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Preparation of Chromium (III) and Copper (II) Liquid Membrane Electrodes using Two Methylcoumarin Derivatives

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Abstract- 4-methylcoumarin-7-yloxy-N-4-nitrophenyl acetamide and 4-methylcoumarin-7-yloxy-N-phenyl acetamide were used as effective ionophores for preparation of chromium (III) and copper (II) selective liquid membrane electrodes, respectively. Optimization of the composition of the membranes and the conditions of the analysis was performed, and under the optimized conditions the chromium (III) liquid membrane electrode has a detections limit of 1.0×10^{-10} with response time 4-6 s and the concentration range 1.0×10^{-4} to 1.0×10^{-10} M chromium (III) with a Nernstian slope of 20.25±0.4 mV/decade over the pH range of 4.0–7.5 and copper (II) liquid membrane electrode has a detection limit of 3.0×10-5 with response time about 5 s and the concentration range 1.0×10^{-1} to 3.0×10^{-5} M copper (II) with a Nernstian slope of 31.08±0.5 mV/decade over the pH range of 4.5–8. The chromium (III) and copper (II) selective electrodes were stable for about 8 and 5 weeks, respectively. They exhibit good selectivity for two ions. They were successfully applied for the direct determination of chromium (III) and copper (II) in wastewater and as indicator electrodes for potentiometric titration of copper ions and chromium ions with EDTA.

Keywords- 4-methylcoumarin-7-yloxy-N-4-nitrophenyl acetamide; 4-methylcoumarin-7-yloxy-N-4-phenyl acetamide; Chromium (III); Copper (II); Liquid membrane; Potentiometry

1. INTRODUCTION

Compounds of heavy metals are widespread [1-3], and industrial activities have greatly enhanced their presence in the environment [4,5]. Chromium is present in water in III and VI oxidation states, both of which come from different sources like tanning, electroplating, oxidative dying, and steel industries [6-8]. The III oxidation state is a vital nutrient, and its shortage can lead to metabolic disorders and diabetes. However, excess of chromium (III) compounds can lead to health conditions as illustrated by various in vitro evaluations on the damages of high levels of such compounds on DNA [9-12].

On the other hand, Cu is a key element for human metabolism, yet its high levels can be toxic, and the World Health Organization (WHO) recommends its levels in drinking water to be less than 2 mgL^{-1} [13]. However, the widespread industrial, and agricultural applications of Cu arising from its considerable electrical conductivity, chemical inertness, and capacity to form alloys [14], has increased its content in various industrial and urban waste waters, which necessitates the development of methods for cheap, facile, quick and on-line analysis [15-17].

Different methods have been used for the analysis of copper (II) and chromium (III) ranging from spectrophotometry [18,19], atomic absorption spectrometry (AAS) with flame or electrothermal atomization [20-23], ICP-AE [24,25], gravimetry and chromatography. Some of these techniques offer acceptable limits of detection and good selectivities, yet they are also costly, time-intensive and complex.

As an alternative ion-selective electrodes (ISEs) offer facile and quick analytical paths for the analysis of different ionic species [26-28], with further advantages of simple instrumentation, easy sample preparation and analysis, broad response range, good selectivity, and low costs. As a result, many commercial electrodes have been constructed and are offered for various analyte. The key ingredient of selective liquid membrane sensors is the complexing agent, also known as the ionophore, that allows for the selective response to an analyte.

This work tends to introduce two new potentiometric liquid membrane electrodes to chromium (III) and copper (II) determination. The electrodes were prepared by using two similar ligands 4-methylcoumarin-7-yloxy-N-4-nitrophenyl acetamide and 4-methylcoumarin-7-yloxy-N-4-phenyl acetamide (Figure 1) as excellent ionophores.

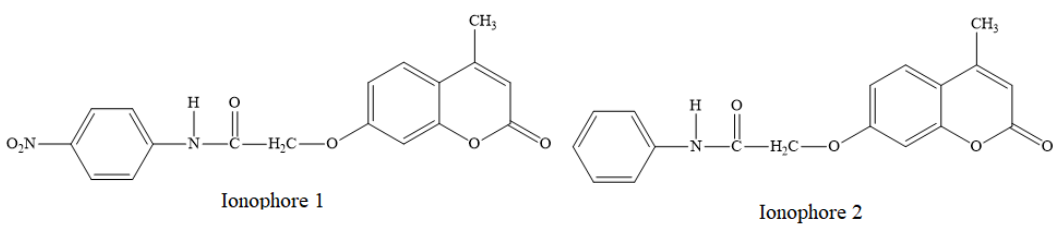

Figure 1. The structure of Ionophore 1 (4-methylcoumarin-7-yloxy-N-4-nitrophenyl acetamide) and ionophore 2 (4-methylcoumarin-7-yloxy-N-4-phenyl acetamide)

2. EXPERIMENTAL SECTION

2.1. Reagents

Benzyl acetate (BA), nitrobenzene (NB) and dibutyl phthalate (DBP), sodium tetraphenyl borate (NaTPB), polyvinyl chloride (PVC) powder, and tetrahydrofurane were obtained from Merck Co. The materials were not treated prior to use. 4-methylcoumarin-7-yloxy-N-4-nitrophenyl acetamide (ionophore 1) and 4-methylcoumarin-7-yloxy-N-4-phenyl acetamide (ionophore 2) were prepared according the procedures reported before [29]. All cation solutions were prepared using nitrate salts obtained Aldrich or Merck using deionized water.

2.2. Apparatus

The reference was a double junction Ag/AgCl. A HIOKI 3256.50 digital milli-voltmeter (±0.1 mV) was used for reading the potentials and pH readings were made using a Metrohm pH-meter and a combined glass electrode.

2.3. Construction of the ISEs

Different quantities of the ionophore 1 or 2, NaTPB (as the additive), PVC powder, DBP, BA, or NB (as the plasticizer) were admixed into 2 mL of THF, followed by aging to allow the solvent to obtain an oily mixture. Next, the tips of plastic tubes (3-5 mm o.d.) were inserted in these mixtures for a short time to allow a transparent membrane (0.3 mm in thickness) to form, which were then allowed to dry for 24 hours in ambient conditions. 1.0×10^{-3} M $Cr(NO_3)_3$ or $Cu(NO_3)_2$ solutions were then filled in the tubes, and the electrodes were soaked in 1.0×10^{-3} M $Cr(NO_3)_3$ or $Cu(NO_3)_2$ solutions for conditioning.

2.4. Emf Measurements

Electromotive force measurements were made using a cell as below:

Ag–AgCl, KC1 (satd.) | internal solution, 1.0×10^{-3} M $Cr(NO_3)_3$ or $Cu(NO_3)_2$| PVC membrane | sample solution | Ag–AgCl, KC1 (satd.)

The Debye- Hückel equation was used for calculating the activities.

3. RESULTS AND DISCUSSION

3.1. Membrane Composition

Membrane composition is key to its selectivity and response behavior. To evaluate the effects of the composition, various mixtures of the components were prepared and the behaviors of the resulting electrodes were monitored and recorded (Tables 1 and 2). Clearly, the chromium (III) selective electrode composed of 12% of the ionophore 1, 2% NaTPB, 30% PVC powder, and 56% DBP (no. 6, Table 1) had the best response behavior (20.25

mV/decade). The optimal copper (II) selective electrode, on the other hand, contained 10% of ionophore 2, 2% NaTPB, 30% PVC, and 58 % BA (no. 5, Table 2) and produced a Nernstian slope of 31.08±0.5 mV/decade.

Table 1. The optimization of the membrane ingredients of chromium (III) selective electrode

Membrane No.	Composition (%)				Slope (mV/ decade)	Working range (M)
	PVC (%wt.)	Plastisizer (%wt.)	Ionophore 1 (%wt.)	NaTPB (%wt.)		
1	35	(DBP)65	0	0	7.3 ±0.5	1×10^{-4} -1×10^{-1}
2	35	(DBP)63	0	2	11.8±0.4	1×10^{-4} -1×10^{-1}
3	33	(DBP)60	5	2	19.97±0.3	1×10^{-9} -1×10^{-5}
4	31	(DBP)59	8	2	17.56±0.3	1×10^{-9} -1×10^{-3}
5	30	(DBP)58	10	2	18.83±0.5	1×10^{-9} -1×10^{-6}
6	30	(DBP)56	12	2	20.25±0.4	1×10^{-10} -1×10^{-4}
7	33	(NB)60	5	2	19.4±0.6	1×10^{-9} -1×10^{-6}
8	31	(NB)59	8	2	18.98±0.4	1×10^{-9} -1×10^{-6}
9	30	(NB)58	10	2	11.5±0.3	1×10^{-9} -1×10^{-7}
10	30	(NB)56	12	2	12.13±0.5	1×10^{-8} -1×10^{-6}
11	33	(BA)60	5	2	10.2±0.5	1×10^{-5} -1×10^{-1}
12	31	(BA)59	8	2	15.9±0.5	1×10^{-5} -1×10^{-1}
13	30	(BA)58	10	2	9.9±0.5	1×10^{-6} -1×10^{-1}
14	30	(BA)56	12	2	6.9±0.5	1×10^{-5} -1×10^{-1}

Table 1, clearly shows that the slopes of the chromium (III) selective sensors containing no 4-methylcoumarin-7-yloxy-N-4-nitrophenyl acetamide (i.e. compositions no. 1, 2) were very low (7.3 and 11.8 mV/decade of concentration), which and were enhanced through increasing the ionophore content up to 12% (no. 6). In the case of the Cu^{2+} electrode, a similar behavior was observed in the absence of 4-methylcoumarin-7-yloxy-N-4-phenyl acetamide Table 2 (No. 1 and 2 Table 1 with respective response slopes of 8.4 and 10.7 mV/decade). Similarly increasing the amount of the ionophore up to 10% (no. 5), enhanced this behavior. Both phenomena reveal the key effects of the presence of these ionophores on the response of the sensors.

Evaluations of the effect of the plasticizer, as a key component of PVC-based membrane electrodes, with considerable lipophilicity allowing for the dissolution and diffusive mobility of the ionophore [30] is also important. Solvents with higher the dielectric constants tend to extract more polar ions, yet they allow for higher interference by undesired ions.

For the chromium (III) electrode, DBP (DC:6.4), and NB (DC:34.8), have produced better results than benzyl acetate (with DC of 5.1) (Table 1), which is probably due to its higher dielectric constant, which increases the possibility of the extraction of trivalent chromium ions. Yet, between these two, nitrobenzene in membrane containing 5% of ionophore has shown a

Nernstian slope 19.4 mV/Decade from 10^{-9} to 10^{-6} M (No. 7). In addition, dibutyl phthalate with the same amount of ionophore has shown a Nernstian behavior of 19.97 mV Decade^{-1} from 10^{-9} to 10^{-5} M (No. 3). Of course, by increasing the amount of ionophore to 12% and using dibutyl phthalate solvent, the slope of 20.25 mV Decade^{-1} has been obtained in a wider linear 10^{-10}-10^{-4} M (No. 6). While in the case of using nitrobenzene, the slope of the electrode has decreased with a further increase in the amount of the ionophore. Therefore, 12% ionophore 1, 56% DBP, 2% sodium tetraphenylborate and 30% PVC was chosen to be the best composition.

Table 2. The optimization of the membrane ingredients of copper (II) selective electrode

Membrane No.	Composition (%)				Slope (mV/decade)	Worjing range (M)
	PVC (%wt.)	plastisizer (%wt.)	Ionophore 2 (%wt.)	NaTPB (%wt.)		
1	35	(BA)65	0	0	8.4 ±0.5	1×10^{-4} -1×10^{-1}
2	35	(BA)63	0	2	10.7±0.4	1×10^{-4} -1×10^{-1}
3	33	(BA)60	5	2	19.15±0.3	1×10^{-8} -1×10^{-6}
4	31	(BA)59	8	2	18.6±0.3	1×10^{-5} -1×10^{-1}
5	30	(BA)58	10	2	31.08±0.5	1×10^{-5} -1×10^{-1}
6	30	(BA)56	12	2	25.8±0.4	1×10^{-3} -1×10^{-1}
7	33	(NB)65	5	2	12.35±0.6	1×10^{-5} -1×10^{-1}
8	31	(NB)63	8	2	12.2±0.4	1×10^{-5} -1×10^{-1}
9	30	(NB)60	10	2	18.78±0.3	1×10^{-9} -1×10^{-5}
10	30	(NB)59	12	2	10.14±0.5	1×10^{-6} -1×10^{-1}
11	33	(DBP)59	5	2	20.2±0.5	1×10^{-5} -1×10^{-1}
12	31	(DBP)59	8	2	15.9±0.5	1×10^{-5} -1×10^{-1}
13	30	(DBP)59	10	2	9.9±0.5	1×10^{-6} -1×10^{-1}
14	30	(DBP)59	12	2	6.9±0.5	1×10^{-5} -1×10^{-1}

Table 2 shows that the copper (II) selective electrode based on BA (no. 5) revealed the best response. Nitrobenzene and dibutyl phthalate, with higher dielectric constants, allow for extraction of high polarity interfering species while lowering the extraction of copper (II). The presence of 4-methylcoumarin-7-yloxy-N-4-phenyl acetamide and its complexation with the copper (II) ions compensates for this effect.

Incorporating ionic additive lowers the electrical resistance of liquid membranes, enhancing their response, and also facilitates the extraction of ionic species into the hydrophobic phase of the membranes [30]. The results in Tables 1 and 2, are in line with this concept. Incorporation of 2% wt. of sodium tetraphenyl borate (NaTPB) boosted the response

slope of both electrodes, due most probably to the facilitation of ion-exchange of chromium (III) and copper (II) between the aqueous and organic membrane phases.

3.2. Effect of pH

The effect of the pH of the test solution on the responses of the chromium (III) and copper (II) electrode response was tested at 1.0×10^{-5} M and 1.0×10^{-3} M chromium (III) and copper (II) ion solution, respectively. Adjustments of the solution pH between 2.0 to 10 were performed through spiking the test solutions with small quantities of concentrated NaOH and HCl solutions. As can be seen in Figure 2, the chromium (III) and copper (II) electrodes produced stable responses between 4.0-7.5 and 4.5-8.0, respectively.

Both ionophores have soft donor nitrogen atoms in their structures, which prefer charge-dipole interactions with chromium (III) and copper (II) ions, to those with H^+ ions. In case the H^+ concentration is considerably higher than those of chromium (III) and copper (II), the role of H^+ become significant. According to the experimental results in Figure 2 in pH values between of 4.0-7.5 and 4.5-8.0, the H^+ concentration was not enough to cause considerable competition complexation reactions with chromium (III) and copper (II). Yet, below the two pH values of 4.0 (for Cr(III)) and 4.5 (for Cu(II)), the concentration of hydrogen ion seems to have been enough to cause significant interference through competition with chromium (III) and copper (II) ions.

At pH values over 7.5 (for Cr(III)) and 8.0 (for Cu(II)), on the other hand, the concentrations of hydroxy ions become high enough to form soluble complexes with chromium (III) and copper (II) ions. Therefore, the pH ranges 4.0-7.5 and 4.5-8.0 were established as the tolerable ranges for the two sensors.

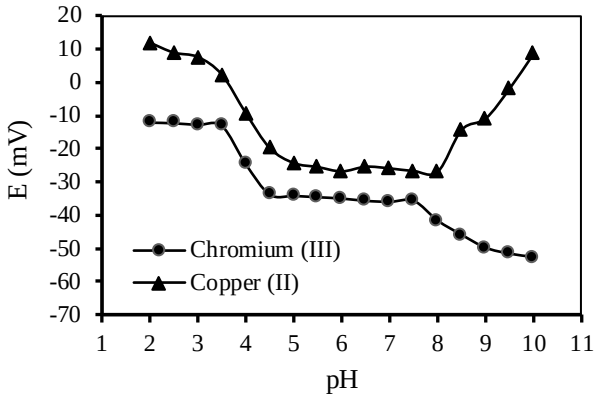

Figure 2. Influnce of pH changes on the response of the chromium (III) and copper (II) selective electrodes

3.3. Response Time

The response time of an electrode is the average time required to reach a value ±0.1 mV of the equilibrium potential of an electrode, upon its immersion in a set solution having concentrations tenfold higher than the previous, is well-established as the response time of the electrode. The other factors influencing the response time include the stirring rate, composition of the test solution, former applications or preconditioning of electrodes, and temperature [31].

The results recorded for the electrodes are illustrated in Figure 3, indicating the response time values to be around 5 s for the copper (II) sensor and about 4-6 s for the chromium (III) electrode (Figure 3).

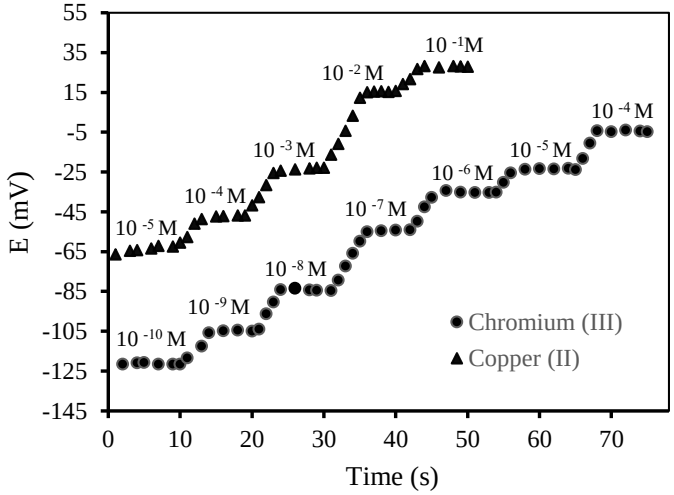

Figure 3. Response times of the chromium (III) and copper (II) selective electrodes

3.4. Sensitivity

The chromium (III) and copper (II) electrodes illustrated Nernstian slopes of 20.25 and 31.08 mV/decade (Figure 4) from 1×10^{-4} to 1×10^{-10} M and 1×10^{-1} to 3×10^{-5} M, respectively. These values clearly indicate the sensitivity of the developed electrodes for the intended target ions.

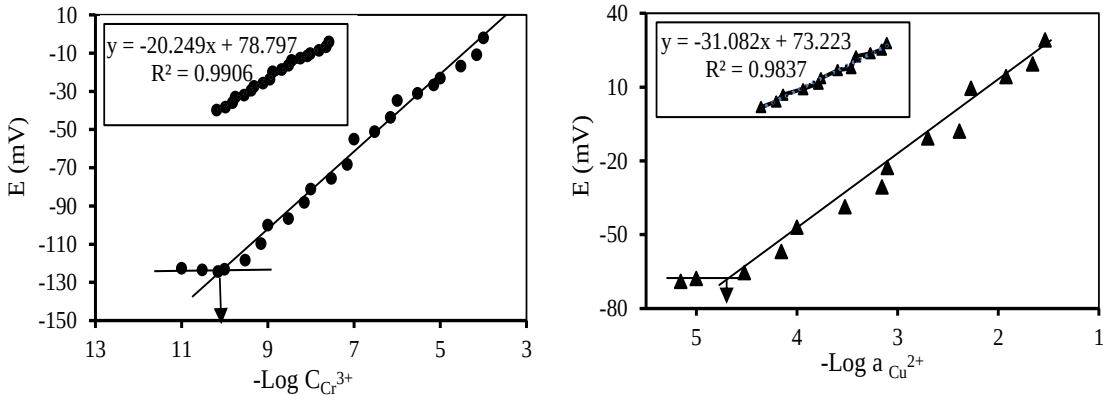

Figure 4. The calibration curves of the chromium (III) and copper (II) selective electrodes

The limit of detection (LOD), was calculated by determining the intersection point of the extrapolated sections of the linear parts of each calibration plot at low concentrations. The respective LODs determined in this fashion were 1.0×10^{-10} M and 3.0×10^{-5} M for the chromium (III) and copper (II).

3.5. Selectivity behavior

The selectivity of an electrode is its relative response to the primary as opposed to a secondary ion, which is expressed in terms of the selectivity coefficients, in such way that lower selectivity coefficients translate into higher selectivity. Here, the matched potential method (MPM) was used to determine the selectivity coefficients (K_{MPM}) [32-38] and the results are presented in Table 3. The results indicate that the maximum interference for chromium (III) is from Cu^{2+} (K_{MPM}:3.2×10^{-4}), while in the case of the copper (II) electrode the maximum interference was caused by Cd^{2+} (K_{MPM}: 9.9×10^{-3}). Yet even these values are acceptable for an ion selective electrode.

Table 3. The selectivity coefficients of chromium (III) and copper (II) selective electrodes for some interfering cations

Ion	K_{MPM}	K_{MPM}
	Chromium (III) selective Electrode	**Copper (II) selective Electrode**
Zn^{2+}	3.1×10^{-5}	4.0×10^{-3}
Ag^{+}	6.3×10^{-5}	1.6×10^{-3}
Pb^{2+}	6.2×10^{-6}	1.0×10^{-3}
Mg^{2+}	6.3×10^{-5}	5.0×10^{-3}
Cd^{2+}	2.5×10^{-5}	9.9×10^{-3}
Cr^{3+}	1	3.2×10^{-3}
Mn^{2+}	1×10^{-4}	1.2×10^{-4}
Cu^{2+}	3.2×10^{-4}	1
Na^{+}	1.6×10^{-3}	2.0×10^{-3}
Ni^{+}	3.0×10^{-3}	2.0×10^{-3}
Co^{2+}	4.0×10^{-5}	1.9×10^{-4}
Fe^{2+}	6.3×10^{-3}	7.4×10^{-4}
Ca^{2+}	2.0×10^{-3}	4.0×10^{-5}
Hg^{2+}	4.0×10^{-5}	1.6×10^{-4}

3.6. Lifetime

The lifetime of a liquid membrane sensor can be limited due to the leakage of the membrane ingredients (i.e. plasticizer, ionophore, or ionic additive) from the liquid membrane during application [30-35].

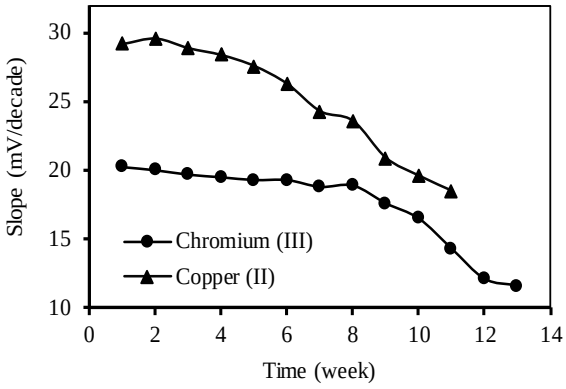

Figure 5. The lifetime of the chromium (III) and copper (II) selective electrodes

To evaluate the lifetime of the proposed electrodes the changes in the slopes of the electrodes were monitored over periods of their application [39-44]. During this period, each electrde was used for 1 hour each day, and its slope was recorded. Figure 5 illustrates the results over a period of 13 weeks, indicating that the developed copper (II) ISE has a lifetime of 5 weeks, without considerable changes in its response slope, while this value was around 8 weeks for the chromium (III) ISE. At the end of the lifetimes, the slopes of both electrodes started to drop at a considerable rate.

3.7. Analytical Applications

The proposed electrodes were successfully used as indicator electrodes in potentiometric titration experiments using 25.0 mL of 1.0×10^{-4} M of Cr(III) and Cu(II) solutions with 1.0×10^{-2} M solutions of EDTA. Figure 6 illustrates the titration plots. The sharpness of the endpoints supports the accuracy of results obtained using the developed electrodes.

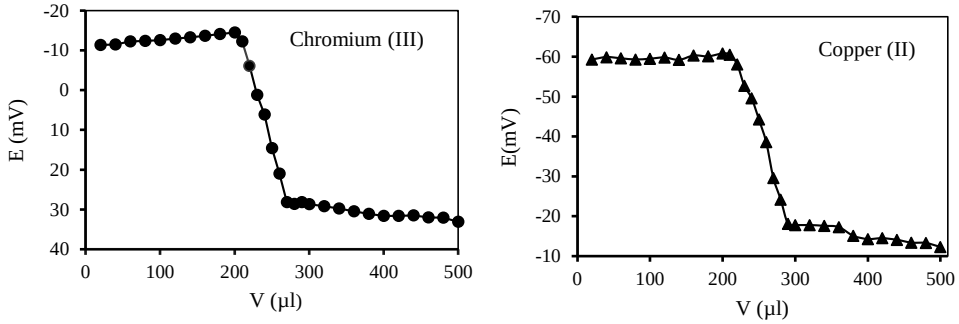

Figure 6. Titration plots of 1.0×10^{-4} M Cr(III) and Cu(II) solutions using 1.0×10^{-2} M EDTA, with the developed potentiometric indicator electrodes

3.8. Chromium (III) and copper (II) determination in real sample

For examining the applicability of the chromium (III) and copper (II) selective sensors to real samples, the sensors were applied in the determination of amounts of Cr(III) and Cu(II)

ions in industrial wastewater samples. The analytical procedures involved diluting the samples 10 folds and adjusting their pH values. The analyses were conducted using the developed electrodes, and control tests were also performed through flame atomic absorption spectroscopy (FAAS) and the results are presented in Table 4.

Table 4. Analysis of chromium (III) and copper (II) in wastewater sample

Sample	Measured by copper (II) selective electrode	Copper (II) Measured by FAAS	Measured by chromium (III) selective electrode	Chromium (III) Measured by FAAS
Wastewater	6.9×10^{-4} (±4.8) M	6.7×10^{-4} (±2.1) M	5.6×10^{-6} (±4.1) M	5.3×10^{-6} (±3.4) M

It can be seen that potentiometric results were comparable FAAS results in the case of both electrodes, reflecting their applicability to real samples.

3.9. Selectivity mechanism

Metal-ionophore interactions can be described based on the Lewis acid-base theory. According to this theory, metal ions act as Lewis acids (electron pair acceptors), while the ionophores act as Lewis bases (i.e. donors of electron pairs). Ralph Pearson classified Lewis acids and bases as being hard or soft [45]. Cu(II) ions tend to have stronger interactions with the relatively soft N atoms present in the Lewis base (4-methylcoumarin-7-yloxy-N-phenyl acetamide), since copper ions are soft acids based on the Pearson classification.

On the other hand, in 4-methylcoumarin-7-yloxy-N-4-nitrophenyl acetamide, an $–NO_2$ (nitro) group is added to the phenyl ring (in comparison to 4-methylcoumarin-7-yloxy-N-phenyl acetamide), which changes to the selectivity of this ion carrier from Cu(II) to Cr(III). This seems to come from the resonant and electron-withdrawing influences of the $–NO_2$ group, enhances the hardness of the N atom in the amide group and its tendency to interact with harder species like Cr(III) ions (i.e. the tendency of ionophore 1 to covalently share its electrons is less than ionophore 2, and hence only more electronegative/stronger acids like Cr(III) can form complexes. These results were also confirmed for the ion selective carbon paste electrodes that were previously prepared using these ionophores [29]. It is noteworthy that changing the type of electrode did not affect the selectivity.

3.10. Comparison study

Table 5 compares key features of the developed sensors with some formerly reported chromium (III) and copper (II) selective electrodes [46-51]. In the majority of cases, the developed sensors showed superiority over the previously reported ones, in terms of response

time, applicability pH range, and Nernstian slope (sensitivity) of the Cu(II) electrode, and Nernstian slope, applicable working range, limit of detection, and response time of the Cr(III) sensor.

Table 5. Comparison of the proposed selective electrode and the some previously reports

Ionophore	Ion	Slope	Detection limit (M)	Linear range (M)	Response time (S)	pH	Ref.
Alkylmethylimidazolium chlorides	Cu^{2+}	28.9	3.2×10^{-8}	1×10^{-7}-1×10^{-1}	5-10	2.5-6	[46]
2-(4-methyl pyperazine-1-yl methyl)-1-cyano cyclohexanone	Cu^{2+}	30.7	1×10^{-6}	1×10^{-6}-1×10^{-2}	10	3.5-8.5	[47]
1-cyano-1-piperidino-2(N- piperidino meth-yl)-cyclohexane	Cu^{2+}	28.4	6.3×10^{-9}	1×10^{-8}-1.5×10^{-2}	10	5-8.5	[48]
4-mehylcoumarin-7-yloxy-N-4-nitrophenyl acetamide	Cu^{2+}	31.08	3×10^{-5}	3×10^{-5}-1×10^{-1}	5	4.5-8	This study
N-(2H-[1,2,4] thiadiazolo[2,3-a]pyridine-2-ylidene)benzamide	Cr^{3+}	19.7	---	8×10^{-6}-1×10^{-1}	5	3.5-8	[49]
N, N-bis(salicylidene)-o-phenylene deaminate chromium(III)	Cr^{3+}	20.1	1.8×10^{-6}	7.5×10^{-6}-1×10^{-2}	8	4.5-7.7	[50]
4-amino-3-hydrazino-6-methyl-1,2,4-triazin-5-one	Cr^{3+}	19.7	5.8×10^{-7}	1×10^{-6}-1×10^{-1}	10	2.7-6.6	[51]
4-methylcoumarin-7-yloxy-N-4-phenyl acetamide	Cr^{3+}	20.25	1×10^{-10}	1×10^{-10}-1×10^{-4}	4-6	4-7.5	This study

4. CONCLUSION

Two novel potentiometric liquid membrane electrodes were fabricated using two derivatives of the 4-methylcoumarin. 4-methylcoumarin-7-yloxy-N-4-nitrophenyl acetamide (ionophore 1) and 4-methylcoumarin-7-yloxy-N-phenyl acetamide (ionophore 2) were prepared as described elsewhere and applied as ionophores for preparation of the chromium (III) and copper (II) selective liquid membrane electrodes, respectively. Ionophore 1 showed good chromium (III) ions selectively, while ionophore 2 tended to copper (II). Given the resonant and electron-withdrawing influence of the $–NO_2$ group in ionophore 1, the hard character of N atom present in the amide group is enhanced compared to the ionophore 2, increasing its affinity to interact with harder ionic species.

In the case of chromium selective electrode, the best liquid membrane composition was 12% ionophore 1, 2% NaTPB, 30% PVC, and 56 % DBP. For the copper sensor, the best liquid

membrane composition was 10% ionophore 1, 2% NaTPB, 30% PVC, and 58 % BA. The chromium (III) selective sensor had a response slope of 20.25 mV/decade of concentration, from 1.0×10^{-10} to 1.0×10^{-4} M, while the copper (II) electrode had a calibration plot slope of 31.08 mV/decade of concentration from 3.0×10^{-5} to 1.0×10^{-1} mol L^{-1}. Selectivity, wide pH range, rapid response time and acceptable linear concentration ranges of the electrodes turn them to desirable tools for the analysis of chromium (III) and copper (II) content in wastewater sample.

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