Heterogeneous precipitate based Cu(II)-ion-selective electrode and its application in the determination of stability constant of Cu(II) complex with 4-(2-pyridylazo)-resorcinol

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A new Cu(II)-ion selective electrode (ISE) based on thiopentone-Cu(II) complex as electroactive material has been described. The selectivity coefficients determined by mixed solution method, reveal that the electrode is selective in the presence of ions Co(II), Ni(II), Zn(II), Ca(II), Mg(II) and Al(III). The stability constant of Cu(II) complex with 4-(2-pyridylazo)-resorcinol (PAR) has been determined by measuring the free metal ion concentration at different pH using this electrode \( \log K = 13.69 \).

Precipitate based ion selective membrane electrodes are well-known\(^1\). The Cu(II) electrodes developed by different authors are listed in several review articles\(^1\)\(^-\)\(^5\). The subsequent work on Cu(II)-ion-selective electrode\(^6\), and macrocyclic polythioethers\(^7\) as electroactive material are well documented. Copper (II) form of cation exchange resin was also employed as the electroactive material in the preparation of Cu(II)-ion-selective electrode\(^8\). A liquid state Cu(II)-ISE containing a complex of Cu(II) with salicylalaniline has also been investigated by Ren\(^9\). Neshkova\(^10\) has described the behaviour of a solid state copper-chalcogenide membrane.

Thiopentone is well-known for its anaesthetic and psychiatric activities and forms an insoluble precipitate with Cu(II) ion. Here, a new Cu(II)-ISE based on thiopentone-Cu(II) complex is described for the first time.

Experimental

Preparation of Cu(II) complex as electroactive material

Thiopentone [sodium-5-ethyl-5-(1-methylbutyl)-2-thiobarbiturate] was chosen as the ligand for the preparation of Cu(II) complex. To a solution of 0.528 g of thiopentone [Abbot Lab. (India)], CuCl\(_2\).2H\(_2\)O (0.1706 g) (Sarabhai Chemicals) solution was added. A green coloured precipitate was obtained which on heating changed to yellow. The solution was allowed to evaporate at room temperature (30°C) for several days. The precipitate was filtered and washed with doubly distilled water and then dried. This precipitate was used as an electroactive material for electrode.

Preparation of membrane

Approximately 150 mg of dried electroactive material was mixed with 600 mg of araldite (Ciba-Geigy) and the paste was applied on Whatman Filter Paper (No. 42). It was spread uniformly over the filter paper to obtain a 0.1 mm thick layer of the electroactive material with matrix and left in air to dry for 48 h. To prepare the electrode, the filter paper was separated from the membrane by dipping the filter paper containing membrane in a solution of Cu(II)-ion. Any portion of filter paper adhering to the surface of the membrane was removed. A portion of the membrane was cut into a disc and fixed with araldite to one end of a glass tube (diameter 1 cm and length 15 cm) and it was dried for 24 h. The tube was filled with 0.1 mol dm\(^{-3}\) Cu(II) ion solution and kept immersed in a solution of 0.1 mol dm\(^{-3}\) for one week. The internal and external reference electrodes were calomel electrodes. The entire electrode system for the measurement can be represented as:

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A Philips pH/mV meter model PR 9405 M with a saturated calomel electrode as reference electrode was used for measurement of electrode potential. All measurements were carried out at room temperature (\(25^\circ \pm 2^\circ \)C). Doubly distilled water was used in all the experiments.

Results and discussion

Electrode response

The electrode was first conditioned in 0.1 mol dm\(^{-3}\) solution of Cu(II) ion till it attained stable equilibrium.
after which it was used for the determination of characteristics of the electrode. The electrode potential for a series of standard solutions of Cu(II) ion were measured. The electrode gave a linear response to Cu(II) ion concentration in the range of 1.0 × 10⁻¹ to 1.0×10⁻³ mol dm⁻³. The slope was found to be 38 mV per decade change in Cu(II) ion concentration.

Response time

To find the response time, the electrode was first dipped in 0.01 mol dm⁻³ of Cu(II) ion solution and suddenly the concentration of solution was changed to 0.001 mol dm⁻³. The values of potential change were noted at every five sec. A constant potential was obtained after 45 sec.

Effect of pH

To study the effect of pH, a series of solutions containing 0.01 mol dm⁻³ Cu(II) ion were prepared in which the pH was varied by the addition of a dilute solution of NaOH or HCl. It was found that the potential remained unchanged within the pH range 2.0 to 5.5, which is the working range of pH for the electrode.

Interference by ions

The cationic interferences due to other ions were studied by the determination of selectivity coefficients by mixed solution method. The electrode potentials were recorded in mixed solution having a fixed concentration of interferent ion, B, (1×10⁻³ mol dm⁻³) and varying concentrations (1×10⁻¹ to 1×10⁻⁶ mol dm⁻³) of Cu(II) ion solution. The selectivity coefficients were calculated from the plot of potential of electrode versus concentration in the usual manner. The selectivity coefficients for different cations determined are: Co(II) - 0.20, Ni(II) - 0.50, Mn(II) - 0.55, Ca(II) - 0.90, Mg(II) - 0.55 and Al(III) - 0.07.

Applications

The ion selective electrodes find wide applications in the metal-ligand equilibrium studies because it is capable of providing the equilibrium concentration of free metal ion or the free ligand concentration. In order to see the application of electrode reported in this work, the Cu(II) complex of pyridylazo resorcinol (PAR) was determined.

Cu(II) forms a 1:1 complex with PAR in the pH range 3-6 (ref. 11) and the reaction can be shown as,

\[
M+H_2L \leftrightarrow ML+2H
\]  \hspace{1cm} (1)

Changes are omitted for simplicity. The formation of 1:1 complex was further confirmed by Job's method of continuous variations. The stability constant, \(K\), is given by

\[
K=K'\phi
\]  \hspace{1cm} (2)

where \(\phi=1+([H]/K_{d1})+([H]^2/(K_{d1}.K_{d2}))\)  \hspace{1cm} (3)

\(K_{d1}\) and \(K_{d2}\) are the first and second dissociation constants of PAR and \(K'\) is the conditional stability constant whose value can be determined at a particular pH and is given by:

\[
K'=[ML]/([M]^2-[ML])\times[L^2]-[ML])\times[ML])\times[M]\phi=L^2\times[M]\phi]
\]  \hspace{1cm} (4)

where \(M^2\) and \(L^2\) are the total metal and ligand concentrations, respectively. On combining and rearranging Eqs (4) and (2), one can arrive at Eq. (5)

\[
[M]/([M^2]\phi)=1/[K.L^0]+[M]/(\phi.L^0)
\]  \hspace{1cm} (5)

If total metal and ligand concentration are kept constant and the pH of the solution are varied, then a plot of \([M]/[M^2].\phi\) against \([M]/\phi\) would give a straight line with slope equal to \(1/L^2\) and intercept equal to \(1/[K.L^0]\), thus enabling one to calculate the true stability constant \((K)\) of 1:1, Cu(II)-PAR complex.

A series of solutions were prepared in which the concentration of metal and ligand were kept constant, but pH was varied in the range 3.5–5.5. The electrode potential of each solution was measured and the corresponding values of Cu(II) ion were obtained from the calibration curve. The dissociation constant being known, the free ligand concentration and therefore the value of \(\log K\) was calculated (log \(K = 13.69\)).

References