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Complexation of the alkaline earth metals perchlorates with 3-hydroxyflavone in acetonitrile: Precise conductometric treatment

Vira N. Agieienko [a,b,*], Natalya A. Otroshko [b,c], Oleg N. Kalugin [b,**]

[a] Laboratory of Advanced Carbon Nanomaterials, Kazan Federal University, 18 Kremlevskaya st., 420008 Kazan, Russia
[b] Department of Inorganic Chemistry, V. N. Karazin Kharkiv National University, 4 Svoboda sq., 61022 Kharkiv, Ukraine
[c] Department of Chemistry, Microbiology and Hygiene of Nutrition, Kharkiv State University of Food Technology and Trade, 333 Klochkivska st., 61051 Kharkiv, Ukraine

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ABSTRACT

The alternative models of ionic equilibria in acetonitrile solutions of alkaline earth percholorates in the presence of 3-hydroxyflavone (HL) were studied by conductometry at 288.15, 298.15, 308.15, 318.15, and 328.15 K. Using a procedure specially developed for this task it was shown that in the solutions containing $Ca(ClO_4)_2$ and $Sr(ClO_4)_2$ the complexation of the cation (M^{2+}) by the HL molecule leads to the formation of the doubly-charged $[M(HL)]^{2+}$ complex species. In contrast to them, in the presence of $Ba(ClO_4)_2$ HL interacts with the ion pair $BaClO_4^+$ forming the singly-charged $[BaClO_4(HL)]^+$ complex. The limiting equivalent conductivities as well as the constants of complexation were estimated. The latter were calculated by taking into account the ion association between cation and anion of initial salts and activity coefficients, that is the 'true' thermodynamic constants were found. The reliability of the proposed approach was additionally checked by analyzing artificially noised model experimental data. It was shown that the fitted parameters can be satisfactorily reproduced even at the noise level equal to 2%. The limiting equivalent conductivities of the $[Ca(HL)]^{2+}$, $[Sr(HL)]^{2+}$ and $[BaClO_4(HL)]^+$ complex species were interpreted in terms of the Stokes radii whose values indicate very weak solvation of the formed complexes. The variation of the constants of complexation among cations was found to be in agreement with the values of primary association constants.

1. Introduction

Studies on the complexation of bio- and poisonous multicharged metal cations with flavonoids –polyphenol derivatives showing peculiar spectroscopic properties– have received an increased interest in the last few decades [1–12]. These investigations concerned among others the development of the high-performance fluorescent probes for the analytical determination of both cations [6,9] and ligands [8,10,13], improvement of the contrast of magnetic resonance imaging (MRI) using flavonoid-based contrast enhancing agents [11], enhancement of the ligands' antioixidant activity by their complexing with *d*-metals [14–16], and representing the metal-binding sites in proteins [12]. These broad applications are mainly due to the ability of flavonoids to undergo an excited-state intramolecular proton transfer (ESIPT) reaction exceedingly sensitive to various factors [1,17–19], including the presence of cations [1–3]. This definitely demands a careful investigation of the complexation processes occurring in the flavonoid-based solutions containing metal salts among which perchlorates are the ones most frequently used [1,2,4,5] due to their good solubility in many solvents [20].

Evidently, most of the relative studies deal with the spectroscopic investigations of the mentioned systems. Roshal et al. investigated the complex formation in the acetonitrile solutions containing 3-hydroxyflavone (flavonol, HL, see Fig. 1) derivatives together with magnesium and barium perchlorates [1,2]. Basing on the absorbance spectra the authors obtained stability constants and a stoichiometric metal:ligand composition (1:1) of the formed complexes. Substantial changes observed in the absorbance and fluorescence spectra of flavonols in the presence of $Mg(ClO_4)_2$ were attributed to the formation of the so-called 'internal' complexes. The authors suppose that in these complexes Mg^{2+} cation interacts with both 3-hydroxyl and carbonyl oxygens of 3-hydroxyflavone and its 4′-dialkylamino derivatives. Moreover the 3-hydroxyl hydrogen is displaced upon the complexation leading to the formation of a singly-charged complex $[Mg·L]^+$ (here L^- is a deprotonated flavonol). In contrast to the discussed above Mg^{2+} containing systems, low-stability 'external' complexes $[M·HL]^{2+}$ where M^{2+} only interacts with carbonyl oxygen are formed in the solutions of $Ba(ClO_4)_2$ with all studied 3-hydroxyfavone derivatives and in the solutions containing $Mg(ClO_4)_2$ and 3-metoxyflavone. This conclusion was based on the fact that no significant changes in the flavonols'

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[*] Correspondence to: V.N. Agieienko, Laboratory of Advanced Carbon Nanomaterials, Kazan Federal University, 18 Kremlevskaya st., 420008 Kazan, Russia.

[**] Correspondence to: O.N. Kalugin, Department of Inorganic Chemistry, V. N. Karazin Kharkiv National University, 4 Svoboda sq., 61022 Kharkiv, Ukraine.

E-mail addresses: VNAgeenko@kpfu.ru (V.N. Agieienko), onkalugin@gmail.com (O.N. Kalugin).

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