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Solvent Influence upon complex formation Between 4-Nitrobenzo-15-Crown-5 and Ni^{2+}, co^{2+} and Cu^{2+} Cations in Acetonitrile-Methanol Binary Mixtures Using the Conductometric Method

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Pedersen's [1] early investigations of the host-guest chemistry of macrocycle crown ethers has led to an explosion of interest in their use as host systems for the study of molecular recognition and inclusion phenomena. Numerous applications of crown ethers arise from their ability to enter into selective complexation with alkali metal cations and to transport these species selectivity across liquid membranes [2, 3].

The complex formation between Ni^{2+}, Co^{2+} and cu^{2+} metal cations with 4-nitrobenzo-15-crown-5 was studied in acetonitrile (AN) - Methanol (MeOH) binary systems at different temperatures using conductometric method. In all cases, 4- nitrobenzo-15C5 forms 1:1 complexes with these metal cations. The stability of the complexes is sensitive to the solvent composition and non-linear behaviour was observed for variation of logk$_f$ of the complexes versus the composition of the binary mixed solvents. The results show that the selectivity order of 4- nitrobenzo-15C5 for the metal cations is pure AN is: co^{2+} > cu^{2+} > Ni^{2+}, but in the case of pure MeOH is: Ni^{2+} > cu^{2+} > co^{2+} and this selectivity order is changed with the composition of the mixed solvents. The values of thermodynamic parameters ($\Delta H_c^{\circ}, \Delta S_c^{\circ}$) for complexation reactions were obtained from temperature dependence of the stability constants and the results show that in most cases, the complexes are enthalpy stabilized, but entropy destabilized and the values of ΔH_c° and ΔS_c° depend strongly on the nature of the medium. A non-linear behaviour is observed between the thermo dynamic parameters and the composition of the mixed solvents.

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