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NEW APPROACH TO MULTIPLY THE SENSITIVITY OF DIRECT POTENTIOMETRY BY USING TWO ION-SELECTIVE ELECTRODE -CONTAINING CELLS: APPLICATION TO KCl $CuCl_2$ AND $CaCl_2$

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SUMMARY

Potentiometric cells containing Cl^- and K^+, Cu^{2+} or Ca^{2+} ion-selective electrodes were used to construct E_{cell} - $\log C_M$ (where M is K^+, Cu^{2+} or Ca^{2+}) calibration graphs of slopes 113.0, 80.5 and 78.0 mV / Concentration decade, at 25 °C, for the three metal ions, respectively. The percent error of the determination corresponding to $\pm$ 1 mV deviation was calculated in each case and found to be much lower than the corresponding value obtained using the conventional M-ion-selective electrode / calomel reference system. The Cl^- and Cu^{2+} ion-selective electrodes employed were made by electroplating silver rod with $AgCl-Ag_2S$ and a platinum plate with CuS, respectively. The effect of pH, foreign ions, and temperature on the characteristics of these electrodes was studies.

INTRODUCTION

Direct potentiometry using the extrapolation method has found a spectacular renaissance during the last decades as a result of the availability of new ion-selective electrodes with their novel and diverse applications to many scientific and technological disciplines[1-3]. Inspite of being simple and rapid, the method has the disadvantage that any minor measurement changes due to systematic or unpredictable errors might lead to a significant error in the concentration value obtained from the calibration graph. The lower the slope of this graph the higher would be the error expected. For example, calibration graphs of triply charged ions exhibits a very low Nernstian slope (19.17 mV / decade at 25 °C) leading to a very high error in direct potentiometry. Therefore, no ion-selective electrode for their determination is known, only indirect determinations has been reported[4].

In the present work a new approach is described to increase the sensitivity of direct potentiometric determination of inorganic salts ($M^{z+} X_z$) by constructing Ecell– log C_M calibration graphs of high slopes (multiple Nernstian values). This approach has been tested using KCl, $CuCl_2$ and $CaCl_2$. Although the method is applicable to almost all potentiometric determinations of ionic salts, the matrix effect should be considered carefully on dealing with real samples, this is due to use of two ion-selective electrodes instead of one as in the normal technique.

This paper describes also a very simple method for the preparation of solid state membrane copper(II) and chloride ion–selective electrodes based on electrodeposition of CuS and AgCl / Ag_2S, respectively, on metallic surface.

This method enables manufactuing the electrode in different shapes, which is very difficult by the conventional methods[5–7]. Moreover, the deposited film being very thin provide a high degree of conductance. Recently, Lakshmi[8] prepared I^- and S^{-2} selective electrodes by coating graphite rods electrolytically with a thin film of silver and chemical conversion of the film into AgI or Ag_2S.

EXPERIMENTAL

Reagents and Electrodes Preparation

All solutions were prepared with doubly distilled water from analytical grade reagents. Potassium (glass type) and Calcium (II) ion–selective electrodes provided by INGOLD, West Germany, were employed. The Cu(II)–responsive electrode was prepared by electrodepositing copper on Platinum plate (0.3 x 0.5 cm) from 0.05 M Cu $(NO_3)^2$ solution using 2 mA cm^{-2} current for 60 min; following this step the copper layer was converted into CuS anodically. The Chloride electrode was prepared electrolytically by partially coating a silver wire with a layer of AgCl (from 0.1 M NaCl), and partially with a layer of Ag_2S (from 0.01 M Na_2S). The Cu^{+2} and Cl^- electrodes were washed thoroughly with distilled water and conditioned by soaking in 0.01 M solutions of $CuCl_2$ and NaCl, respectively.

Apparatus

Potentials were measured, at constant temperature, with Phillps type PW 9409 digital pH / mV meter. The conventional cell consisting of the ionselective electrode and a satureted callomel electrode (Tacussel, type–8) was used to investigate the performance characteristics of the home–made Cu^{2+} and Cl^- ion–selective electrodes. The multiple Nernstian slope calibration graphs for the MCl_z salts, where M^{z+} is K^+, Cu^{2+} or Ca^{2+}, were constructed using the following two ion–selective electrodes–containing cell:

M^{z+}–ion–selective electrode / test solution / Cl^-–ion–selective electrode. The latter was connected to the "reference" terminal of the potentiometer.

Selectivity

The selectivity of the prepared Cu^{+2} and Cl^- –ion–selective electtrodes was studied by applying the seperate solution method[9] for determination of the selectivity coefficients. A series of ions that would constitute a possible interference in the response of the investigated electrodes was tested. In the case of the Cu–electrode the series included Na^+, K^+, Ag^+ and $NH4^+$; divalent Mn, Fe, Co, Ni, Hg and Zn; and trivalent Al, Cr and Fe cations; while in the case of the Cl–electrode in included F^-, Br^-, CN^-, NO^-_3, S^{-2} and SO_4^{-2}.

Effect of pH

The working pH ranges of the prepared Cu^{2+} and Cl^- electrodes have been determined by following the electrode potential as a function of pH in a cell containing 10^{-3} M solution of KCl or $CuCl_2$. The pH value was varied between 1–12 by adding the appropriate amount of HCl or NaOH solutions.

Effect of temperature

To study the effect of temperature on the Cu^{+2} and Cl^- electrode potentials, 50 ml of 10^{-3} M of the test solution was transferred to the measuring cell containing the respective ion–selective electrode and a calomel electrode as the reference. The emf of the cell was recorded at different temperatures ranging from 20 to 70 °C.

Construction of (Ecell – log C_M) graph of high sensitivity

To the test solution (10^{-6} M) a standard solution of the respective chloride salt was added in suitable increments so as to cover the concentration range 10^{-6} – 3.2×10^{-2}M. The two ion–selective electrode–containing cell was employed.

RESULTS AND DISCUSSION

The results (Table 1) show that the performance characteristics of the present home-made Cu^{2+} and Cl^- ion-selective electrodes are comparable with those previously reported for their corresponding solid state[4] and heterogeneous membrane[6-7] electrodes. The temperature coefficients (dE / dt) of these electrodes were determined by plotting the electrode potential as a function of temperature in the range 20–70 °C, the slope (dE / dt) of the linear part of the obtained plot (Fig. 1) was substituted in the following equation[9]: $dE^\circ / dt = dE / dt \pm 2.3R / F \log C_x$, where C_x is the concentration of the ion X in the test solution, the plus and minus signs are used in case of $X = Cl^-$ and Cu^{2+} solutions, respectively. It has been found from Fig. 1A that the temperature coefficient of the Cu^{2+}-electrde is –0.0014 V / °C within the temperature range 35–64 °C. At $t > 35$ °C, the temperature change has a negligible effect on the electrode potential while at $t > 64$ °C the electrode seems to be no longer thermally stable as its potential increases sharply with the increase in temperature. This most probable due to interference of additional interfacial potential arising as a result of excessive thermal agitation and / or to enhancement of membrane conductance. In case of the Cl^--responsive electrode potential–temperature plot (Fig. 1B), the temperature coefficients were $+7.9 \times 10^{-4}$, -1.39×10^{-3} and -1.70×10^{-3} V / °C within the temperature ranges 20–37, 37–58 and 62–70°C, respectively. These results reflects a high thermal stability of the electrode over a relatively wide range of temperature.

Table 1. Performence charecteristics of the home-made Copper (II) and chloride electrodes at 25°C and their working pH ranges.

Electrode	Concentration range, M	Slope mV / decade	S* %	Response time, s	Interfering** ions j
Cu^{2+}	2.5×10^{-6}– 1.6×10^{-2}	29.8	1.8	< 5	Ag^+, Hg^{2+}, Cr^{3+}, Fe^{3+}
Cl^-	3.1×10^{-2}– 3.2×10^{-2}	-53.5	0.4	Instantaneous	Br^-, I^-, CN^- and S^{2-}

* Relative standard deviation (three preparations).

** Selectivity Coefficients $K_{xj}^{pot} > 10^{-2}$, where $x = Cu^{2+}$ or Cl^-.

The working pH range for the two electrodes was 1–12.

Ecell / log C_M Calibration Graphs using Two Ion-selective Electrodes.

A cell containing the metal ion (Mz^+)– and Cl^- selective-electrodes was employed to obtain Ecell / log C_M calibration graph of slope S =

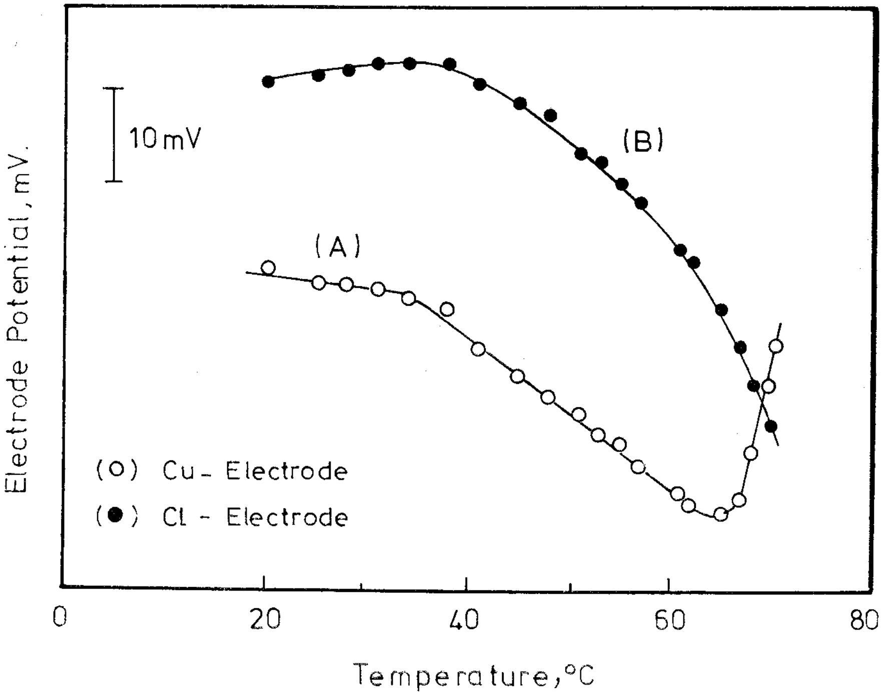

Fig. 1. Effect of temperature on the potential of the Cu^{2+} (– + –) and Cl. (–●–) electrodes in 10^{-3} M solutions of $Cu(NO_3)_2$ and NaCl, respectively.

SM + S_{Cl}, where S_M and S_{Cl} are the Nernstian slopes obtained using the metal ion-and Cl^- selective electrodes, respectively. The potential of such a cell can be related to the metal ion concentration as follows:

$$E_{Cell} = E_{Mz^+} - E_{Cl^-}$$

$$E_{Cell} = E^\circ_M + S_M \log C_M) - (E^\circ_{Cl} - S_{Cl} \log C_{Cl})$$

Substituting for $C_{Cl} = zC_M$

$$E_{Cell} = (E^\circ_M + S_M \log C_M) - (E^\circ_{Cl} - S_{Cl} \log zC_M)$$

$$E_{Cell} = K + (S_M + S_{Cl}) \log C_M$$

where K is a constant equals ($E^\circ_M - E^\circ_{Cl} + S_{Cl}$ log z). From the last equation, it is evident that E_{Cell} / log C_M relationship is a straight line with a slope of ($S_M + S_{Cl}$) and intercepting with $E_{Cell} = K$ at C_M = unity. Representative E_M / log C_M, E_{Cl} / log C_{Cl} and E_{Cell} / log C_M calibration graphs are shown in (Fig. 2). Collective results of the

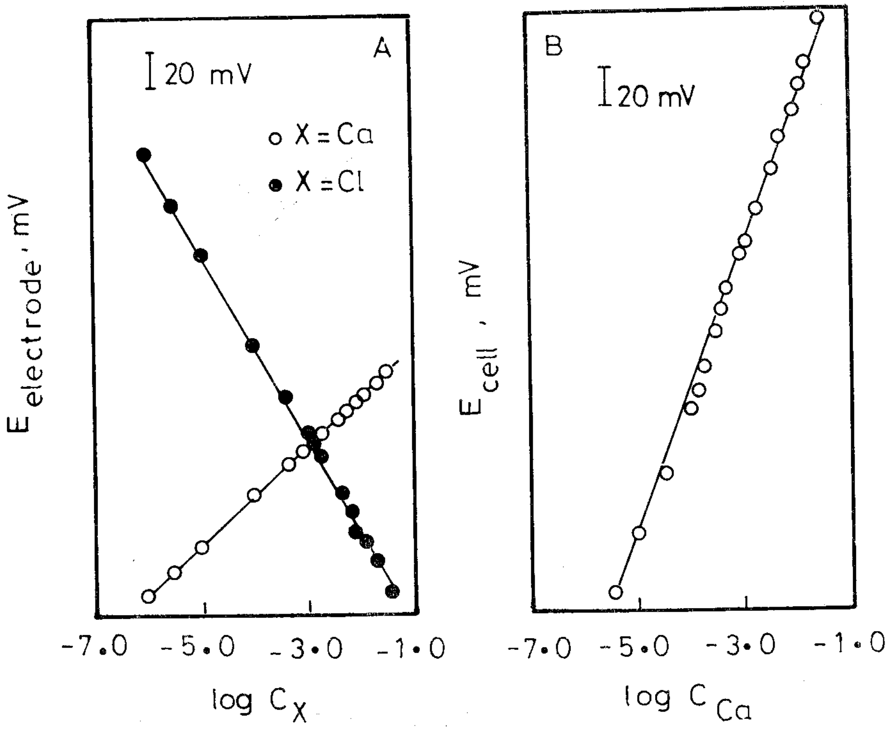

Fig. 2. A) Electrode potential vs log X (X = Ca or Cl) calibration graphs for Ca^{2+} and Cl^- ion-selective electrodes using calomel as the reference.

B) E_{cell} vs log C_{ca} calibration graph using a cell containing Ca^{2+}– (indicator) and Cl (reference) ion-selective electodes.

calibration graph's slope, coefficient of variation and percent error corresponding to a probable measurement error $\pm \delta E = 1$ mV are given in (Table 2). The percent error $\pm (\delta C / C_T)\ 100$, where C_T is the correct concentration, is callculated by aid of the following equation which is derived from Nernstian equation:

$$\pm (\delta C / C_T)\ 100 = (10 \pm \delta E / S - 1)\ 100$$

δ E and S are the measurement error and slope of the calibration graph employed, respectively. From (Table 2), it is evident that although the reproducibility of E_{Cell} / log C_M is nearly of the same order as that of E_M / log C_M plots, the percent error due to a given measuremeent is much less in case of the E_{Cell} / log C_M than in case of E_M / log C_M calibration graphs.

Table 2. Potentiometric responce using the conventional (reference electrodeindicator) cell and using the two ion-selective electrode-containing cell (t = 25°C).

		M-ISE[a] vd SCE[b]			M-ISE vd Cl^--ISE		
	Salt	Slope,mV	S%[c]	R%[d]	Slope,mV	S%	R%
Na^+	NaCl	53.5	1.6	4.2	113.1	0.1	2.0
Cu^{2+}	$CuCl_2$	29.8	1.8	8.0	80.5	1.7	2.9
Ca^{2+}	$CaCl_2$	26.5	1.5	9.1	78.0	1.3	3.0

a. Metal Ion-Selective Electrode.
b. Saturated Calomel Electrode.
c. Coefficient of variation (3 determinations).
d. Relative determination error corresponding to ± 1 mV measrement error.

CONCLUSION

It has been shown that in direct potentiometric measurements of inorganic salts, the use of a proper two ion-selective electrode-containing cell would highly increases the sensitivity of the calibraion graph, due to the obtained multiple Nernstian slope.

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