Sulfate-selective Electrode Based on a Complex of Copper

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A new sulfate-selective electrode based on the complex *N,N'*-bis(2-amino-1-oxo-phenelenyl)phenylenediamine copper(II) (CuL) as the membrane carrier was developed. The electrode exhibited a good Nernstian slope of -29.5 ± 0.5 mV/decade and a linear range of 1.0×10^{-7} – 1.0×10^{-1} M for sulfate. The limit of detection was 1.0×10^{-8} M. It has a fast response time of 10 s and can be used for more than three months. The selective coefficients were determined by the fixed interference method (FIM). The electrode could be used in the pH range 3.5–8.0. It was employed as an indicator electrode for direct determination of sulfate in pharmacy and cement samples.

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Sulfate is a major anion with relevance to industrial chemistry, environmental chemistry including pollution studies, biochemistry and mineralogy, as well as several other areas. The fact that sulfur in several other forms is ultimately determined after conversion to sulfate further enhances the importance of sulfate determination. Acid rain is a very serious problem closely connected with the fast development of industries and economics in the world. In order to clarify and evaluate the effect of acid rain on the acidification of the natural environment, the development of chemical sensors for measuring the primary components of acid rain is important.

Among chemical sensors ion-selective electrodes (ISEs) are mainly used for routine applications because they have a number of advantages over other methods of ion determination, such as analysis speed, portability, no sample destruction, and a wide measuring range. The essential property of ISEs is their selectivity, except for cases in which they are employed as detectors in connection with a separation method. In such a case, the best performance does not require selectivity, but only a short response time. Although the majority of the approximately 60 ions for which ionophore based polymeric membrane ion-selective electrodes have been described up to now are cations,^{1,2} a series of a new anion-selective electrodes were introduced recently as a result of the growing interest in the host-guest chemistry of anions.^{3–5} Classical liquid membrane electrodes for anions are based on quaternary ammonium salts and exhibit the Hofmeister selectivity sequence based on the analyte lipophilicity.^{6,7} Recently, a series of new anion-selective electrodes has been described, which display a selectivity deviating from the Hofmeister sequence as a result of unique interactions between the carriers and the anions. It has been well documented that the selective complexation of anions by synthetic ionophores can be used to design anion selective electrodes. For sulfate, so far, the most promising ISE is based on a bis(thiourea) derivative that forms four hydrogen bonds in a 1:1 complex with sulfate.⁸ Recently, a bis(imidazole) derivative was reported to exhibit a similar selectivity for sulfate with respect to major interferences along with a strong pH dependence.⁹ The synthetic hydrotalcite have been used as

ionophore for sulfate.¹⁰ For a truly anion-selective electrode, a strong interaction between the ionophore and the anion is required in order to complex the anion in a selective fashion. The potentiometric response of the membranes doped with these complexes is believed to be based on the coordination of analyte anion axial ligand to the metal center of the carrier molecule.^{11,12}

Recently, we have used ionophores in the construction of ISEs for NO_3^- ^{13,14} and SCN^- .¹⁵ In the present paper, we report the use of *N,N'*-bis(2-amino-1-oxo-phenelenyl)phenylenediamine copper(II) as an excellent ionophore for the preparation of a high selective ISE for the potentiometric determination of sulfate ion over a wide concentration range. The potentiometric response properties, reproducibility and selectivity of ISE were evaluated by the response potentials and selectivity coefficients. The ion which has been considered is sulfate, since it is difficult to recognize this species by potentiometric methods due to its highly hydrophilic character. A sulfate ISE, which displayed the best performance, was used for a rapid determination of sulfate concentration in samples.

Experimental

Reagents

PVC of high relative molecular weight, trioctylmethyl ammonium chloride (TOMAC) and dibutyl phthalate (DBP), were used as received from Aldrich. Potassium or sodium salts of all anions, tetrahydrofuran (THF) and all other chemicals were of the highest purity available from Merck, and were used without further purification, except THF, which was distilled before use. The ionophore of *N,N'*-bis(2-amino-1-oxo-phenelenyl)phenylenediamine copper(II) (CuL) (Fig. 1) was prepared essentially as described previously¹⁶ and used after purification. The pH adjustments were made with dilute hydrochloric acid and sodium hydroxide solutions as required. Wastewater samples were filtered through a filter paper. A stock solution of sulfate was prepared by dissolving the appropriate amount of sodium sulfate in 100 mL of water. Working solutions were prepared by successive dilutions with water. Both standard stock and working solutions of the anions tested were prepared in carbonate free doubly distilled water.

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Fig. 1 The structure of *N,N'*-bis(2-amino-1-oxo-phenelenyl)-phenylenediamine copper(II) (CuL).

Electrode preparation

The membrane ion-selective electrodes were prepared according to a previously reported method.¹⁷ A mixture of PVC, plasticizer (DBP), and the membrane additive (TOMAC), with a total mass of 200 mg was dissolved in approximately 10 mL of freshly distilled THF. To this mixture was added the electroactive material (CuL) and solution was then mixed well. The resulting mixture was poured into a small flat-bottom dish of 2 cm diameter; this was covered with a piece of filter paper and the solvent was allowed to evaporate at room temperature. The resulting membrane (*ca.* 0.2 mm thick) was then sectioned with a cork borer and mounted across the opening of a PVC tube of about 7 mm i.d. and 1.5 cm length using a PVC glue in THF. The PVC tube with the membrane was then filled with an internal solution of in 1.0×10^{-3} M Na_2SO_4 . The filled electrode was conditioned by soaking in 1.0×10^{-3} M sulfate solution. The first conditioning time was approximately 24 h, until a stable potential value was obtained and then 30–40 min intervals were employed for successive uses. A silver/silver chloride electrode was used as an internal reference electrode.

Potential measurement and calibration

The potential build up across the membrane electrode was measured using a galvanic cell of the following type: $\text{Ag}|\text{AgCl}|\text{KCl}$ (3 M) internal solution (1.0×10^{-3} M Na_2SO_4)|PVC membrane|test solution||SCE. All potentials were measured at $25 \pm 1^\circ\text{C}$ using a digital pH/mV meter, Model 691 Metrohm. A saturated calomel electrode (SCE, Metrohm) with a fiber junction was used as the external reference electrode. Activities were calculated according to the Debye-Hückle procedure¹⁸ for the calibration curve, concentration instead of activity was used. The pH of the sample solution was monitored simultaneously with a conventional glass pH electrode (Metrohm).

Before the measurements were started, the electrode was preconditioned in stirred water until a steady potential was obtained. The performance of the electrode was investigated by measuring its potential in sodium sulfate solutions prepared in the concentration range 1.0×10^{-7} – 1.0 M by serial dilution. All solutions were freshly prepared by dilution from the stock standard solution, 2.0 M, with doubly distilled water. The solutions were stirred and the potential readings were recorded when they became stable. The data were plotted as observed potential *vs.* the logarithm of the SO_4^{2-} concentration. Potentiometric titration of 20 mL 1.0×10^{-4} M SO_4^{2-} solution was carried out with 0.01 M Ba^{2+} solution using the sulfate-selective electrode as the indicator electrode in conjunction with a fiber function SCE electrode.

Results and Discussion

Response behavior

The plasticized PVC-based membrane electrode containing the CuL carrier generated stable potential responses in solutions

containing sulfate. Therefore, we studied in detail the performance of the membrane electrode based on this carrier for sulfate in aqueous solutions.

In preliminary experiments, membranes with and without carrier were constructed. The membrane with no carrier displayed insignificant selectivity toward sulfate and the response was not reliable, whereas, in the presence of the proposed carrier, the optimized membrane demonstrated Nernstian response and remarkable selectivity for sulfate over several common inorganic and organic anions. The preferential response toward SO_4^{2-} is believed to be associated with the coordination of sulfate with the central metal ion of the carrier.

The influence of membrane composition

A membrane is a phase, finite in space, which separates two other phases and exhibits individual resistance to the permeation of different species.

A polymer membrane gives a unique opportunity to obtain a variety of electrodes selective towards particular ions by doping each membrane with a certain ionophore. A polymer matrix provides mechanical stability of the membrane, chemical stability, clean surface of the resulting membrane, and chemical inertness and can be adjusted to fit extra requirements, *i.e.*, physiological fluids samples, biocompatibility, adhesion, *etc.*

Initially, plasticizers were applied to a polymer matrix in order to decrease its viscosity and provide mobility of membrane constituents within the membrane phase. In PVC membranes, plasticizer acts as a membrane solvent, affecting membrane selectivity through both extracting of ions into organic phase and influencing their complexation with the ionophore. Typical PVC plasticizers used for ISE membranes are 2-nitrophenyl octyl ether (*o*-NPOE, polar) and bis(2-ethylhexyl)sebacate (DOS, apolar).

Lipophilic ionic additive is a salt of a non-exchangeable lipophilic anion/cation and an exchangeable counter ion. Ionic sites provide electro-neutrality of the membrane with neutral ionic carriers, so that no significant amount of counter ions can be co-extracted into the membrane together with the primary ion. Therefore, the membrane is permeable only for ions of the same charge sign as the primary ion (Donnan exclusion) and demonstrates theoretical Nernstian response. Moreover, lipophilic ionic sites reduce electrical resistance of the membrane, which is especially important for micro-dimensional electrodes.

Ion carriers as a class of ionophores are lipophilic complexing agents having the capability of binding ions reversibly and of transporting them across organic membranes by carrier translocation. For an analytically relevant application of ionophores in solvent polymeric membranes for ion selective electrodes at least four requirements: 1) lipophilicity of ionophore, 2) ionophore exchange kinetics, 3) ion selectivity of membranes, and 4) intrinsic selectivity of ionophores, have to be met simultaneously. It is well known that the sensitivity, linear dynamic range, and selectivity of the ISEs depend not only on the nature of the carrier used, but also significantly on the membrane composition and the properties of the additives employed.^{19,20} Thus, the influences of the membrane composition and nature, the amount of plasticizer, and the lipophilic additives on the potential response of the membrane were investigated. Several membranes were prepared with different compositions. The optimized membrane compositions are summarized in Table 1. The blank membrane without ligand containing PVC, DBP and TOMAC was also prepared and its potential response toward varying concentrations of SO_4^{2-} ion was measured. As is obvious from Table 1, the

Table 1 Optimization of membrane ingredients

No.	Percent (w/w) of various components				HTAB	Slope/mV decade ⁻¹	Linear range/M	Detection limit/M
	PVC	DBP	Ionophore	TOMAC				
1	30	65	0	5	—	—	—	—
2	25	67	3	5	—	-5.5	$1.0 \times 10^{-5} - 1.0 \times 10^{-3}$	1.0×10^{-5}
3	23	71	6	0	—	-12.0	$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$	1.0×10^{-5}
4	30	67	3	0	—	-16.8	$1.0 \times 10^{-4} - 1.0 \times 10^{-1}$	1.0×10^{-4}
5	36	58	6	0	—	-21.6	$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$	5.0×10^{-6}
6	31	61	5	3	—	-29.5	$1.0 \times 10^{-7} - 1.0 \times 10^{-1}$	7.0×10^{-8}
7	30	60	6	4	—	-25.5	$1.0 \times 10^{-5} - 1.0 \times 10^{-3}$	5.0×10^{-6}
8	30	65	5	0	—	-31.1	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	1.0×10^{-5}
9	32	61	5	2	—	-20.0	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	1.0×10^{-5}
10	20	70	6	4	—	-10.6	$1.0 \times 10^{-6} - 1.0 \times 10^{-3}$	1.0×10^{-6}
11	31	61	5	—	3	-21.5	$1.0 \times 10^{-4} - 1.0 \times 10^{-1}$	1.0×10^{-4}
12	30	63	5	—	2	-12.7	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	1.0×10^{-5}
13	22	70	5	—	3	-27.1	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	1.0×10^{-6}

membrane without the ionophore displayed insignificant selectivity toward sulfate whereas, in the presence of the ionophore, the membrane shows remarkable selectivity for sulfate. Among the different compositions studied, the membrane incorporating 31% PVC, 61% DBP, 3% TOMAC and 5% CuL exhibits the best response characteristics. Increases in %PVC strongly influence the diffusion coefficients of the carriers and other components in the membrane phase. Therefore, this composition was used to study various operation parameters of the electrode, such as working concentration range, sensitivity, lifetime, response time and pH.

It is well known that the presence of lipophilic sites in anion-selective membrane electrodes not only reduce the ohmic resistance²¹ and improve the response behavior and selectivity^{22,23} but also, in cases where the extraction capability of the ionophore is poor, enhance the sensitivity of the membrane electrode.²⁴ Moreover, the lipophilic additives may catalyze the exchange kinetics at the sample-membrane interface.²⁵ In order to investigate the effect of ionic sites in the membrane system with DBP as plasticizer, we studied the influence of the TOMAC concentration. The potentiometric response of the membranes was greatly improved in the presence of lipophilic cationic additives. It is known that lipophilic salts not only reduce the membrane resistance, but also enhance the response behavior and selectivity, and reduce the interference from the sample.^{26,27} Previous studies have shown that there is an optimal concentration of lipophilic ionic additives in the membranes that gives the best electrode performance. The effect of TOMAC concentration in the membranes was investigated at several carrier/additive mole ratios. Better response characteristics, *i.e.* Nernstian response and improved selectivity, were usually observed with an ionophore/TOMAC weight ratio of approximately 1.7, which corresponds to a mole ratio of approximately 1.6. The presence of lipophilic ionic sites is beneficial for both neutral carrier and charged carrier-based ion-selective electrodes.^{21,28} However, for the charged carrier-based ion-selective electrodes, the charge sign of the ionic sites that gives the highest potentiometric selectivities depends on the charge of the ionophore and the charges of the primary and interfering ions as well as on the stoichiometry of their complexes with the ionophore.²⁹

The plasticizer/PVC ratios of 1.6–3.5 were examined. The membrane prepared with a plasticizer/PVC ratio of about 2.0 was found to have the best sensitivity and the widest linear range.

Fig. 2 Calibration graph of the SO_4^{2-} -selective electrode based on CuL.

Response characteristics of the electrodes

The potential response of the optimized sulfate-selective electrode to varying concentration of SO_4^{2-} ions was examined. All the emf values were corrected for liquid junction potential using the Henderson equation. The average slope of the calibration plot was -29.5 ± 0.5 mV/decade. The calibration plot is shown in Fig. 2; it indicates a linear range from 1.0×10^{-7} to 1.0×10^{-1} M ($R = 0.999$). The practical limit of detection, defined as the concentration of sulfate ion obtained from the intersection of two extrapolated segments of the calibration graph, was about 7.0×10^{-8} M. The optimum equilibration times for sulfate-selective electrode in the presence of 1.0×10^{-3} M potassium sulfate was 24 h, after which the electrode would generate stable potentials in contact with SO_4^{2-} solutions. The characteristic properties of the optimized membrane are summarized in Table 2.

The stability and reproducibility of the electrodes were also tested. The standard deviation of 20 replicate measurements at 1.0×10^{-2} , 1.0×10^{-3} and 1.0×10^{-4} M SO_4^{2-} were ± 0.3 , ± 0.5 and ± 0.7 mV, respectively. The long-term stability of the electrode was studied by periodically re-calibrating in standard solutions and calculating the response slope over the range of 1.0×10^{-7} – 1.0 M.

The influence of the concentration of internal solution on the potential response of the sulfate-selective electrode was studied. The results showed that the concentration of the internal solution does not cause any significant difference in the potential response of the electrodes, except for an expected

Fig. 3 Effect of pH of the test solution on the potential response of the SO_4^{2-} -selective electrode based on CuL at the concentrations of: a, 1.0×10^{-3} M; b, 1.0×10^{-2} M.

Fig. 4 Response time of the membrane electrode for sulfate with change of concentration from: a, 1.0×10^{-8} M to 1.0×10^{-7} M; b, 1.0×10^{-7} M to 1.0×10^{-6} M; c, 1.0×10^{-6} M to 1.0×10^{-5} M; d, 1.0×10^{-5} M to 1.0×10^{-4} M; e, 1.0×10^{-4} M to 1.0×10^{-3} M; f, 1.0×10^{-3} M to 1.0×10^{-2} M; g, 1.0×10^{-2} M to 1.0×10^{-1} M.

change in the intercept of the resulting Nernstian plots.

The effect of the pH of the test solution (1.0×10^{-2} and 1.0×10^{-3} M) on the response of the membrane electrode was examined at two SO_4^{2-} concentrations. The pH value was adjusted with dilute hydrochloric acid and sodium hydroxide as required. As illustrated in Fig. 3, the potentials remain constant within a pH range of approximately 3.5–8.0. Variation of the potential at $\text{pH} < 3.0$ could be related to protonation of CuL in the membrane phase, which results in a loss of its ability to interaction with SO_4^{2-} ions. At higher $\text{pH} > 8.0$, the potential drop (negative slope) may be due to interference from hydroxide ions. In high pH media, hydroxyl ion will compete with sulfate ion for the cation sites in the membrane.

The response time, defined as the time elapsed from the dipping of the electrode in the solution until the equilibrium potential was reached, varied from 5 to 10 s, depending on the analyte concentration, being faster when the concentration was higher. The signal stability was good, *i.e.* 3 mV h^{-1} .³⁰ The actual potential *versus* time traces are shown in Fig. 4. The sensing behavior of the membrane electrode did not depend on whether the potentials were recorded from low to high concentrations or *vice versa*.

The optimum equilibration time for the membrane electrode in the presence of 1.0×10^{-3} M K_2SO_4 was 24 h, after which the electrode would generate stable potentials in contact with sulfate solution. The potentiometric response of the membrane

Table 2 Characteristics of optimized SO_4^{2-} -ISE

Linear range/M	$1.0 \times 10^{-7} - 1.0 \times 10^{-1}$
Slope/mV decade ⁻¹	-29.5
pH range	3.5–8.0
Precision	At concentrations of 1.0×10^{-2} , 1.0×10^{-3} and 1.0×10^{-4} M SO_4^{2-} , standard deviations of ± 0.3 , ± 0.5 and ± 0.7 mV
Detection limit/M	7.0×10^{-8}
Life time/month	>3
Response time/s	5–10

Table 3 Stability and reproducibility of the SO_4^{2-} -ISE ($n = 5$)

Time/day	Slope/mV decade ⁻¹	Linear range/M
1	-29.5 ± 0.5	$1.0 \times 10^{-7} - 1.0 \times 10^{-1}$
7	-29.5 ± 0.5	$1.0 \times 10^{-7} - 1.0 \times 10^{-1}$
14	-29.5 ± 0.5	$1.0 \times 10^{-7} - 1.0 \times 10^{-1}$
21	-29.5 ± 0.5	$1.0 \times 10^{-7} - 1.0 \times 10^{-1}$
35	-29.5 ± 0.5	$1.0 \times 10^{-7} - 1.0 \times 10^{-1}$
49	-29.5 ± 0.7	$5.0 \times 10^{-7} - 1.0 \times 10^{-1}$
60	-29.0 ± 1.0	$5.0 \times 10^{-7} - 1.0 \times 10^{-1}$
70	-29.0 ± 1.2	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$
90	-28.5 ± 1.5	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$

Table 4 Selectivity of coefficients, determined by use of the fixed interference method for the SO_4^{2-} -ISE

Interference ion	$\log K_{\text{sul}, A}^{\text{pot}}$	Interference ion	$\log K_{\text{sul}, A}^{\text{pot}}$
F^-	-2.7	PO_4^{3-}	-4.1
Cl^-	-3.0	Citrate	-3.9
Br^-	-2.6	IO_3^-	-4.0
I^-	-4.0	CO_3^{2-}	-2.5
CN^-	-3.2	$\text{S}_2\text{O}_3^{2-}$	-2.1
SCN^-	-2.4	ClO_3^-	-2.5
$\text{Cr}_2\text{O}_7^{2-}$	-2.9	CrO_4^{2-}	-3.8
OAc^-	-2.0	NO_2^-	-4.0
NO_3^-	-4.6	HPO_4^{2-}	-3.5

electrode to different concentrations of SO_4^{2-} was examined using the optimized membrane composition and the conditions described above. In the traditional procedure, the membrane is conditioned in a solution that contains a relatively high concentration of the primary ion. This ensures stable and reproducible electrode behavior and is recommended for practical use of the sensor. However, the presence of these primary ions is often the reason for the non-Nernstian response toward highly discriminated ions. The calibration plot is shown in Fig. 2, which shows the linear range to be from 1.0×10^{-7} – 1.0×10^{-1} M; the Nernstian slope is -29.5 ± 0.5 mV decade⁻¹ of SO_4^{2-} concentration. The practical limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph was 7.0×10^{-8} M.

The electrode was tested over a period of three months to investigate stability. During this period the electrode was in daily use and was stored in 1.0×10^{-4} M SO_4^{2-} solution when not in use. Before each measurement, the electrode was conditioned in 1.0×10^{-3} M K_2SO_4 for approximately 30 min. No significant change in the performance of electrode (slope, linear range) was observed during this period (Table 3). Storage of the electrode in solution for extended periods, however, especially in stirred solution, resulted in a slight

Table 5 Comparison of the potentiometric parameters of the proposed SO_4^{2-} -ISE with those of other SO_4^{2-} -ISEs

A^-	The proposed SO_4^{2-} -ISE	Ref. 10	Ref. 9	Ref. 35	Ref. 36
Nernstian slope/mV decade ⁻¹	-29.5 ± 0.5	I, -26.2 ± 0.6 ; II, -26.4 ± 0.7 ; III, -29.6 ± 0.8^a	-28.5	-28.9 ± 0.5	-29.2 ± 0.3
Linear range/M	$1.0 \times 10^{-7} - 1.0 \times 10^{-1}$	I, $4.0 \times 10^{-5} - 2.0 \times 10^{-2}$; II, $4.0 \times 10^{-5} - 3.0 \times 10^{-2}$; III, $4.0 \times 10^{-5} - 4.0 \times 10^{-2}$	$3.16 \times 10^{-5} - 5.0 \times 10^{-1}$	$1.0 \times 10^{-6} - 1.0 \times 10^{-2}$	$1.0 \times 10^{-6} - 1.0 \times 10^{-2}$
Limit of detection/M	7.0×10^{-8}	(I, II, III), 4.0×10^{-5}	3.16×10^{-5}	8.0×10^{-7}	8.0×10^{-7}
Response time/s	5 – 10	I, 60 – 360; II, 60 – 180; III, 60	—	10	10
Interfering ion	—	(I, II, III), SCN^- , $\text{C}_2\text{O}_4^{2-}$, $\text{S}_2\text{O}_3^{2-}$, HCO_3^- , HSO_3^-	NO_3^- , NO_2^- , Br^-	—	—
$K_{\text{sul}, \text{A}^-}^{\text{pot}} > 1.0 \times 10^{-2}$					

a. Electrodes I, II and III include similar ionophore Mg/Al- SO_4 with different plasticizer (DBP, NPOE and Silopren K 1000, respectively).

gradual decrease in the slope, as is usual for many plasticized PVC membranes, probably as a result of leaching of the ionophore from the membrane.

Potentiometry selectivity

The selectivity behavior is obviously one of the important characteristics of ion-selective electrodes, determining whether reliable measurement in the target sample is possible. The selectivity of the proposed sulfate ion selective electrode over other anions (A^-) was important; their potential responses were investigated in the presence of a wide variety of interfering foreign anions using the mixed solution method (MSM).^{31,32} Potentiometric selectivity coefficients ($K_{\text{sul}, \text{A}^-}^{\text{pot}}$) describing the preference of the membrane for an interfering ion A^- relative to SO_4^{2-} were determined by the fixed interference method (FIM). The selectivity coefficients for various anions were evaluated by the mixed solution method with a fixed concentration of interferent (0.10 M), and varying amounts of SO_4^{2-} concentrations. Table 4 lists the potentiometric selectivity coefficient data of the sensor for several anions relative to SO_4^{2-} . The selectivity coefficients clearly indicate that the electrode is selective to sulfate over a number of other inorganic and organic anions. As it is evident from the data in Table 4, the electrode based on CuL has relatively high selectivity toward SO_4^{2-} relative to anions such as nitrate, bromide, and several common anions. The compound of CuL, seems to higher than interaction with the SO_4^{2-} ion to any of the remainder anion tested. It is interesting to note that the observed selectivity pattern for the SO_4^{2-} -ISE significantly differs from the so-called Hofmeister selectivity sequence.

The interfering effect of the ions is in the following order: $\text{OAc}^- > \text{S}_2\text{O}_3^{2-} > \text{SCN}^- > \text{ClO}_3^- = \text{CO}_3^{2-} > \text{Br}^- > \text{F}^- > \text{Cr}_2\text{O}_7^{2-} > \text{Cl}^- > \text{CN}^- > \text{HPO}_4^{2-} > \text{I}^- = \text{NO}_2^- = \text{IO}_3^- > \text{NO}_3^-$.

The electrode demonstrates a significant deviation in selectivity from the Hofmeister series:³³ large lipophilic anions $> \text{ClO}_4^- > \text{SCN}^- > \text{I}^- > \text{NO}_3^- > \text{Br}^- > \text{N}_3^- > \text{NO}_2^- > \text{Cl}^- > \text{OAc}^- > \text{SO}_4^{2-}$. A theoretical treatment of liquid anion-exchanger membranes has shown that this kind of behavior is typical of dissociated anion-exchangers, in which the complexation between the cationic sites and the counter ions in the membrane phase is negligible. The reasons that the selectivity coefficients proposed for the sulfate electrode do not comply with the Hofmeister series may involve specific interaction of the anions with the metal center in the carrier used in this study, *i.e.* chemical recognition of the anions, and especially of sulfate, by the complex. The selectivity is completely described by the distribution coefficients of the various anions between the sample solution and the membrane phase³⁴ from the data given in Table 4; it is

immediately obvious that the SO_4^{2-} -ISE is highly selective with respect to other inorganic and organic anions. This is most probably due to the weak interaction between these anions and the ionophore. According to hard-soft acid and base (HSAB) theorem, interaction of sulfate with complex is *via* nitrogen. Thus, according to hard-soft acid and base theory, Cu^{2+} is a borderline acid, but coordination of the nitrogen atoms of chelate lead to hardening this cation and so it can interact with the oxygen atoms on the sulfate anion (hard base).

Table 5 lists the linear range, detection limit, slope, response time and selectivity coefficients of some of other sulfate-selective electrodes against proposed sulfate-selective electrode for comparative purposes.^{9,10,35,36} As can be seen from the table, the selectivity coefficients obtained for the proposed electrode are superior to those reported for other SO_4^{2-} -selective electrodes listed in Table 5. It is noteworthy that the limit of detection, linear range, slope and response time of the proposed electrode is also considerably improved with respect to those of previously reported SO_4^{2-} -selective electrodes.

Analytical applications

The proposed membrane electrodes were found to work well under laboratory conditions. The sulfate-selective electrode was used as an indicator electrode in the successful titration of a SO_4^{2-} solution (20.0 mL, 1.0×10^{-4} M) with a Ba^{2+} solution (1.0×10^{-2} M). The resulting titration curve is shown in Fig. 5. It is seen that the amount of sulfate ion can be accurately determined with the electrode. The electrode was also successfully applied to the direct determination of sulfate content in a fixed amount of cement. To 0.5 g of the cement sample was added 20 mL of concentrated HCl and the mixture was boiled for 30 min. The resulting mixture was then filtered and the filtrate was neutralized with 0.1 M sodium hydroxide solution and diluted to 50.0 mL with distilled water. The sulfate content of the final solution was determined by the proposed electrode using the standard addition method and also by gravimetric method as a reference method. The comparison of the results obtained from three measurements ($0.74 \pm 0.03\%$) and the certified value (0.75%) shows that the present electrode can be used in determination of SO_4^{2-} in real samples. Also, an attempt was made to determine sulfate ions in samples water. The samples were analyzed without any treatment. The comparison of the results obtained from five measurements by SO_4^{2-} -selective electrode (13.4 ± 0.5 mg/lit), by electrothermal atomic absorption spectrometry (ETAAS) (12.8 ± 0.6 mg/lit) and the certified value by gravimetric method (12 mg/lit) shows good agreement between the potentiometric, ETAAS and gravimetric procedures. The sulfate-selective electrode has also been

Fig. 5 Potentiometric titration curve of 20.0 mL of 1.0×10^{-4} M Na_2SO_4 with 1.0×10^{-2} M Ba^{2+} , using the SO_4^{2-} -selective electrode as an indicator electrode.

applied to the determination of sulfate in drugs. To 0.2 g of the drug sample was added 20 mL of concentrated HNO_3 . The resulting mixture was then filtered and the filtrate was neutralized with 0.1 M sodium hydroxide solution and diluted to 50.0 mL with distilled water. The sulfate content of the final solution was determined by the proposed electrode using the standard addition method and also using a gravimetric method as a reference method. The comparison of the results obtained from five measurements (131 ± 2 mg/tablet) and the certified value obtained by the gravimetric method (129 mg/tablet) shows good agreement between the potentiometric and gravimetric procedures.

Conclusion

The membrane SO_4^{2-} -selective electrode, prepared with N,N' -bis(2-amino-1-oxo-phenelenyl)phenylenediamine copper(II) under optimal PVC-membrane ingredients revealed a Nernstian response over a wide sulfate concentration range, fast response time, reproducibility and long lifetime. The present sulfate ion-selective electrode displayed very good selectivity for SO_4^{2-} ion with respect to NO_3^- , I^- and other halide ions. The electrode was used as an indicator electrode for determination of SO_4^{2-} solution with Ba^{2+} solution. The membrane electrode was successfully applied for the determination of sulfate content in real samples.

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