemical sensors for wastewater analysis in industrial areas. The design and study of such polymers would allow environmental monitoring to be carried out quickly and efficiently. It would be also reasonable to obtain polymers whose fluorescent chain units are of natural origin, less expensive than synthetic luminophores and having low toxicity.

It should be noted that one of the promising materials for the creation of polymer luminescent chemical sensors are network polymers based on glycidyl ethers of 3,5,7,3',4'-pentahydroxyflavone (quercetin) [4]. The quercetin molecule has five hydroxyl groups, which makes it possible to chemically modify quercetin over a wide range. In addition, quercetin is extracted from renewable raw materials, which removes the issue of the raw material base for its production. The most of quercetin derivatives have no own fluorescence, but it is able to form chelate complexes of different structure, which demonstrate an intense light emission. Possible complex formation sites of quercetin (I, II, III) are depicted in Fig.1.
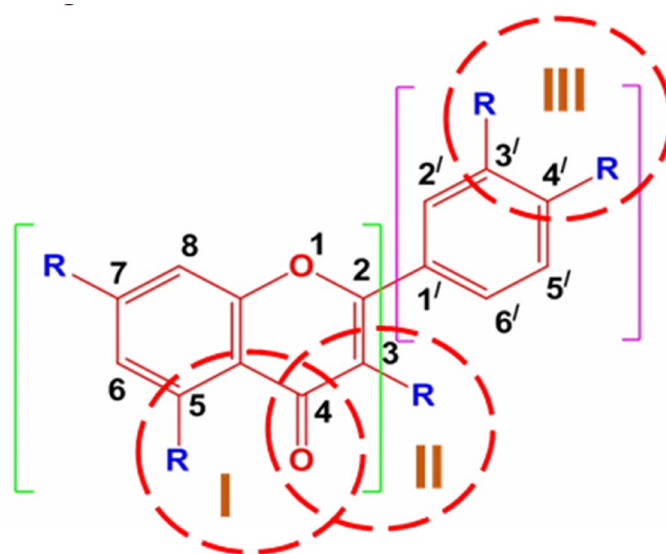

Fig.1. Structure of quercetine moiety. R are OH or glycidyloxy groups. I, II, III – probable chelation centers (for R = OH only)

The purposes of our work were:

- the simulation of quercetin-containing polymeric matrices, obtained based on and 7,4'-diglycidyloxyquercetin (2GEQ), 7,3',4'-triglycidyloxyquercetin (3GEQ), and 3,7,3',4'-tetraglycidyloxyquercetin (4GEQ) cured with diethylenetriamine (DETA);
- the structural analysis of chelate complexes which could be formed with some M^{2+} and M^{3+} cations.

Model epoxy-resin-like polymers – poly(2GEQ), poly(3GEQ) and poly(4GEQ) are of different cross-link density; the quercetin fragments in such polymer matrices have different number of chelating sites, different conformations (first of all, dihedral angles between phenyl and bicyclic chromone fragment) and are in different environment. All these factors affect spectral properties and complexation ability of the polymers under investigations.

2. Computer details

The quantum chemical geometry optimization of the glycidyl ethers of quercetine [5,6], DETA, obtained polymer matrices and their complexes metal ions Be^{2+}, Mg^{2+}, Zn^{2+}, Al^{3+} were carried out using semi-empirical PM3 method implemented into Gaussian 09w program software. The choice of the semi-empirical method is due to low efficiency of DFT calculations for polymer matrices and the presence of the PM3 parameterization for cations mentioned above.

Since fluorescence of polymers was investigated in solvent-free thin polymer films, solvation effects and metal ions coordination with solvent molecules was not studied. To simplify optimization procedure the counter ions effect were neglected. According the experimental data quercetin analogs form complexes of ML stoichiometry, therefore the calculation were done for one-ligand complexes only.

3. Results and Discussion

Previously, it was found that in native 3,5,7,3',4'-pentahydroxyflavone the complex formation is possible for three chelating sites: 5-hydroxy-4-carbonyl (site I), 3-hydroxy-4-carbonyl (site II) and 3',4'-dihydroxy (site III) groups (Fig.1) [7]. The stability of complexes formed with participation of the site I (ML^5) and II (ML^3) is much higher than that obtained with the site III, and the complex formation with the last one is unlikely. In addition, in most glycidyl ethers of quercetin 3' and 4' hydroxyl groups are substituted and hard to reach due to sterical hindrances. The structures of ML^5 and ML^3 complexes are depicted in Fig.2.
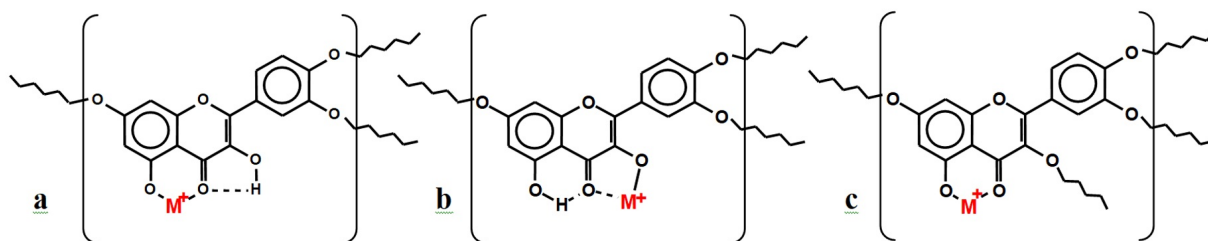

Fig.2. Structures of complexes ML^5 (a) and ML^3 (b) of poly(3GEQ) and ML5 (c) of poly(4GEQ).

All studied polymer matrices contain six quercetin moieties. The enthalpies of complexation reactions (ΔH_R) were calculated from enthalpies of formations of polymer complexes, free polymer matricies (polymer-ligands), metal ions. The obtained values were divided by number of quercetin moieties. Then the molar fractions of ML^5 and ML^3 complexes were compared, too. The obtained enthalpies of formation were compared with values for

complexes of monomers – glycidyl ethers of quercetine. Geometrical parameters of chelates were analyzed.

Molar fractions of ML^5 and ML^3 complexes of monomers and polymers were listed in Table 1 (except 4GEQ and poly(4GEQ), were ML^3 complexes cannot be formed).

The data presented in Table 1 show that, not depending on monomer or polymer matrix, Be^{2+} ion forms complexes of ML^5 type, and Mg^{2+} – complexes of ML^3 type. Zn^{2+} and Al^{3+} ions can form complexes of both types, but on going from monomers to corresponding polymer matrices the fractions of ML^5 complexes increases. It could be explained by rotation of the side phenyl ring of quercetin fragment due to sterical hindrances creating by cross-linked polymer chains. In turn, that leads to deviation of 3-hydroxy group from the molecular plain and its moving away from carbonyl group, that worse conditions for ML^3 chelate formation.

Table 1

Molar fraction of ML^5 and ML^3 complexes

		2GEQ	Poly(2GEQ)	3GEQ	Poly(3GEQ)
Be^{2+}	ML^5	100.0%	100.0%	100.0%	100.0%
	ML^3	0.0%	0.0%	0.0%	0.0%
Mg^{2+}	ML^5	0.0%	0.0%	0.0%	0.0%
	ML^3	100.0%	100.0%	100.0%	100.0%
Zn^{2+}	ML^5	38.0%	88.3%	6.5%	45.8%
	ML^3	62.0%	11.7%	93.5%	54.2%
Al^{3+}	ML^5	0.2%	82.0%	0.4%	50.0%
	ML^3	99.8%	18.0%	99.6%	50.0%

Comparing values of complexation enthalpies, it is possible to conclude that these values increase on going from poly(2GEQ) to poly(3GEQ), i.e. from matrix of low cross-linking density to that of higher cross-linked density. When forming both ML^5 and ML^3 complexes the growth of ΔH_R is similar (Fig.3). On going from poly(3GEQ) to poly(4GEQ) matrix does not result in changing ΔH_R values, consequently further changing density of polymer network does not lead to additional structural changes of built-in quercetin moieties.
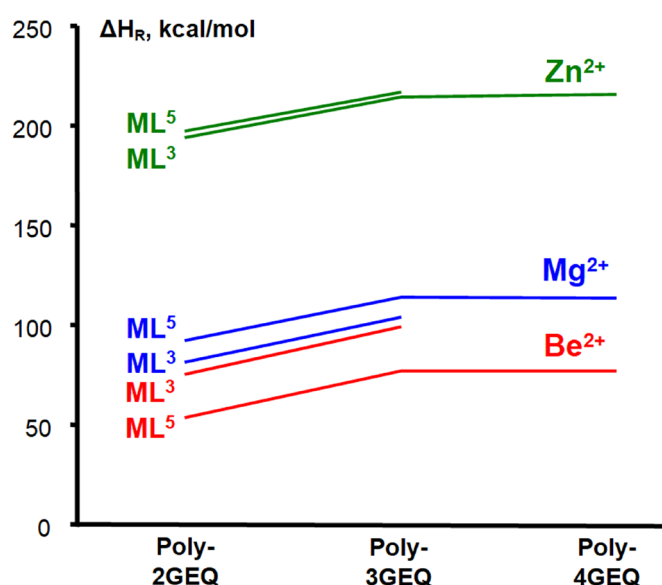

Fig.3. Complexation enthalpies for polymer complexes

Conclusions

The results of quantum chemical simulations of GEQ polymer matrices and their complexation with Be^{2+}, Mg^{2+}, Zn^{2+}, Al^{3+} ions are presented. It is shown that metal ions can form complexes with different chelating sites of the quercetin derivatives. Thus, depending on metal ion parameters, the complexes of ML^5 and ML^3 types can be obtained. Structural changes of quercetin moiety in polymer matrices increase probability of ML^5 complex formation. As cross-link density of polymer matrices increase, complexation enthalpies first increase and then do not change.

Acknowledgments

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