

**Construction of Sr²⁺-Selective Electrode and Thermodynamic Study of
the Ternary Aqueous Mixed Electrolyte System (SrCl₂, KCl, H₂O)
Using Potentiometric Method**

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ABSTRACT

In order to preparing strontium ion selective electrode 6-(4-nitrophenyl)-2-phenyl-4,4-dipropyl-3,5-diaza-bicyclo [3, 1, 0] hex-2-ene (NPDBH) was used as an ionophore. This electrode responds to Sr (II) ion with a sensitivity of 28.2 ± 0.5 mV/decade over the range 1.0×10^{-6} to 1.0 M at pH 3.0-10.0. The limit of detection was 2.4×10^{-7} M. The influences of membrane composition, the pH of the test solution, the temperature effect and the interfering ions on the electrode performance for the proposed electrode were investigated. In the next step, electrolyte solution system SrCl₂, KCl, H₂O in the high concentration range were thermodynamically investigated. The thermodynamic investigations were performed by evaluation of potentiometric experimental data, successfully.

Keywords: Ion selective electrode; Thermodynamic investigation; Ternary electrolyte system; Potentiometric method

INTRODUCTION

In the area of membrane-based ISEs, emphasis has been focused on the development of new ionophores and on the composition of the membrane phase, aiming at enhancing the potentiometric responses of the ISEs. Fabrication of a new, ion-specific ISE with high selectivity and sensitivity, wide linear concentration range, long lifetime, good reproducibility and low cost, is always in need. The introduction of new ion-selective membrane electrodes has played a fundamental role in the development of potentiometric measurements. The advantages of ISEs over many other methods are their easy handling, nondestructive analysis and inexpensive sample preparation. Electrolyte solution system consist of SrCl₂, KCl, H₂O in the wide concentration range were thermodynamically investigated [1-7]. Using a Sr²⁺-selective electrode with together an Ag-AgCl electrode on the galvanic cell without liquid junction performed thermodynamic investigations of

ternary system. The ion selective electrode used for investigation of electrolyte system of SrCl₂, KCl, H₂O was the PVC based Sr (II) ion selective electrode. The application of pair electrodes used (Sr²⁺-selective electrode and Ag-AgCl) was confirmed by comparing potentiometrically determined mean activity coefficients of single electrolyte and mean activity coefficients calculated by theoretical model.

EXPERIMENTAL

Reagents and materials

Relative molecular weight PVC (all from Merck), CH₃COONa and absolute EtOH (from Fluka or Aldrich) were used as received. Chloride and nitrate salts of all other cations (all from Merck) were of the highest purity available and used without any further purification. Double distilled deionized water was used throughout the experiments.

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Preparation of Membrane

Membranes containing different compositions were studied and the optimum found was 30.0 wt. % of powdered PVC, 57 wt. % of plasticizer (AP), 6 wt. % of additive (OA) and 7 wt. % of the corresponding ionophore (NPDBH). These were mixed in 2.0 ml of THF. The solvent was evaporated slowly until an oily concentrated mixture was formed. A Pyrex tube (4 mm o.d.) was dipped into the mixture for about 15 s so that a transparent membrane of about 0.4 mm thickness was formed. The tube was then pulled out from the solution and kept at room temperature for about 2 h. The tube was then filled with internal solution. The electrode was finally conditioned for 24 h. Fig. 1 shows a flow diagram for preparation of membrane. The ratios of various ingredients, concentration of equilibrating solution and time of contact were optimized to provide a membrane that was reproducible, noiseless and stable potential.

Potential measurement

The structure of ionophore is shown in Fig. 2. and the electrode cell assembly of the following type

was used:

- (a) Ag | AgCl | SrCl₂ (m_A), H₂O | Sr-ISE
 (b) Ag | AgCl | SrCl₂ (m₁), KCl (m₂), H₂O | Sr-ISE

RESULTS AND DISCUSSION

Theoretical calculations

Some ab initio quantum mechanical calculations were carried out using second-order Moller-Plesset (MP2) perturbation theory with Gaussian 98 program package. The lan12dz basis set for all atoms was used for optimizing molecules. The optimized structure of complex between ionophore and Sr²⁺ ion is shown in Fig. 3.

Interaction energies for ionophore and some metal ions were calculated and are listed in Table 1. From the data given in Table 1 it is obvious that the interaction energy calculated decreases in the order: Sr²⁺ > Al³⁺ > La³⁺ > Cu²⁺. Thus, based on the above results, ionophore could possibly be used as a suitable ionophore in preparation of a Sr²⁺ ion-selective membrane electrode.

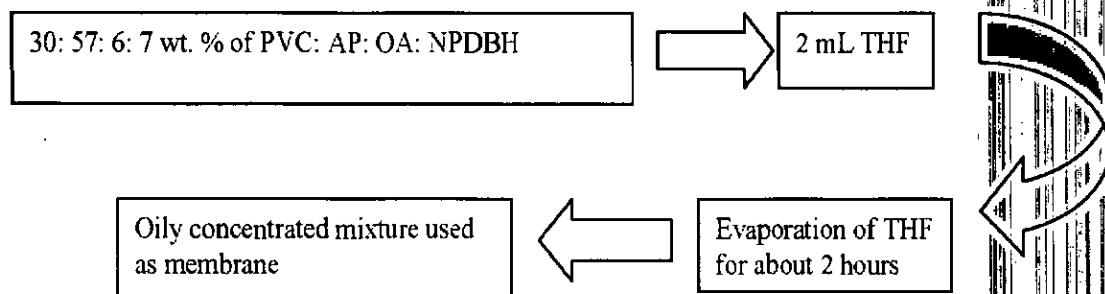


Fig. 1. Flow diagram for preparation of membrane.

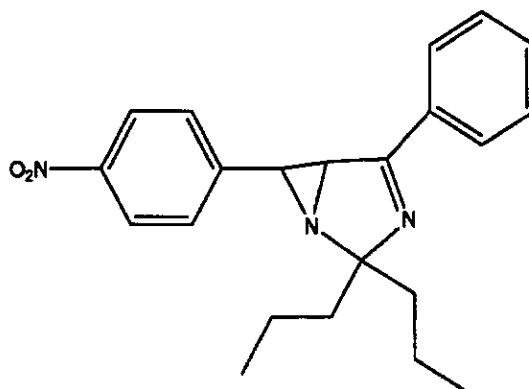


Fig.2. Structure of 6-(4-nitrophenyl)-2-phenyl-4,4-dipropyl-3,5-diaza-bicyclo [3.1.0] hex- 2-ene (NPDBH) used as ionophore.

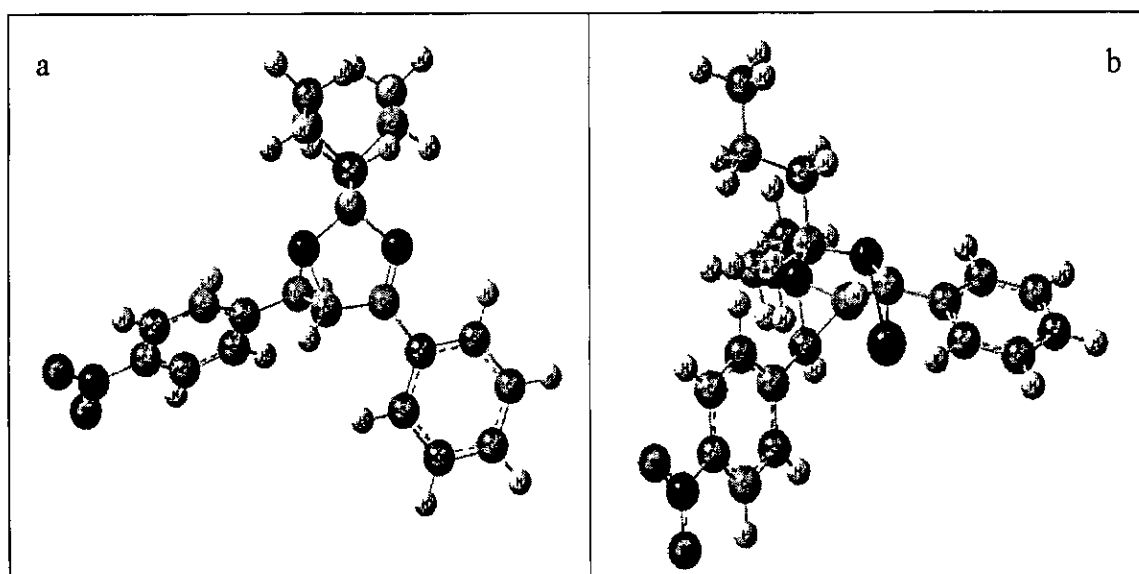


Fig. 3. Optimal conformation of ionophore before (a) and after (b) complexation with Sr^{2+} .

Table 1. Interaction energy between metal ions-ionophore

Metal ions	Interaction energy (kcal/mol)
Sr^{2+}	-19.10679
Al^{3+}	-18.94573
La^{3+}	-18.63801
Cu^{2+}	-18.51219

Potential response of Sr^{2+} -selective electrode

The potential responses of various ion-selective electrodes are shown in Fig. 4. Except for the Sr^{2+} ion-selective electrode, in all other ions the slope of the corresponding potential-pM plots is much lower than the expected Nernstian slopes. Therefore, this electrode is suitable for determination of Sr^{2+} ion. Fig. 5

shows the response of mentioned sensor in high concentrations. This figure confirms that the electrode performs successfully.

Fig. 6 indicates Plot of the values of natural logarithm mean activity coefficients for SrCl_2 versus total ionic strength at different molal ratio. It can be concluded that the good agreement exists between mean activity coefficients.

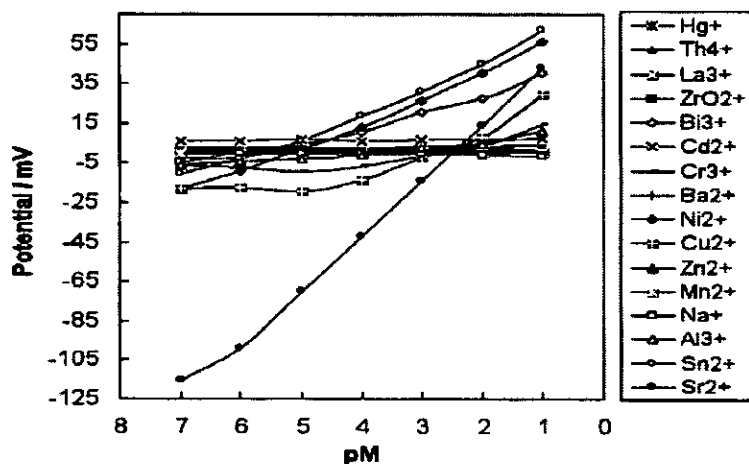


Fig.4. Potential response of various ion-selective membranes based on NPDBH.

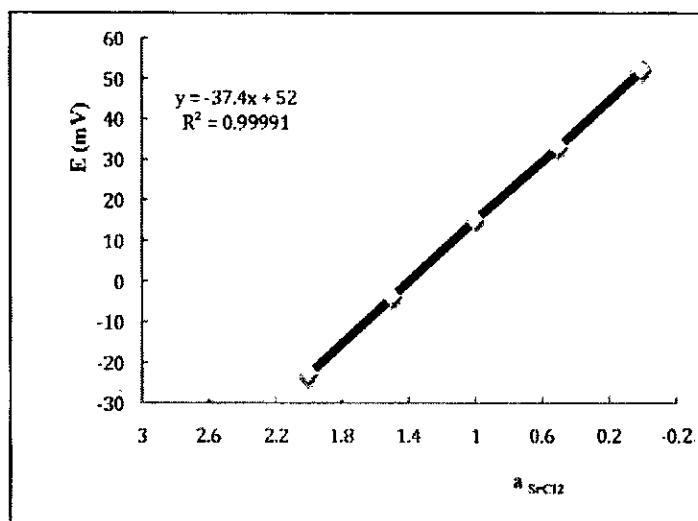


Fig.5. Potential response of Sr^{2+} -selective membranes in high concentrations.

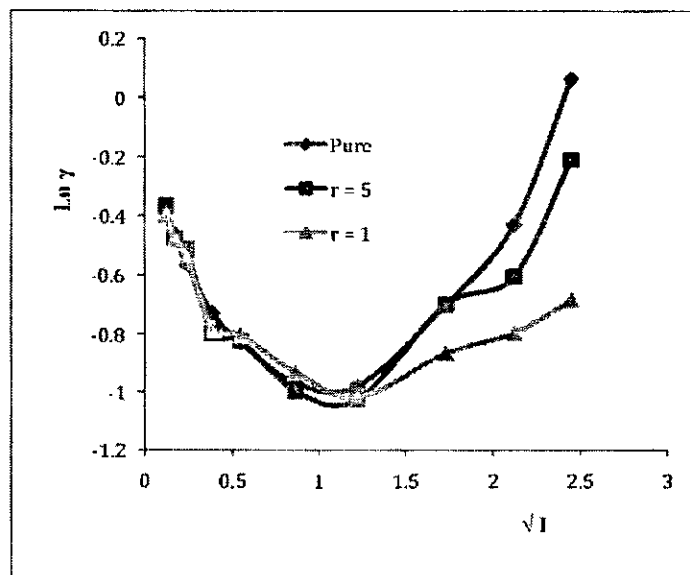


Fig. 6. Variation of mean activity coefficient with ionic strength.

CONCLUSIONS

The new compound, 6-(4-nitrophenyl)-2-phenyl-4,4-dipropyl-3,5-diaza-bicyclo[3,1,0]hex-2-ene (NPDBH), was used as an ionophore for construction of Sr^{2+} -ion selective electrode. This electrode responds to Sr (II) ion with a good sensitivity over the wide concentration range at pH 3.0-10.0. These observations confirm theoretical calculations, which compare interaction energies. Using a Sr^{2+} -selective electrode with together an Ag-AgCl electrode on the galvanic cell performed thermodynamic investigations of electrolyte system. The ion selective electrode used for investigation of electrolyte system of SrCl_2 , KCl, H_2O was the PVC based Sr (II) ion selective electrode. The results show that potentiometric method is successful in evaluation of the mean activity coefficient in mix electrolyte solutions.

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