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Electrochemical study of sulfide solution in the presence of surfactants*

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Abstract—Voltammetric curve studies on aqueous Na_2S solution in the presence of three types of surfactants were presented. Presence of anodic surfactant (HTAB) increases anode current density and makes the corresponding anode peak potential shift to more negative. Potentials of the reduction of elemental sulfur to intermediates S_x^{2-} shift to more negative with the increasing of HTAB concentrations. In the presence of HTAB, the anode current density at 77℃ increases more than at 34℃. The electrolysis indicates that anodic product sulfur loosely adhered to the graphite electrode surface when HTAB is added to the anolyte. The total efficiency of producing sulfur is high after several times of cycle electrolysis. The results showed that anode passivation is minimized in the presence of HTAB. The depassivation effect of HTAB was discussed.

Keywords: surfactant; sulfur; sulfide; voltammetry.

1 Introduction

Hydrogen sulfide is a toxic gas present as a contaminant in natural gas wells as well as in other fossil energy resources. With an expected increase of more than 75% on the production of this gas in the next decade, remove of hydrogen sulfide from sour gas and subsequent recovery of its constituents will be of greater importance to environmental conservation and utilization of resources. Claus process, which has widely used to remove H_2S from these fuels, still suffers from many disadvantages (Mao, 1991). Electrochemical oxidation of aqueous H_2S solution has been investigated for many decades as an alternative process to the Claus process. The waste gas H_2S is at first absorbed in aqueous NaOH solution (Hai, 1986), then the absorption liquid is electrolyzed to produce sulfur at anode and hydrogen gas at cathode. The new process used to treat hydrogen sulfide gas has some economic benefits (Noring, 1982). However, with the proceeding of electrolysis of H_2S solution, insulated anode product sulfur produced at anode results in sharp decreasing of current. In other words, sulfur deposited at the anode block further electrochemical oxidation of species S(− 2) to sulfur. This phenomenon is called anodic passivation during electrolysis of hydrogen sulfide solution. Some methods were proposed to overcome this problem, including the organic solvent stripping process (Shih, 1986; Bolmer, 1968), and the controlling of electrolysis conditions (Anani, 1990) and so on. In addition, F. Castaneda *et al*. (Castaneda, 1987) reported the electrochemical oxidation of sodium sulfide in water at pH 8 in the presence of cationic, neutral and anionic surfactants. The results showed that a cationic surfactant CTAB, combined with the increasing temperature to 80℃, could hinder anodic passivation caused by sulfur deposition.

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F. Castaneda *et al*. discussed only a low concentration Na_2S solution of pH 8. However, what used in practical electrolysis should be a more concentrated Na_2S solution so as to increase production efficiency. So we reported electrochemical oxidation of 0.5 mol/L Na_2S solution in the presence of surfactants, and the pH of this solution is about 13.3 figured out from dissociation constants of hydrogen sulfide solution. The effects of cationic, neutral and anionic surfactants on potential-current curves of anolyte Na_2S in water will be discussed in this article.

The stripping of sulfur deposit in the presence of surfactants may be due to adsorption of the surfactants at the electrode surface and dissolution of the precipitate inside the micelle which is formed above the critical micelle concentration (CMC). However, it is not easy to explain the mechanism about depassivation effect of the surfactants, which will be commented in the results and discussions.

2 Experimental details

Both anolyte and catholyte used in these experiments were prepared from deionized water and A.R.-grade materials. The glass electrolytical cell is consisted of two compartments separated by a cation-selective membrane which can be crossed freely by cations. Anode material here used is graphite. Cathode material is nickel. Saturated Calomel Electrode (SCE) was connected to the anode compartment via Luggin capillary and was utilized for monitoring half cell potentials. The potentials reported in this article are on the SCE scale.

All experiments were conducted at constant temperature water bath. The electrode potential was controlled by a HDV-7B potentiostat programmed with a KS-1 sweep generator. Current-potential relationships were recorded on a new model 3086 XY1Y2 recorder. Before experiments, both anode and cathode were polished carefully using golden phase carbide paper, following washed by acetone and deionized water.

Current efficiency for sulfur production was estimated from the amount of solid product collected in the anolyte and on the anode surface. However, the efficiencies were lower due to both product losses during washing, filtering and formation of polysulfides in the anolyte. If the anolyte either was used to be electrolyzed in cycles or neutralized by a dilute HCl solution, the total efficiency will be near 100%. The *X*-ray diffraction spectrum was conducted in the XRD-R3m/E system with the data gathering software used for analysis.

3 Results and discussions

Three types of surfactants are discussed here. They are cationic (HTAB), neutral (PEG polyethyleneglycol 400) and anionic (SCS sodium cetylbenzenesulfonate) surfactants.

3.1 Anodic polarization studies

Voltammetry at graphite anode is shown in Fig.1. The result shows that neutral surfactant PEG almost has no effect on polarization curves. Presence of anionic surfactant SCS makes current peak wider. With the increasing of SCS concentrations, the peak potentials progressively shift to more positive and a shoulder peak arises at a more negative potential (Fig.1).

The extent of following reaction proceeding to right is higher because of strong hydrolysis of S^{2-} ion:

$$S^{2-} + H_2O = HS^- + OH^-, \tag{1}$$

its hydrolysis constant is 1.4. Calculation shows that concentrations of S^{2-} and HS^- ions are about

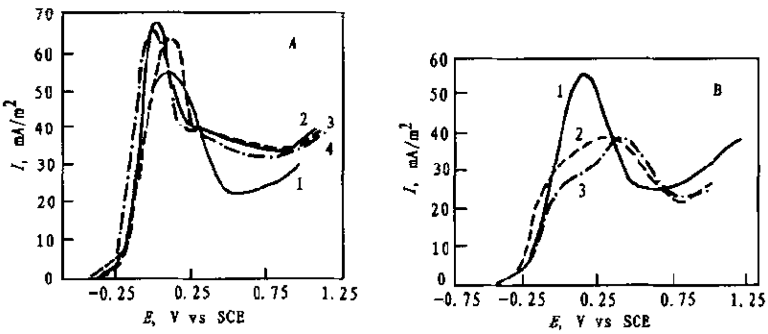

Fig.1 Anode voltammetric curves for 0.5 mol/L Na_2S solution at 34℃
A: (1) C_{HTAB}(mol/L) = 0; (2) C_{HTAB}(mol/L) = 7.1×10^{-4}; (3) C_{HTAB}(mol/L) = 1.41×10^{-3}; (4) C_{HTAB}(mol/L) = 2.4×10^{-3}; B: (1) C_{SCS}(mol/L) = 0; (2) C_{SCS}(mol/L) = 5.9×10^{-4}; (3) C_{SCS}(mol/L) = 2.4×10^{-3}
anode-graphite, cathode-Ni, Catholyte-1.0 mol/L NaOH, potential sweeprate-10 mV/s
(The curve in the presence of PEG is the same as curve 1)

0.11 and 0.39 mol/L, respectively, in 0.5 mol/L Na_2S solution. Electrochemical oxidations of S^{2-} and HS^- ions become more difficult because of repulsive force of anionic surfactant SCS adsorbed on electrode to the negative ions S^{2-} and HS^-. In other words, following reactions may be conducted at more positive potentials:

$$S^{2-} = S + 2e; \quad (2)$$

$$HS^- + OH^- = S + H_2O + 2e. \quad (3)$$

These cause the peak potentials to shift towards more positive potentials in current-potential curves. According to different repulsive forces of SCS to S^{2-} and HS^-, it can be explained that the current peak becomes wider with the increasing of SCS. The potential corresponding to the shoulder peak shifts to more positive with SCS concentrations.

Concentrations of S^{2-} and HS^- ions on the electrode surface will decrease in the presence of anionic surfactant SCS. This leads to lower the anode current. Polysulfides S_x^{2-} are present as intermediates in electrochemical oxidations of S^{2-} and HS^-, and their presence is controlled by dynamics (Yi, 1997), and they are further oxidized to elemental sulfur (Briceno, 1990):

$$xS^{2-} = S_x^{2-} + (2x-2)e; \quad (4)$$

$$xHS^- = S_x^{2-} + xH^+ + (2x-2)e; \quad (5)$$

$$S_x^{2-} - xS + 2e. \quad (6)$$

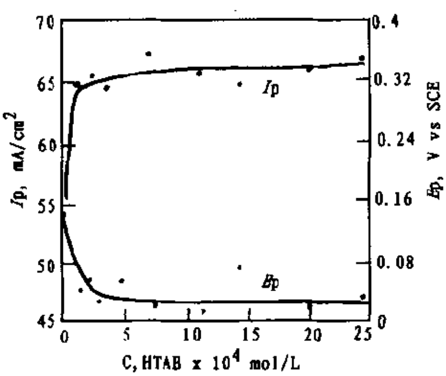

Fig.2 Variations of Ep and Ip against C_{HTAB}
(the same conditions as Fig.1)

Anode peak current increases in the presence of cationic surfactant HTAB. Because HTAB is absorbed on the electrode surface and it attracts S^{2-} and HS^- ions, concentrations of electrode reaction active species, i.e. S^{2-} and HS^-, and peak current increase. Plateau current after anode peak in the presence of HTAB is also higher than in the absence of HTAB. Relationships of anode peak potentials (Ep) and currents density (Ip) with HTAB concentrations are shown in Fig.2.

Attraction of HTAB with S^{2-} and HS^- ions make S^{2-} and HS^- be oxidized electrochemically at less positive potentials with the increase of HTAB concentrations, so the peak potentials shift to more negative and peak currents increase. When HTAB concentration is about 2×10^{-4} mol/L, *Ep* and *Ip* are not changed almost. This shows that whole anode surface is coated by HTAB.

3.2 Cycle voltammetric studies

The discussion above shows that only cationic surfactant HTAB can increase anode current density. Compared with HTAB, neutral or anionic surfactant has not the effect in the same conditions as HTAB. So the effective surfactant HTAB will be studied with cycle voltammetries.

Potential *Epc*(a) corresponding to reduction peak(a) is -0.367V in the absence of HTAB. *Epc*(a) shifts to more negative with the increase of HTAB concentrations and the peak current density becomes more negative, too.

According to Hamilton (Hamilton, 1983), reduction peaks are resulted from following electrochemical reduction processes on negative-going scan:

$$xS + 2e = S_x^{2-}; \quad (7)$$

$$S_x^{2-} + (2x-2)e = xS^{2-}; \quad (8)$$

$$(2x-2)e + S_x^{2-} + xH^+ = xHS^-. \quad (9)$$

Reduction peak(a) corresponds to reaction (7), i.e. formation of intermediates S_x^{2-}. When HTAB concentrations increase, elemental sulfur produced in anode reaction is "surrounded" with more HTAB and activation energy of reaction (7) increases. This results in the reaction (7) more difficult to take place and *Epc*(a) to shift more negative. However, more sulfur gathers near the anode with HTAB concentrations, so peak (a) current on negative-going scan becomes more negative (Fig.3).

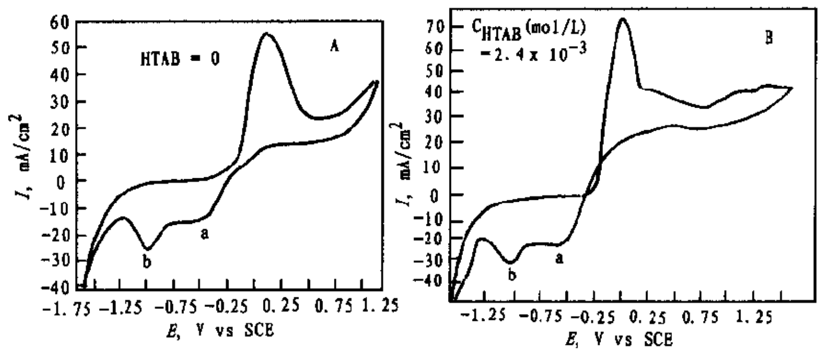

Fig.3 Cycle voltammograms for 0.5 mol/L Na_2S solution in the presence of HTAB
A: HTAB=0; B: C_{HTAB}(mol/L) = 2.4×10^{-3}
(other conditions the same as Fig.1)

If the potential sweep is applied from open-circuit potential to 0.5 or 0V, peak current of the reduction peak(a) is reduced or disappears (Fig.3). This phenomenon shows that less amount of sulfur formed on positive-going scan make peak current of the corresponding reduction lower (Fig.4). If the vertex potential on positive-going scan is limited to the potential before anode peak (Fig.4), the reduction peak (a) disappears but reduction peak (b) is still present. It can be concluded from the discussion that S^{2-} or HS^- ion is firstly oxidized to polysulfides S_x^{2-} and the reduction peak(b) is corresponding to reduction of intermediates S_x^{2-} to S^{2-} or HS^- ion. The little changed potentials corresponding to reaction peak(b) in Fig.3A and Fig.3B may be resulted from rapid reduction rates of intermediates S_x^{2-} to S^{2-} and HS^- ions.

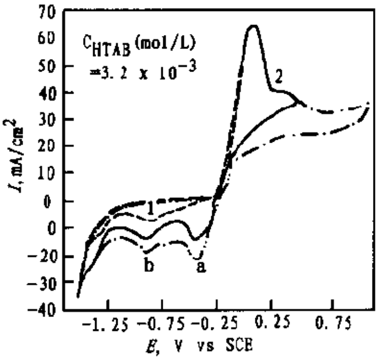

Fig.4 Cycle voltammorgrams for 0.5 mol/L Na_2S
The vertex potential: 0.5 V——(2); 0 V——(1) C_{HTAB}(mol/L) = 3.2×10^{-3}
(other conditions the same as Fig.1)

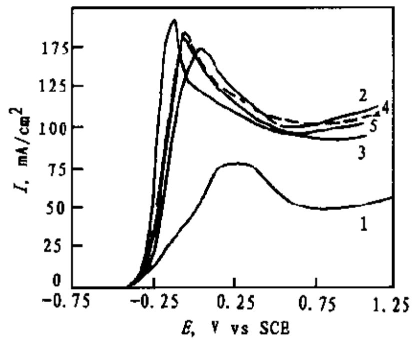

Fig.5 Current-potential curves at 77℃
1, 2, 3, 4 and 5: C_{HTAB}(mol/L) are 0, 6.6×10^{-4}, 1.6×10^{-3}, 3.4×10^{-3} and 5.5×10^{-3}, respectively
(other conditions the same as Fig.1)

3.3 Electrolytical results for aqueous Na_2S solution

It favors electrolysis of aqueous hydrogen sulfide to produce sulfur and hydrogen gas when anodic current density increases in the presence of HTAB. When 0.5 mol/L Na_2S solution was electrolyzed, the anolyte changed its colour from colourless to orange red. Elemental sulfur is loosely adhered to the electrode surface when 4×10^{-4} mol/L HTAB is added to the anolyte. When the electrolysis was terminated, current efficiency resulted from the sulfur collected in both anode and anolyte is 30%—45%. If the residue anolyte was neutralized with a dilute acid (HCl or HAc), total current efficiency for sulfur production will be about 95%. In addition, the residue anolyte can also be electrolyzed in cycles. The cycle numbers and efficiencies are listed in Table 1.

Table 1 Current efficiencies of cycle electrolysis

Run number	Numbers of cycle electrolysis and current efficiencies, %					Total current efficiency, %
1	1—17.5	2—98.6	3—94.1	4 97.9	5—93.0	80.3
2	1—30.6	2—95.2	3—92.5	4—93.2	5—90.5	80.4
Condition	Water-bath temp. 63.5℃, Anolyte: 0.5 mol/L Na_2S, Catholyte: 1.0 mol/L NaOH, V_{cell} = 0.9—1.2 V					

If numbers of cycle electrolysis continue to increase, the total efficiency will be greater than those shown in Table 1. The result shows that passivation was hindered in the presence of HTAB. XRD of product sulfur is shown in Fig.6 which indicates the sulfur being present as sulfur.

3.4 Effect of surfactants

The effect of surfactants is not easy to understand (Castaneda, 1987). Although sulfur can be dissolved inside HTAB micelles or absorbed on the surface of micelles and the CMC of HTAB is unknown, it well be expected that the CMC of HTAB should be lower because of the low concentrations of HTAB used in our experiments. The CMC of HTAB can be estimated to be about

2×10^{-4} mol/L from the Fig. 2. So low concentration of CMC is insufficient to dissolve sulfur. Therefore, dissolution of sulfur into HTAB micelles is certainly not the main cause to reduce anodic passivation. This conclusion is supported by rising electrolysis temperature. The CMC of HTAB decreases with the increase of temperature, but anode current density at 77℃ increases more than at 34℃ (Fig. 5). This phenomenon shows that increasing electrolysis temperature to 77℃ is favorable to electrochemical oxidation of alkaline hydrogen sulfide solution.

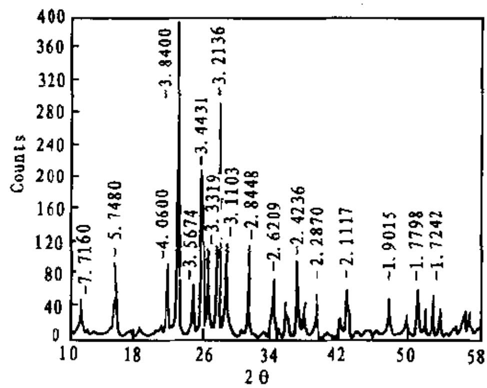

Fig. 6 XRD of anode product sulfur

Depassivation of HTAB may be explained by the adsorption of HTAB at the electrode surface. The adsorption effect would be related to the potential of zero charge (PZC) of the graphite electrode. Though the PZC is unknown in our experimental conditions, one can reasonably suppose that the graphite electrode is negatively charged at open-circuit potential. This will explain adsorption of HTAB at the electrode surface and preventing a surface deposit to be formed. However, it is difficult to understand the adsorption of SCS at the graphite surface. In a word, it is necessary to further search the mechanism of the surfactant effects.

4 Conclusions

Only cationic surfactant HTAB increases the anode current density especially at 77℃ in our experimental conditions. The mechanism of surfactants effect may be due to their adsorptions at the anode. Anode product sulfur can be obtained and the anode passivation was not obvious when Na_2S solution was electrolyzed in the presence of HTAB. Total current efficiencies for production of sulfur were high.

References

Anani A, Mao Z, White R E. J Electrochem Soc, 1990, 137 (9): 2703—2709
Bolmer P W. U S Pat, 1968, 3409520
Briceno A, Chander S. J Appl Electrochem, 1990, 20: 506—511
Castaneda F, Pezeron E, Plichon V. Bull de da Soc Chim de France, 1987, 1: 34—36
Hai M T. Absorption kinetics of H_2S gas by aqueous NaOH solution. Changsha: Central South University of Technology, 1986
Hamilton Z C, Woods R. J Appl Electrochem, 1983, 13: 783—794
Mao Z, Anani A, White R Z. J Electrochem Soc, 1991, 138(5): 1299—1303
Noring J E, Fletcher E A. Energy, 1982, 7: 651—653
Ven-Shiang Shih, Jeou-Long lee. Ind Eng Chem Process Des Dev, 1986, 25: 836—838
Yi Q F, Chen Q Y. Trans Nonferrous Met Soc China, 1997, (1): 27—32

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