Density functional theoretical tailoring of electronic effect through various substituent on Calix[4]arene-crown-6 for efficient Cs+ ion encapsulation and extraction

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Abstract

The structure, energetic and quantum chemical descriptors of Cs+ complexes of calix[4]arene-crown-6 (C4C6) and substituted C4C6 i.e 1,3 alternate-diethoxy C4C6 are reported here based on the analysis of results using density functional theory. Substitution of benzo group to both C4C6 and 1,3 alternate-diethoxy C4C6 resulted in reduction of binding energy (BE). Further substitution on benzo group with methyl, methoxy and amino groups leads to increase in BE and nitro substitution leads to decrease in BE for C4C6, whereas in the case of 1,3 alternate-diethoxy calix[4]arenebenzocrown-6, methoxy substitution leads to highest BE compared to other complexes. The calculated Gibbs free energy, ΔGgas also followed the same order as BE in the case of 1,3 alternate-diethoxy C4C6 and their substituted ligands. Furthermore, the ΔG of complexation were computed using thermodynamic cycle with conductor like screening model (COSMO) in different solvents: toluene, chloroform, octanol and nitrobenzene. The values of ΔGext are found to be increased with increase in the dielectric constant of the solvent and found to be highest in the nitrobenzene. The Atoms in Molecule (AIM) analysis reveals partial ionic character in Cs-O bond. Among all the studied complexes, 1,3 alternate-diethoxy calix[4]arene 3'-methoxy benzo crown-6 displays highest ΔGext in nitrobenzene. The calculated value of [?][?]Gext ([?][?]G= [?]GCs+-[?]GNa+) is found to be -41.82 kcal/mol with 1,3 alternate-diethoxy calix[4]arene 3'-methoxy benzocrown-6 which is higher than that obtained with calix [4] bis-crown-6 (-5.24 kcal/mol). The newly designed ligand might be suitable for the selective extraction of Cs+ over Na+ in the reprocessing of nuclear waste and thus invites the experimentalists for testing this DFT finding in the laboratory.

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