



three dimensional interior cavity of a cryptand provides a binding site - or nook - for "guest" ions. Cryptands form complexes with many "hard cations" including NH_4^+ , lanthanoids, alkali metals, and alkaline earth metals. In contrast to crown ethers, cryptands bind the guest ions using both nitrogen and oxygen donors. Many cryptands are commercially available under the tradename "Kryptofix" [4]. In this paper, we report the results of thermodynamic study of complexation reactions between kryptofix 21 with Y^{3+} and Ce^{3+} cations in methanol-acetonitrile (MeOH/AN) and methanol-methyl acetate (MeOH/MeOAc) binary mixtures and their pure solvents at different temperatures using conductometric method. Kryptofix 21 forms a 1:1 [M:L] complex with Y^{3+} and Ce^{3+} cations in most solvent systems, but in the case of Y^{3+} cation, in addition of formation of a 1:1[M:L] complex, 2:1[M₂L] and also 1:2[ML₂] complexes are formed in pure MeOAc solution at all studied temperatures, which shows that the stoichiometry of the complexes may change by the nature of the solvent. The order of stability of the metal-ion complexes in (MeOH/AN) binary solution, at 25°C was found to be: (kryptofix21.Y)³⁺ > (kryptofix21.Ce)³⁺, but in the case of (MeOH/MeOAc) binary solution at the same temperature, it changes to: (kryptofix21.Ce)³⁺ > (kryptofix21.Y)³⁺. The values of stability constants of the 1:1[M:L] complexes were determined from conductometric data using a GENPLOT computer program. The thermodynamic parameters (ΔH°_c and ΔS°_c) for formation of (kryptofix21.Y)³⁺ and (kryptofix21.Ce)³⁺ complexes were obtained from temperature dependence of the stability constant using the vant Hoff plots. The results show that the values of standard enthalpy (ΔH°_c) and standard entropy (ΔS°_c) change with the nature of the non-aqueous solvents.

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Sensitive Voltammetric Determination of Clozapine Based on Electrodeposited Nickel Oxide Nanoparticles on MWCNT Modified Carbon Paste Electrode

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Clozapine, 8-chloro-11-(4-methyl-1-piperazinyl)-5H-dibenzo[b,e][1,4]diazepine, a tricyclic dibenzodiazepine neuroleptic with a piperazinyle side chain, is used to treat positive and negative symptoms of schizophrenic patients who do not respond well to traditional neuroleptic drugs. Several analytical methods including chromatography and spectrophotometry have been reported for determination of the drug in its pure and dosage forms [1-3]. Due to the excellent electrocatalytic activity and good antifouling properties of electrodes modified with nickel oxide, these modified electrodes have been used for electrocatalytic oxidation and determination of insulin, thiols, disulfides, mercaptans, and sulfur oxoanions [4].

In this study, conventional carbon paste electrode is prepared with a specific amount of MWCNT to increase its sensitivity and conductivity properties, and then the constructed electrode surface is modified by electrodeposition of nickel oxide nanoparticles. The fabricated electrode showed superior electrochemical response to the different concentrations of clozapine. The linear range is 2×10^{-5} to 9×10^{-9} , and detection limit of 3.34 nM is obtained. To increase the reproducibility of the electrode response, an effective and simple method was developed for the regeneration of electrode surface after each running process. The proposed electrochemical sensor was successfully used for the determination of clozapine in pharmaceutical preparations.

Keywords: Nickel Oxide Nanoparticles, Clozapine, Electrodeposition, MWCNT

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Conductance study of the thermodynamics of Co^{2+} , Ni^{2+} , Cu^{2+} cryptates in mixed acetonitrile-ethylacetate binary solvent solutions at different temperatures

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The discovery of the crown ethers was followed by synthesis of macro bicyclic poly ethers containing three poly ether strands joined by two bridge head nitrogen atoms [1]. These compounds have three-dimensional cavities which can accommodate a metal ion of a suitable size and form an inclusion complex. These ligands which developed by Lehn and his co-workers [2], were called 2-cryptands where 2 indicates the bicyclic ligand such as kryptofix-222. It is important to mention that the macrocyclic crown ethers have many applications such as in biological activity, corrosion chemistry, analytical chemistry, phase-transfer catalysis and industrial production such as nuclear energy, electronics and electro-chemical photosensitive materials [3-4]. For better understanding of the interactions between macrocyclic crown ethers and metal cations in solutions, it requires the study of various parameters governing these interactions. The thermodynamic studies of these interactions give important information about their complexation reactions and the selectivities of these ligands towards different metal cations [5]. In this paper, we report the results of a conductance study of the interactions between Co^{2+} , Ni^{2+} , Cu^{2+} metal cations with cryptand 222 in acetonitrile-ethylacetate binary mixtures at various temperatures. The conductance data show that in most cases, the stoichiometry of the complexes is 1:1 [M:L], but in the case of complexation of Co^{2+} and Cu^{2+} cations with C222, in addition of 1:1 [M:L] complexes 1:2 [M:L₂] complexes are formed in some solvent systems. The stability constants of the 1:1[M:L] complexes were determined using a computer program, GENPLOT. The stability order of complexes between C222 and Co^{2+} , Ni^{2+} and Cu^{2+} cations at 25°C in the binary solution of AN-EtOAc (mol % AN 20) is: (C222. Co)²⁺ > (C222. Ni)²⁺ > (C222. Cu)²⁺, but in case of another AN-EtOAc binary solvent solution (mol % AN 25) it was found to be: (C222. Ni)²⁺ > (C222. Co)²⁺ > (C222. Cu)²⁺ and in case of AN-EtOAc binary mixed systems (mol % AN 50 and 75) the stability order changes as: (C222. Cu)²⁺ > (C222. Ni)²⁺ > (C222. Co)²⁺. The order of the stability of the complexes in pure AN is: (C222. Cu)²⁺ > (C222. Co)²⁺ > (C222. Ni)²⁺. The results obtained in this study, reveal that the selectivity of cryptand 222 for the studied cations in binary mixed non-aqueous solvents changes with the nature and composition of the solvent system. A non-linear behavior was observed for variation of the stability constants (log K) of complexes versus the composition of the binary solvent solution. This behavior is due to solvent-solvent interaction and also it may be due to preferential solvation of the cation and ligand in the binary mixed solvent system. The value of thermodynamic quantities, (ΔH°_c , ΔS°_c) show that in most solvent systems, the studied cryptates are enthalpy stabilized but with the exception of a few cases, they are enthalpy destabilized.