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A Conductometric Study of Complexation Reactions Between 4-Nitrobenzo-15-Crown-5 with Ag⁺, Hg²⁺, Ti⁴⁺ and La³⁺ Metal Cations in Acetonitrile-Methanol Binary Solutions

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Pollution by toxic heavy metals remains a serious environmental and public concern all over the world [1]. Various efficient technologies, including chemical precipitation [2], adsorption onto activated carbon [3], membrane processes [4] and ion exchange [5-7] were developed to improve their removal from the polluted media. These methods, however, display one or more limitations such as covering high operational costs or appearing to be insufficient to meet strict regulatory requirements as for chemical precipitation. To overcome these limitations, chemists have been devoted to developing materials capable of removing low concentrations of toxic metal ions such as polymers[8] or silicates[9], mesoporous molecular sieves[10] and metal complexing groups(e.g., crown ethers)[11-12].

The complex formation between Ag⁺, Hg²⁺, Ti⁴⁺ and La³⁺ metal cations with macrocyclic ligand, 4-nitrobenzo-15-crown-5 (NB15C5) was studied in acetonitrile(AN)-methanol(MeOH) binary systems at different temperatures using conductometric method. The obtained results show that the stoichiometry of the complexes is 1:1(ML), but in the case of Hg²⁺ cation, in addition to a 1:1 complex, a 1:2(ML₂) complex is formed in solutions. The stability constants of the complexes were obtained from fitting of molar conductivity curves using a computer program, Genplot. A non-linear behaviour was observed for changes of logK_f of the complexes versus the composition of AN-MeOH binary solution. The results show that the selectivity of NB15C5 for the metal cations changes with the composition of the mixed solvent. The values of standard enthalpy changes(ΔH°_c) for complexation reactions were obtained from the slope of the van't Hoff plots and the changes in standard entropy(ΔS°_c) were calculated from the relationship: $\Delta G^\circ_c = \Delta H^\circ_c - 298.15 \Delta S^\circ_c$. The obtained results show that, the complexes are entropy stabilized but from the enthalpy view point, depending on the solvent system the metal ion complexes are stabilized or destabilized, and the values of ΔH°_c and ΔS°_c depend strongly on the nature of the medium.

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