



Electrical Conductance study of interactions of Cu^{2+} , Co^{2+} and Ni^{2+} metal cations with kryptofix-21 in acetonitrile - ethanol binary solvent solution

Banafsheh Sefati, Gholam Hossein Rounaghi*, Mahmood Ebrahimi

Department of chemistry, Faculty of sciences, Islamic Azad University of Mashhad, Mashhad branch, Mashhad, Iran
Email*: ronaghi0970@mshdiau.ac.ir , ghrounaghi@yahoo.com

The main characteristic of a crown ether is the complexation of the ether oxygens with various ionic species. The factors which influence the stability of the metal cation-crown ether complexes include: the relative size of the cation and the cavity of the crown ether, the number of oxygen atoms in the ring, the coplanarity of the oxygen atoms, the symmetrical placement of the oxygen atoms, the basicity of the oxygen atoms, steric hindrance in the polyether ring, the nature of the cation and electrical charge on the cation [2,3]. The ability of the solvent molecules to compete with the donor atoms of the ligand towards the coordination sites of the cation and also the solvation of the ligand and the resulting complex are another factors that can thermodynamically influence the complexation process between such macrocyclic ligands and the metal cations [4,5]. The complexation reactions between Co^{2+} , Cu^{2+} , Ni^{2+} metal cations with the macrocyclic ligand, kryptofix-21, in pure acetonitrile, ethanol and also in acetonitrile-ethanol (AN-EtOH) binary mixtures have been studied at different temperatures using conductometric method. The conductance data show that the stoichiometry of the complexes in most cases is 1:1 [ML]. But in the case of Cu^{2+} cation a 1:2 [ML₂] complex is formed in pure EtOH, which shows that stoichiometry of the complexes may be changed by the nature of the medium. The stability constants of the 1:[M:L] complexes were determined using a computer program, GENPLOT. The stability order of complexes between kryptofix-21 and Co^{2+} , Ni^{2+} , Cu^{2+} cations at 25°C in the binary solvent solution of AN-EtOH (mol % AN 0) is: (kryptofix-21. Ni)²⁺ > (kryptofix-21. Cu)²⁺ > (kryptofix-21. Co)²⁺, but in case of another AN-EtOH binary solvent solution (mol % AN 25) it was found to be: (kryptofix-21. Cu)²⁺ > (kryptofix-21. Co)²⁺ > (kryptofix-21. Ni)²⁺ and in case of AN-EtOH binary mixed systems (mol % AN 50 and 75) the stability order changes as: (kryptofix-21. Co)²⁺ > (kryptofix-21. Cu)²⁺ > (kryptofix-21. Ni)²⁺. The order of the stability of the complexes in pure AN is (kryptofix-21. Co)²⁺ > (kryptofix-21. Ni)²⁺ > (kryptofix-21. Cu)²⁺. The values of stability constants of complexes, which were obtained from conductometric data, show that the stability of complexes is affected by the nature and composition of the binary mixed solvents and a non-linear behavior was observed for variation logK_f of the complexes versus the composition of the solvent system. The values of thermodynamic parameters (ΔH_c^0 , ΔS_c^0) for formation of complexes show that in most solution systems, the complexes are enthalpy destabilized but entropy stabilized.

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Study of complexation processes between kryptofix 222 with Cd^{2+} and Y^{3+} metal cations in some pure and binary mixed non-aqueous solvents using conductometric method

S. Eskandari Naddaf, G.H. Rounaghi*, M. Mohajeri

Department of Chemistry, Faculty of sciences, Islamic Azad University, Mashhad Branch, Mashhad, Iran
*e-mail: ronaghi0970@mshdiau.ac.ir , ghrounaghi@yahoo.com

Crown ethers which first synthesized in 1967 by Pederson [1], are macrocyclic polyethers which are noted for their remarkable selectivity towards specific cations [2] and formation of stable and selective complexes with them [3]. Cryptands are three dimensional analogues of crown ethers [4]. Most of them are available as the commercial name 'kryptofix'. In the present work, the complexation reactions between Cd^{2+} and Y^{3+} metal cations with the macrocyclic ligand, kryptofix222 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8] hexacosane), were studied in acetonitrile-ethanol (AN-EtOH), acetonitrile-ethylacetate (AN-EtOAc) binary mixed solvent solutions, and in pure acetonitrile (AN), pure ethanol (EtOH) and pure ethylacetate at different temperatures using conductometric method. The conductance data show that in most solvent systems, kryptofix222 forms a 1:1 complex [M:L] with Cd^{2+} and Y^{3+} cations, but in some of the solvent systems, in addition of formation a 1:1 [M:L] complex, 1:2 [M_2L_2] and 1:3 [M_3L_3] complexes are probably formed in solutions. The stability order of (kryptofix222.Cd)²⁺ and (kryptofix222.Y)³⁺ complexes in pure studied solvents at 25°C was found to be: AN > EtOH.

The stability constants of the 1:1 complexes were determined using a computer program, Genplot [5]. The results obtained in this study, show that the (kryptofix222.Cd)²⁺ complex is more stable than (kryptofix222.Y)³⁺ in most solvent systems at various temperatures and the stability constants of the 1:1 complexes are affected by the nature and also the composition of the binary solvent solutions. A non-linear behavior was observed for the changes of logK_f of the complexes versus the composition of the binary mixed solvents. The values of the standard thermodynamic parameters (ΔH_c^0 , ΔS_c^0) were obtained from temperature dependence of the equilibrium constants of (kryptofix222.Cd)²⁺ and (kryptofix222.Y)³⁺ complexes using the van't Hoff plots. The obtained results show that the complexation processes between Cd^{2+} and Y^{3+} cations with C222 in all cases are entropy stabilized but from the enthalpy view point, depending on the nature and composition of the mixed solvents they are exothermic and endothermic or athermic.

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Complexation ability of kryptofix 21 with Y^{3+} and Ce^{3+} cations in some pure and binary mixed non-aqueous solvents

Shahzad Mehdizadeh, Gholam Hossein Rounaghi*, Massoumeh Mohajeri

Department of Chemistry, Faculty of Sciences, Islamic Azad University, Mashhad Branch, Mashhad, Iran
*Email: ronaghi0970@mshdiau.ac.ir , ghrounaghi@yahoo.com

Crown ethers and cryptands have attracted significant attention from various fields of science [1]. Crown ethers are macrocyclic polyethers which form stable and selective complexes with suitable cations [2]. The binding ability and selectivity of crown ethers to metal cations depend on several factors: such as the size of the crown ether cavity, metal ion radius, type of donor atoms, conformation of the crown ether, the nature of the solvent and etc [3]. Cryptands are three dimensional analogues of crown ethers but are more selective and complex the guest ions more strongly. The resulting complexes are lipophilic. The