



MWCNTs can increase current response by improvement of electron transfer of these compounds on the electrode surface. The presence of the chitosan in the modified electrode could be enhanced the repeatability of the sensor by its antifouling effect. Application of the differential puls voltammetry (DPV) showed that the linear dynamic ranges for MO and AR were in the range of  $2 \times 10^{-5}$  to  $2 \times 10^{-3}$  mol L<sup>-1</sup> and  $1 \times 10^{-6}$  to  $2 \times 10^{-4}$  mol L<sup>-1</sup>, respectively. The relative standard deviations of the proposed method for MO and AR were 2.8% and 2.1% (n=10), respectively. At the end, the proposed method was successfully applied for the simultaneous determination of MO and AR in the waste water samples collected from different industrial places of Iran.

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### Selective Polymeric Membrane Sensor for Determining Lanthanum(III) Based on 4',4''(5'')-Di-tert-butylidibenzo-18-crown-6 as Ionophore

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Macrocyclic compounds, due to their selective receptor properties and ease of structural modification, have been employed as ionophores in construction of ion selective electrodes for the determination of alkali, alkaline earth and many transition metal ions [1-4]. In the present paper, we introduce a new ion selective electrode based on the incorporation of 4',4''(5'')-Di-tert-butylidibenzo-18-crown-6 (DtBDB18C6) that is selective to lanthanum (III) cations was evaluated electrochemically, and a Nernstian slope ( $20.2 \pm 2$  mV decade<sup>-1</sup>) over a concentration range of  $1.0 \times 10^{-2}$ – $0 \times 10^{-6}$  M and a detection limit of  $5.6 \times 10^{-6}$  M were observed. The electrode reached equilibrium in a short period of time (10 s) due to the fast exchange kinetics of the complexation–decomplexation of La(III) cations with the ion carrier at the test solution–membrane interface and most significantly, very good selectivity with a number of ions the transition and heavy metal ions as well as some mono, di and trivalent cations such as K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Pb<sup>2+</sup>, Ni<sup>2+</sup>, Ba<sup>2+</sup>, Zn<sup>2+</sup>, Sr<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>3+</sup>, Al<sup>3+</sup> and Cr<sup>3+</sup> ions. The potentiometric selectivity coefficient values as determined by Mixed solution method (MSM) indicate excellent selectivity for La<sup>3+</sup> ions over interfering cations. In addition, it can be used at least for a period of 9 weeks without any significant divergences in its potential response. In the present study, the effect of the nature and amount of plasticizer on the potential response of the proposed La(III) potentiometric sensor was investigated, the potential remained constant over a pH range of 7.0–11.5. Therefore, the working pH range of the proposed electrode is 7.0–11.5. In our preliminary studies, to examine the interactions between La (III) cations and the ligand, complex formation between the ligand and lanthanum(III) cations was investigated. For this purpose, a conductometric titration was performed, and the change in molar conductivity ( $\Lambda_m$ ) versus the ligand to cation molar ratio ( $[L]_0/[M]_0$ ) was studied to determine the stability constant of the complexation of 4',4''(5'')-Di-tert-butylidibenzo-18-crown-6 (DtBDB18C6) with lanthanum(III) cations in methylacetate (MeOAc). The stoichiometry of the complex formed between lanthanum(III) cation and DtBDB18C6 was 1:1. Additionally, the proposed sensor was used as an indicator in the potentiometric titration of EDTA and titration of sodium hydroxid.

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### Thermodynamic study of complex formation between 4',4''(5'')-Di-tert-butylidibenzo-18-crown-6 and lanthanum(III) ion in some binary non-aqueous solvents using a conductometric method

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Crown ethers have been demonstrated to be highly selective complexing agents for many metal ions and can potentially be applied in their separation and determination [1]. Thermodynamic studies of macrocyclic complexation reactions with metal ions not only result in important information on the thermodynamics of complexation reaction, but also lead to a better understanding of the high selectivity of these ligands towards different metal cations. It is well known that the stability and selectivity of complexations strongly depend on the solvating ability of the solvent [2,3]. The complexation reaction between a macrocyclic polyether, 4',4''(5'')-Di-tert-butylidibenzo-18-crown-6 (DtBDB18C6) and lanthanum(III) ion was studied in methylacetate (MeOAc)-acetonitrile (AN) and tetrahydrofuran (THF)-acetonitrile (AN) binary solvent systems at different temperatures using a conductometric method. It was of interest to us, therefore, to investigate the dependence of the stability constant and thermodynamic parameters of the DtBDB18C6-La<sup>3+</sup> complex on the composition of several binary solvent mixtures in order to see how the thermodynamics of complexation are affected by the solvent composition. In addition it was found that the stability of the 1:1 complex formed between La<sup>3+</sup> ion. A Non-linear behavior was observed for the variation of  $\log K_f$  of the complexes versus the composition of binary mixed solvents, which was discussed in terms of heteroselective solvation and solvent-solvent interactions in binary solutions. It was found that the stability order of the complexes changes with changing the composition of the mixed solvents. Standard enthalpies and standard entropies of the complex formation were obtained from the temperature dependence of the stability constant. In all cases negative  $\Delta H_c^\circ$  and  $\Delta S_c^\circ$  values characterize the formation of DtBDB18C6-La<sup>3+</sup> complex. The results obtained show that the stability of the complex is governed by the solvent medium and the thermodynamic parameters  $\Delta H_c^\circ$ ,  $\Delta S_c^\circ$  and  $\Delta G_c^\circ$  are sensitive to the composition of the mixed solvents. The values of stability constants of the 1:1 [M:L] complex was determined from conductometric data using a GENPLOT computer program [4]. The results revealed that, the stability constant of (DtBDB18C6.La)<sup>3+</sup> complex in pure organic solvents varies in the order: AN>MeOAc>THF and in the case of binary mixed solutions at 25°C it follows the order: AN>MeOAc>AN-THF.

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