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Construction of Cu^{2+} -selective electrode and thermodynamic study of the ternary aqueous mixed electrolyte system (CuCl_2 , KCl , H_2O) using nanocomposite-based potentiometric sensor

ABSTRACT

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A nanocomposite membrane Cu^{2+} ion-selective electrode has been constructed using a new compound ethyl 1,2,3,4-tetrahydro-4-(4-methoxyphenyl)-6-methyl-2-oxopyrimidine-5-carboxylate (ETMOC) as a neutral ionophore. The electrode works properly. It responds to Cu^{2+} ion with a sensitivity of 29.5 ± 0.2 mV/decade over the range 1.0×10^{-9} to 5.0×10^{-1} M at pH 3.0-8.0. The limit of detection was 4.5×10^{-10} M. It has a response time of < 6 s and can be used for at least 3 months without any divergence in potentials. The proposed electrode shows fairly good discrimination of Cu^{2+} ion from several cations. Then, electrolyte solution system, CuCl_2 , KCl , H_2O in the concentration range from dilute to near saturate from the thermodynamic viewpoint was investigated. The thermodynamic investigations were performed based on Pitzer ion-interaction model by processing experimental data of potentiometric. The thermodynamic investigations were successfully performed by the evaluation of potentiometric experimental data.

Keywords: Activity Coefficient; Pitzer Model; Cu^{2+} -Selective Electrode; Nanocomposite.

INTRODUCTION

Copper is an important element for all plants and animals. It functions at low concentration as bacteriostatic substances, fungicides, and wood preservatives. In addition, it is found in a variety of enzymes [1]. Copper is widely used in many industries, such as electroplating, paint, metal finishing, electrical, fertilizer, wood manufacturing and pigment industries. 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.

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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 consisting of CuCl_2 , KCl , H_2O in the wide concentration range were thermodynamically investigated [2-8]. Using a Cu^{2+} -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 the investigation of electrolyte system of CuCl_2 , KCl , H_2O was the nanocomposite- based Cu(II) ion selective electrode. The application of pair electrodes used (Cu^{2+} -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 [9-13].

EXPERIMENTAL

Reagents and materials

Reagent grade acetophenone (AP), oleic acid (OA), tetrahydrofuran (THF), nitrophenyl octyl ether (NPOE), Sodium tetra phenyl borate (NaTBP) (all from Merck), p-methoxy benzaldehyde, β -keto ester, urea or thiourea, $\text{Fe}(\text{HSO}_4)_3$, 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.

Synthesis of Ionophore (ETMOC)

ETMOC was synthesized under solvent-free conditions: A mixture of the p-methoxy benzaldehyde as substrate (1 mmol), β -keto ester (1.2 mmol) urea or thiourea (1.2 mmol) and $\text{Fe}(\text{HSO}_4)_3$ (1 mmol) was heated in an oil bath (100°C) for 2h. After completion (monitored by TLC), the reaction was cooled to room temperature and poured onto crushed ice and the solid product separated was filtered and recrystallised from ethanol.

Preparation of Membrane

Membranes containing different compositions were studied and the optimum found was 30.0 wt. % of Nano Composite Silica Perchloric Acid Poly (2- Methyl Aniline) (NSPPMA), 56 wt. % of plasticizer (NPOE), 5 wt. % of additive (NaTPB) and 9 wt. % of the corresponding ionophore (ETMOC). 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 1.0×10^{-4} M Cu^{2+} . The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} M Cu^{2+} solution. Figure 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 and stable potential.

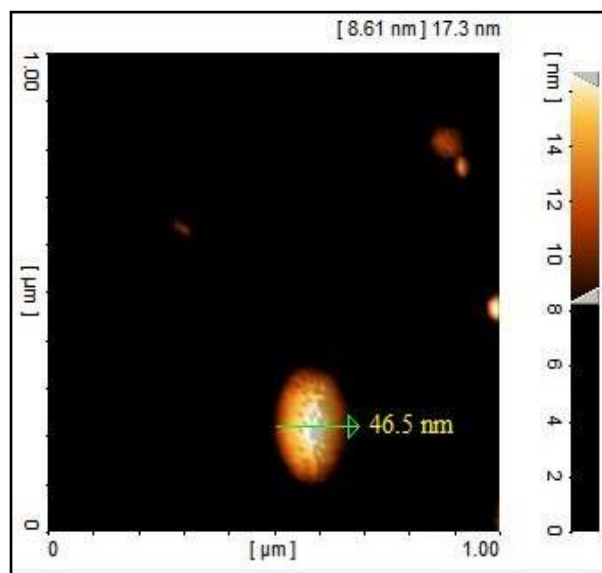


Fig. 1. AFM images of Nano Composite Silica Perchloric Acid Poly (2- Methyl Aniline)

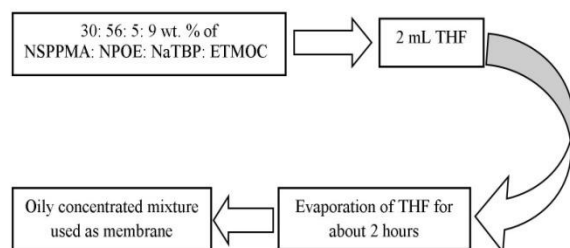


Fig. 2. Flow diagram for preparation of membrane.

Potential measurement

The electrode cell assembly of the following type was used:

- (a) Ag | AgCl | CuCl₂ (m_A), H₂O | Cu-ISE
 (b) Ag | AgCl | CuCl₂ (m₁), KCl (m₂), H₂O | Cu-ISE

RESULTS AND DISCUSSION

Theoretical calculations

Some ab initio quantum mechanical calculations were carried out using second-order Møller–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 Cu²⁺ ion is shown in Figure 3.

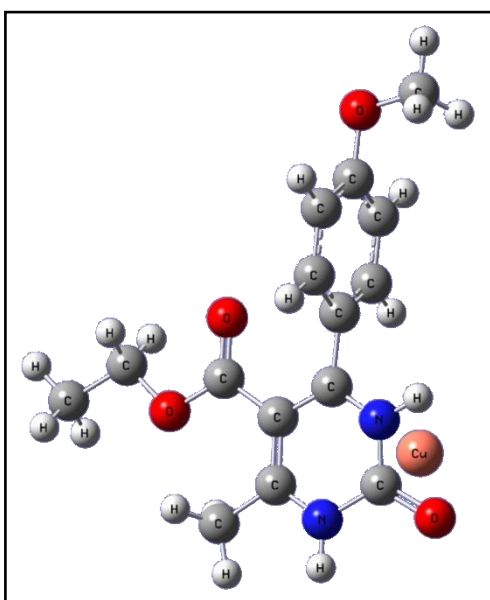


Fig. 3. Optimal conformation of ionophore after complexation with Cu²⁺

Potential response of Cu²⁺-selective electrode

The potential responses of various ion-selective electrodes are shown in Figure 4. Except for the Cu²⁺ 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 Cu²⁺ ion. Figure 5 shows the response of mentioned sensor in high concentrations. This figure confirms that the electrode performs successfully.

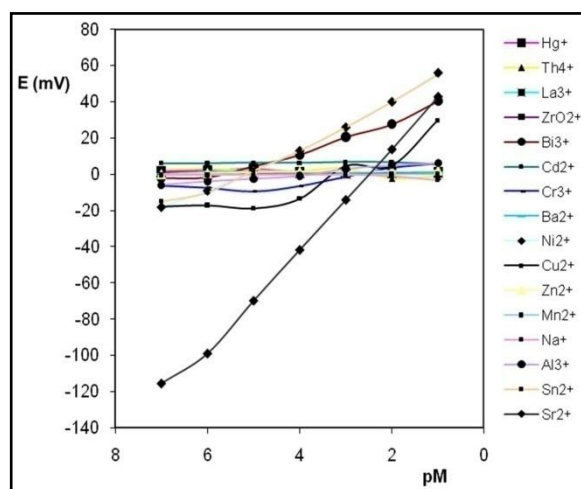


Fig. 4. Potential response of proposed ion-selective electrode based on ETMOC to different ions.

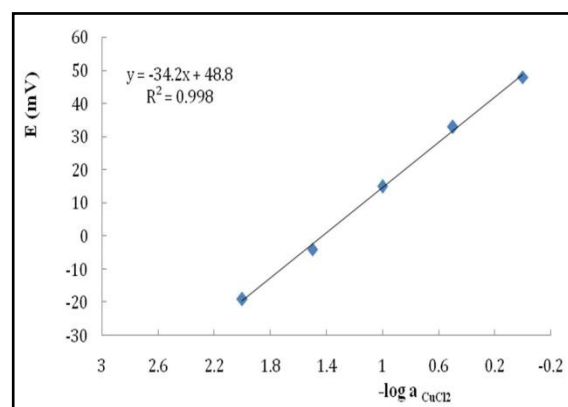


Fig. 5. Potential response of Cu²⁺-selective membranes in high concentrations.

Figure 6 indicates Plot of the values of natural logarithm mean activity coefficients for CuCl₂ versus total ionic strength at different molal ratio. It

can be concluded that the good agreement exists between mean activity coefficients.

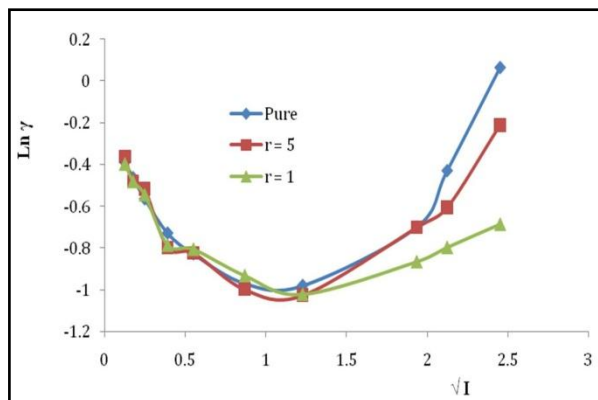


Fig. 6. Variation of mean activity coefficient with Ionic strength.

CONCLUSION

The new compound, ethyl 1,2,3,4-tetrahydro-4-(4-methoxyphenyl)-6-methyl-2-oxopyrimidine-5-carboxylate (ETMOC), was used as an ionophore for the construction of Cu^{2+} -ion selective electrode. This electrode responds to $\text{Cu}(\text{II})$ ion with a good sensitivity over the wide concentration range at pH 3.0-8.0. These observations confirm theoretical calculations, which compare interaction energies. Using a Cu^{2+} -selective electrode with together an $\text{Ag}-\text{AgCl}$ electrode on the galvanic cell performed thermodynamic investigations of electrolyte system. The ion selective electrode used for investigation of electrolyte system of CuCl_2 , KCl , H_2O was the PVC based $\text{Cu}(\text{II})$ 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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REFERENCES

- [1] Pitzer K.S., (1973), Thermodynamics of electrolytes 1. Theoretical basis and general equations. *J. Phys. Chem.* 77: 268-277.
- [2] Pitzer K.S., Kim J.J., (1974), Activity and Osmotic Coefficients for Mixed Electrolytes. *J. Am. Chem. Soc.* 96:5701-5707.
- [3] Pitzer K.S., (1991), Activity Coefficients in Electrolyte Solutions, second ed., *CRC Press, Boca Raton, FL*, 99-110.
- [4] Jun Zh., Shi-Yang G., Shu-Ping X., Yan Y., (2004), Study of thermodynamic properties of quaternary mixture $\text{RbCl} + \text{Rb}_2\text{SO}_4 + \text{CH}_3\text{OH} + \text{H}_2\text{O}$ by EMF measurement at 298.15 K. *Fluid Phase Equilib.* 226:307-312.
- [5] Jun Zh., Shi-Yang G., Shu-Ping X., (2003), Determination of thermodynamic properties of aqueous mixtures of RbCl and Rb_2SO_4 by the EMF method at $T=298.15$ K. *J. Chem. Thermodyn.* 35:1383-1392.
- [6] Deyhimi F., Salamat-Ahangari R., Karimzadeh Z., (2007), thermodynamic investigation of KCl in the ternary $\text{KCl}/\text{LiCl}/\text{H}_2\text{O}$ mixed electrolyte system based on potentiometric method. *Calphad* 31:522-528.
- [7] Zanjanchi M.A., Arvand M., Mahmoodi N.O., Islamnezhad A., (2007), Novel potentiometric membrane sensor based on 6-(4-nitrophenyl)-2-phenyl-4,4-dipropyl-10,3,5-diazabicyclo[3,1,0]hex-2-ene for detection of strontium (II) ions at trace levels. *Talanta* 74: 125-131.
- [8] Shahrokhian S., Fotouhi L., (2007), Carbon paste electrode incorporating multiwalled carbon nanotube/cobalt salophen for sensitive voltammetric determination of tryptophan. *Sens. Actuators B* 123:942-949.
- [9] Fiorucci A.R., Cavalheiro E.T.G., (2002), The use of carbon paste electrode in the direct voltammetric determination of tryptophan in pharmaceutical formulations. *J. Pharm. Biomed. Anal.* 28:909-915.
- [10] Walcarius A., (2006), Zeolite-modified paraffin-impregnated graphite electrode. *J. Solid State Electrochem.* 10:469-478.
- [11] Mazloum-Ardakania M., Beitollahi H., Amini M.K., Mirkhalaf F., Mirjalili B.F., (2011), A highly sensitive nanostructure-based

electrochemical sensor for electrocatalytic determination of norepinephrine in the presence of acetaminophen and tryptophan. *Biosens. Bioelectronics* 26:2102-2106.

- [12] Park S.K., Kim K.D., Kim H.T., (2002), Preparation of silica nanoparticles: determination of the optimal synthesis conditions for small and uniform particles. *Coll. Surf. A: Physicochem. Eng. Aspects*, 197:7-17.

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