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Modified solid ion-selective electrode for potentiometric determination of sulfide in oil refineries water

Key words: ion-selective electrode, silver sulfide, oil refineries, water

Introduction

A scientist, developed electrode membranes at the beginning of the twentieth century with the discovery of the glass electrode, which is one of the important tools in laboratories, as it response to hydrogen ions (Skoog, Holler & Nieman, 1998). Among the different analytical techniques (Mahajan, Kaur, Sharma & Kumar, 2002) and as a result of the development of research, advances in this area began in the 1960s, when Rokosing and Pungor developed a new type of solid sensor (Cattral, 1997). The field of ion-selective electrodes has experienced rapid growth since the past two decades (Arida, Ahmed & El-Saied, 2003), and chemical sensors are miniature analytical devices that can provide information about the presence of specific compounds or ions in complex samples (Wroblewski, 2009), which are dependent on the development of static electricity potential difference across a membrane. It separates two phases. When placed in a solution containing ions (Cattral, 1997), it is one of the most importantly fast and simple modern electrolysis techniques that require the current passing through them to be equal to zero (Othmer, 1981).

The use of ion-selective membrane electrodes is a good analytical technique. Due to its several advantages over conventional analysis methods for example they provide accurate, repeatable, fast, and often selective identification of different ions (Liu, Zhao, Chen & Che, 2000). Sulfide is an anion that is widely present in both natural, wastewater, and industrial waters, and it is one of the most important factors to monitor in water due to its high toxicity to aquatic organisms. The sulfide toxicity is attributed to the release of hydrogen sulfide (H_2S) (Huang et al., 2010) and hydrogen sulfide (H_2S) is one of the most dangerous highly cor-

rosive media (Lusk, Gupta, Boinapally & Cao, 2008). Because sulfide solutions can attack metals and concrete causing corrosion problems (Shao, Ying & Ping, 2020). It is now known that corrosion can have some effects on the chemistry of the specific process, and the product of corrosion can affect the reaction and purity of the reaction products (Popoola, Grema, Latinwo, Gutti & Balogun, 2013). Recent industrial disasters indicate that many industries have lost several billion dollars as a result of corrosion (Oyelami & Asere, 2011).

The ion-selective sulfide electrode has been applied to monitor sulfide in industrial waters, and Ag/Ag_2S electrode is the solid-state that uses this type of ion-selective electrode (S^{-2}) (Zaidan, 2007; Ding, Pan, Huang, Chen & Ye, 2015). These electrodes contain in their crystal membranes only two crystalline compounds, they are the responsible materials for the electrochemical behavior of the membranes, and they are monocrystalline, where the membrane can be got by pressing or dissolving salt powder and then attaching it to the end of the electrode body made so it is not affected by air temperatures and is not subjected to cracking because of heat or rag and resists chemical changes such as the selective fluoride electrode (LaF3). The other such electrodes are the polycrystalline which can be prepared from Ag_2S, CuS, CdS, AgCl, AgI, or AgBr powder selective for sulfide ions, chloride, iodide, or bromide respectively (Anfalt & Jagner, 1969; Vesely et al., 1972). These films have been developed to prepare ion-sensitive selective membranes, where they are used to identifying many of the same ions as an internal solution for a con-

ductor (Dulkiewicz, 1989; Bűhlmann, Pretsch & Bakker, 1998).

The aim of this study is to manufacture a selective electrode to determine the sulfur ions prepared from the reaction of sodium sulfide with silver nitrate to form silver sulfide by sedimentation method and apply it to measure sulfur ions in industrial waters in the production units of oil refineries of North Oil Refineries Company, Iraq, and compared with sensitivity and response of Sindie sulfur analyzer (model 7039 G3).

Material and methods

Instrumentations

The following instruments were used: pH/mV meter (3310 Jenway); silver-silver chloride electrode as working electrode (Jenway); reference calomel electrode (Hanna); PVC tubing; balance (BL 210S Sartorius); magnetic stirrer with hotplate (LMS-1003 LabTech); drying oven (Memmert); test sieve (analysensieb) (200 mm, dia. ×50 mm, ASTM E1175 micron) (D-42781 Haan); sulfur analyzer (7039 G3 Sindie).

Reagents and solutions

All reagents were of high purity grade supplied by Fluka, BDH, and MUMBAI. Sodium sulfide 0.1M Na_2S was used to prepare the standard solution, nitric acid HNO_3, NaOH. The sulfide anti--oxidant buffer SAOB containing 2M NaOH, 0.2M ascorbic acid, and 0.2M disodium EDTA (Dulkiewicz, 1989). Standard staggered ionic solutions were prepared at a concentration of 0.1M of KBr, $BaCl_2$, $SnCl_2·2H_2O$, $CuSO_4·5H_2O$,

$Pb(NO_3)_2$, $CrCl_3$ in a volume of 100 ml distilled water.

Preparation of Ag_2S electrodes

The Ag_2S electrodes used in this study were fabricated by slow addition of 200 ml of 0.5 ml of silver nitrate solution using a burette, at a rate of 100 drops per minute to 100 ml of 0.5M sodium sulfide solution with continuous stirring, and after completing the addition process, it was filtered. The resulting sediment was washed several times with distilled water, and then with diluted 0.1M nitric acid, the sediment was dried in an oven at 120°C for 3 h. The sediment was collected, milled, and homogenized using ceramic mortar until it became a very fine powder and it was made using a 300 μm sieve, the material was pressed in the form of hard disks using a medicinal pill making machine and it became a compact hard disk with a thickness of 0.7 mm, a diameter of 11.9 mm and a weight of 0.8639 g.

Construction of ion-selective electrodes

A PVC diameter was cut into 3–4 cm long pieces. An Ag_2S disk was placed in one end and the other end of the PVC tube was connected to an empty and open Ag/AgCl (Fig. 1).

Cell design and calculation of electrode potential

The selective electrode potential can be calculated depending on the voltage of the membrane that separated different solutions containing the same concentrations of the metal since the response of these membranes depends on the ion

FIGURE 1. The installation of the manufactured electrode

exchanges present in them and has a selectivity of the desired ion. Without the other ions, depending on two main factors the size and charge of the ion, and given that the current passing through these electrodes is equal to zero, the cell used to measure the voltage of this type of electrode is shown in the following:

Ag/AgCl | internal solution of Na_2S (10^{-6}M) | membrane (Ag_2S) | external solution of Na_2S (X M) | SCE

Results and discussion

In this study, the sedimentation method was used to prepare silver sulfide (Ag_2S), which is the material from which the membrane electrode is made, because this method works to accomplish chemical reactions in a fast, simple, and highly efficient way Energy and less time consuming and the properties as shown in Table 1.

TABLE 1. Properties of the prepared electrode

Lifetime/ /month	Response time [s]	Slope [mv·decade^{-1}]	Detection limit [M]	Working pH range	Linear range [M]	Working pH range
4	5-17	28.229	$2.28 \cdot 10^{-7}$	6.0–12.0	10^{-1}–10^{-6}	S^{-2}

Effect of temperature

The best range of temperature without significantly affecting the electrode voltage was 25–35°C, and there is an increase in the voltage difference values at higher temperatures of 35°C, which may occur because of the increase in the movement of S^{-2} in and out of the electrode and the increase in the surface area of the fabricated electrode membrane as the increase in the movement of the solution particles is directly proportional to the increase in the surface area directly with the temperature (Fig. 2).

Response time

Figure 3 shows the response time of the electrode, it could be noticed that the response time within a range of concentrations between 10^{-2} and 10^{-6}M was between 5 and 17 s, and it is noticed that the response time is inversely proportional to the concentration of ions in the external solution. The concentration of ions increases in the external test solution, the response time decreases due to the easy access of the ions to the outer membrane of the electrode, and vice versa, as the concentration of ions decreases, the number of ions in the external solution will decrease, so it takes longer to reach a state of equilibrium in the electrode voltage.

Calibration curve

The standard calibration curve can be measured by preparing a series of solutions in question at concentrations ranging from $0.1 \cdot 10^{-1}$ to $0.1 \cdot 10^{-6}$M, then measuring the voltage by the prepared
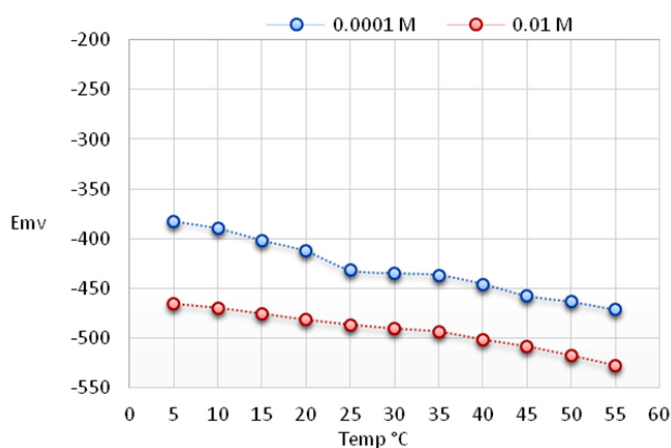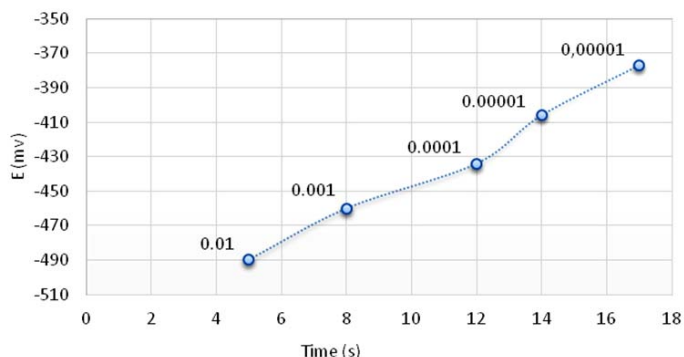

FIGURE 2. Effect of temperature on electrode response

FIGURE 3. The response time of the electrode

selective electrode and drawing the relationship between the electrode voltage versus $-\log[S^{-2}]$, while observing the movement of the model to affect the state of equilibrium. Figure 4 shows the effect of the concentration of the internal filling solution on the electrode response

per decade, which was close to the theoretical value 29.58 mv per decade, to be the concentration, and the electrode calibration curve the linear response of the opposites ranged between $1.00 \cdot 10^{-6}$ and $1.00 \cdot 10^{-1}$M and the minimum Nernst response $2.28 \cdot 10^{-7}$.
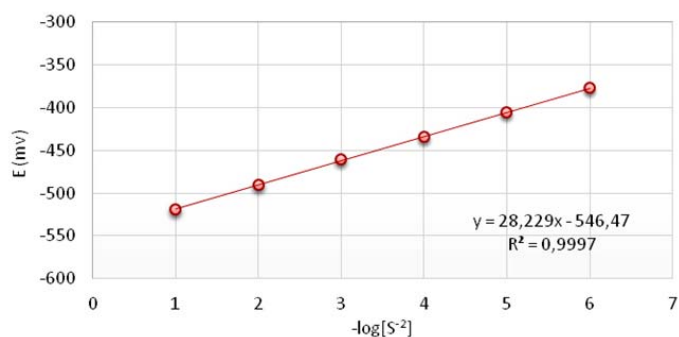

FIGURE 4. Standard curve of an electrode

after fixing the other conditions, temperature and pH where it was observed that the concentrations less than 10^{-6}M did not show any linear response and it was neglected in the subsequent experiments, and the internal filling solution was at concentration 10^{-6}M is the best internal packing solution because the best Nernst slope response 28.229 mv

Selectivity

Selectivity is the most important characteristic that determines the nature of an electrode and the extent to which it can be used successfully. The values of the selectivity coefficient (Table 2) were determined against the number of interfering ions, using the mixed solution method, the selectivity coefficient can be

TABLE 2. Selectivity values of $K_{A,B}^{Pot}$

Concentrations of Na₂S [M]		Interfering species 10^{-2}M
$K_{A,B}^{Pot}$ values		
10^{-4}	10^{-2}	
0.0470	0.0390	K^{+1}
0.0046	0.0320	Cu^{+2}
0.0081	0.0300	Zn^{+2}
0.0069	0.0490	Pb^{+2}
0.0053	0.0082	Cr^{+3}
0.0048	0.0270	Cl^{-1}
0.0064	0.0880	Br^{-1}
0.0710	0.0540	SO_4^{-2}

expressed by the relative error and concentration of the ion to be analyzed to the interfering ion by Eq. (1):

$$K_{A,B}^{Pot} = \frac{C_{A\min} \cdot P}{C_{B\max} \cdot 100} \qquad (1)$$

$K_{A,B}^{Pot}$ – selectivity coefficient of the ion selection electrode (A) in the presence of the interfering ion (B),

$C_{A\min}$– the lowest expected concentration of the ion to be analyzed,

$C_{B\max}$– maximum expected concentration of the interfering ion,

P – permissible relative error when analyzing the ion (A) due to ion interference (B).

Accuracy and precision

Table 3 shows the accuracy and agreement of the results of the standard curve of the electrode, noting that the extent of convergence between the real value and the laboratory values of the concentrations: 10^{-2}, 10^{-4}, 10^{-6}M, and that the percentage recoverable values in

TABLE 3. Accuracy and compatibility of the results of the standard curve of the electrode

%REC	%RE	%RSD	Concentration thoughtful [M]	Electrode
99.9	–0.1	0.5772	10^{-2}	S^{-2}
103.7	3.7	0.7430	10^{-4}	
98.0	2.0	0.6352	10^{-6}	–

TABLE 4. Comparison method between the electrode and sulfur analyzer

%RE	Concentration of S^{-2} [mol·l⁻¹]		Sample
	Ag₂S electrode	sulfur analyzer	
3.92	$2.69 \cdot 10^{-2}$	$2.8 \cdot 10^{-2}$	S1
3.44	$3.00 \cdot 10^{-2}$	$2.9 \cdot 10^{-2}$	S2
–5.66	$2.83 \cdot 10^{-3}$	$3.0 \cdot 10^{-3}$	S3
0.50	$1.47 \cdot 10^{-2}$	$1.4 \cdot 10^{-2}$	S4
–3.25	$3.87 \cdot 10^{-4}$	$4.0 \cdot 10^{-4}$	S5
–5.68	$8.96 \cdot 10^{-4}$	$9.5 \cdot 10^{-4}$	S6
–3.88	$3.46 \cdot 10^{-4}$	$3.6 \cdot 10^{-4}$	S7
4.25	$8.32 \cdot 10^{-4}$	$8.0 \cdot 10^{-4}$	S8
6.15	$1.38 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$	S9
5.38	$2.74 \cdot 10^{-4}$	$2.6 \cdot 10^{-4}$	S10

the range of 98–103.7% for the concentrations chosen from the standard curve, and the highest value of the relative standard deviation (0.7430%). These results indicate high precision and electrode compatibility.

Applications

The method of comparison with the sulfur ion analyzer and the electrode that was the results was very close and the relative error was very small between the two methods, and this gives evidence of good selectivity and high sensitivity of the electrode as shown in Table 4.

Conclusion

The Ag/Ag$_2$S electrode proved to be a suitable tool for measuring the concentrations of sulfur ions in solutions as well as in industrial water that used in the petroleum industries. It is characterized by ease of manufacturing and use, and it has a fast response time, long life, good selectivity, and high sensitivity.

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Summary

Modified solid ion-selective electrode for potentiometric determination of sulfide in oil refineries water. A selective electrode was manufactured to determine the sulfur ions by sedimentation method in industrial waters in oil refineries of North Refineries Company, Baiji, Iraq. The linear response on a wide range of concentration (from $1.0 \cdot 10^{-1}$ to $1.0 \cdot 10^{-6}$M) Na_2S with a Nernst response of 28.229 mv per decade, theoretical value for slope of 29.58 mv per decade, correlation factor of 0.9998, detection limit of $2.287 \cdot 10^{-7}$ at 25–35°C, pH 6.0–12.0, and the best concentration of the filling solution of 10^{-6}M with a fast response time (5–13 s). The direct method were %RSD for 0.5772––0.7430, %RE for –0.1, 3.7 and %REC for 99.9, 103.7.

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