COMPUTATIONAL STUDY ON THE STRUCTURE AND PROPERTIES OF TERNARY COMPLEXES OF Ln^{3+} (Ln = La, Ce, Nd AND Sm) WITH 5,7-DICHLOROQUINOLINE-8-OL AND 4-VINYL PYRIDINE

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In the present research, we have mainly concentrated on the survey of interactions in Ln^{3+} (Ln = La, Ce, Nd and Sm) ternary complexes of 5,7-dichloroquinoline-8-ol (DCQ) and 4-vinyl pyridine (VP), [Ln(VP)$_2$(DCQ)$_3$]$^{3+}$ by means of density functional theory, Hartree-Fock and Sparkle/PM3 semi-empirical computational methods. For VP and DCQ ligands, the cation binding energy sequence follows the order La^{3+} > Ce^{3+} > Nd^{3+} > Sm^{3+} as expected based on increasing in the hardness and decreasing in the ionic radius of this lanthanide cation series. A similar trend was observed in the calculated binding energy of the aforesaid ligands with the hydrated lanthanide cation series [Ln(H$_2$O)$_9$]$^{3+}$, while the computed values of deformation energy of ligands upon complexation demonstrated an opposite order in the lanthanide cation series. Moreover, the solvent effects are considered via a polarized continuum model and provided a significant increase in the binding strength while the relative magnitude of binding energies is the same as that in the gas phase. Combining quantum and statistical mechanical calculations, we have also determined quantitatively a reliable estimate of the conformational distribution of the [Sm(VP)$_2$(DCQ)$_3$]$^{3+}$ complex at various temperatures in the gas phase by computing the molecular partition functions and consequently the analysis of the conformational equilibrium constants.

K e y w o r d s: ion imprinting, lanthanide complexes, density functional theory, polarized continuum model, conformational distribution.

INTRODUCTION

In contrast with a large amount of theoretical studies on alkali and earth alkali cations, transition metals and metalloids, computational reports dealing with actinides and lanthanides are rather scarce. In the present work, we have provided a computational study on Ln^{3+} (Ln = La, Ce, Nd and Sm) ternary complexes of 5,7-dichloroquinoline-8-ol and 4-vinyl pyridine (hereafter denoted by DCQ and VP respectively; Fig. 1) to assess the intrinsic interaction energies and structural features of the complexes. The main motivation of our study on this system was the technological and fundamental importance of the ternary complexes of metal cations with DCQ and VP functional monomers that recently have been synthesized for selective separation of some metal cations on the basis of ionic imprinting process [1—6].

Molecular imprinting is a versatile technique for preparing polymeric SPE (solid phase extraction) adsorbents capable of high molecular recognition. This method involves the arrangement of functional monomers around a template molecule. Subsequent polymerization results in trapping the tem-