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Short Communication

UV-ATR Spectroscopy Study of the Speciation in Aqueous Polysulfide Electrolyte Solutions

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The distribution of species, dissolution of sulfur as polysulfide and oxoanions in aqueous polysulfide electrolytes at room temperature was investigated. The dissociation of sodium sulfide in water produces equal molar concentrations of OH^- and HS^- ions. The addition of elemental sulfur produces a variety of speciation in this polysulfide electrolyte. In this study the formation of oxidised sulfur species by the reaction of elemental sulfur with the large quantity of OH^- ions present in the Na_2S aqueous sulfide solution was investigated. The adopted UV-ATR technique shows a much better response down to the 200nm region. The UV-ATR spectra of pure aqueous solutions of sodium thiosulfate, sulfate and sulfite were recorded and compared with the spectra of aqueous polysulfide electrolytes to report the presence of oxoanions.

Keywords: Polysulfide, Sulfide, Sulfur, Aqueous electrolyte, redox flow battery

1. INTRODUCTION

The dissociation of Na_2S in water produces equal molar concentration of HS^- and OH^- species according to following equations.

$$Na_2S + H_2O \leftrightarrows 2Na^+ + HS^- + OH^- \qquad (1)$$

The formation of polysulfide species by the reaction of elemental sulfur with HS^- ions in Na_2S solutions is well known and follows the equation 2.

$$nS^{(0)} + HS^- + OH^- \rightarrow S_{n+1} + H_2O \qquad (2)$$

Various opinions are held regarding the ionic composition of polysulfide solutions. On the one hand, it is believed that a dynamic equilibrium of polysulfide ions is observed in solution, with a considerable variation of chain length [1]; on the other hand, it has been demonstrated experimentally that, regardless of the overall degree of polysulfidity, only the penta, tetra, and monosulfide ions exist in solution, in the corresponding equilibrium concentrations [2]. In sodium polysulfide; the maximum degree of polymerization quite likely corresponds to no more than five sulfur atoms [2, 3]. Giggenbach [4] identified the presence of four S_n^{2-} species where "n" varied between 2 and 5, assumed that no gap exists in the series S_nS^{2-}. The equilibria between polysulfide ions in aqueous solution can generally be described by the following equation (3).

$$nS_mS^{2-} + HS^- + OH^- \leftrightarrows mS_nS^{2-} + H_2O \qquad (3)$$

$$n = m-1$$

The study of Giggenbach has long been considered as the main reference for polysulfide speciation. Licht et al. [5] improved the analysis of equilibrium constants reported by Giggenbach by using optical absorbance spectra. The computer iterative technique is applied to the calculation of the various species in aqueous alkali-metal polysulfide solutions, including OH^-, H^+, H_2S, HS^-, S^{2-}, S_2^{2-}, S_3^{2-}, S_4^{2-}, and S_5^{2-}, water, and alkali-metal cations. The distribution of polysulfide forms in an electrolyte determined by the equilibrium constants from spectral data by Giggenbach [4] and refined by Licht [5] has been denied by Vorobets [6].

Teder [3] studied the variation in the stoichiometric composition of sodium polysulfide with alkalinity in the pH range 9-14. The author considered that the equilibria between polysulfides were strongly dependent on the alkalinity of the solution, according to the following equilibrium [7].

$$S_{m+n}S^{2-} + HS^- + OH^- \leftrightarrows S_mS^{2-} + S_nS^{2-} + H_2O \qquad (4)$$

The possibility of formation of thiosulfate, sulfate and sulfite in aqueous polysulfide solution prepared at room temperature has been ignored in the literature.

It is hard to locate much literature on the dissolution of sulfur in sodium hydroxide solution. As early as 1846 [8] it was found that sulfur reacted with hydroxide solutions and formed polysulfide and thiosulfate species The experiment was repeated in 1930 by Pearson and Robinson [9] and all early observations were summarised by Mellor [10] who suggested that the reaction probably occurred as follows:

$$(2n+2)S + 6\ NaOH \rightarrow 2Na_2S_n + Na_2S_2O_3 + 3H_2O \qquad (5)$$

Meux [11] reported the evidence of the above reactions using potentiometric titration. The authors showed that the stoichiometric reaction of sulfur and hydroxide resulted in the formation of pure S_4^{2-} species. The solubility of sulfur in alkaline solution was studied in details by Amston et al.

[12] in 1960. The authors established the (S, NaOH, H_2O) three phase diagrams at 25°C and found that equilibrium was attained within a few days for concentrations of NaOH between 0.23 and 1.85 mol kg^{-1}. The conclusions in the literature based on equilibrium constants have ignored the possibility of sulfur oxidation by OH^- ions in sodium sulfide solutions. The most valid studies [4, 5, 13] for the analysis of polysulfide solutions utilised mainly a standard UV spectrophotometers techniques. However the accuracy of the study was limited by the overlapping of the observed polysulfide spectra. The standard UV technique and its accuracy have been recently reviewed [14-16] for the analysis of sulfide and polysulfide solutions which shows a great uncertainty in literature. Furthermore, small compositional changes in polysulfide electrolyte can affect largely the electrochemistry e-g presence of oxanion in polysulfide electrolyte can cause problems especially in redox flow cell by blocking membranes. In this work, the use of UV-ATR probe allows a much better response down to 200nm wavelength region for polysulfide solutions which are previously considered to be partly solved.

2. EXPERIMENTAL

2.1. Materials and Methods

An immersion ATR probe of 12.5 mm diameter from Hellma Worldwide Ltd (labeled 661-802) was used for the highly absorbing polysulfide electrolyte analysis. The probe was connected to a Cary 50 UV spectrophotometer from Varian.

The ATR probe was a three bounce geometry, which allows three reflections at the probe-solution interface at the same angle of 60^o. The baseline correction was carried out using water as a blank sample, during measurement of the absorption of polysulfide solutions.

Polysulfide solutions were prepared by adding elemental sulfur to sodium sulfide solutions. The elemental sulfur used in this study was a sublimed orthorhombic form from Aldrich. The sodium sulfide nona-hydrate of 99.99% purity ($Na_2S.9H_2O$) ACS grade from Aldrich was used. The NaOH 97.5% used was ACS regents from Aldrich. Furthermore for the pure solutions of sodium sulfite, salt from Aldrich of 98.5% purity while thiosulfate penta-hydrate of 99.5% purity ($Na_2S_2O_3.5H_2O$) from BDH were used. All samples of materials used were prepared in deionised water (purite) in laboratories at ambient temperature and normal atmospheric conditions unless otherwise stated. The results are interpreted as S: Na ratio, where S represents total sulfur (sulfide sulfur + added elemental sulfur).

3. RESULTS

To investigate the formation of polysulfide species and oxidized sulfur species together, a comparative UV-ATR study for the dissolution of elemental sulfur in pure NaOH and separately in Na_2S was undertaken. A concentrated polysulfide solution was prepared by the addition of 4.5 mol dm^{-3} of elemental sulfur in aqueous solution of 14 mol dm^{-3} of NaOH. The UV-ATR spectrum was recorded for this solution and compared with the polysulfide solutions of S: Na ratio 1.4 and 1.8

prepared in aqueous 1.8 mol dm^{-3} Na_2S by the addition of elemental sulfur as shown in figure 1. The UV-ATR spectra of polysulfide solutions prepared in Na_2S shows a total of five peaks as shown in figure 1.

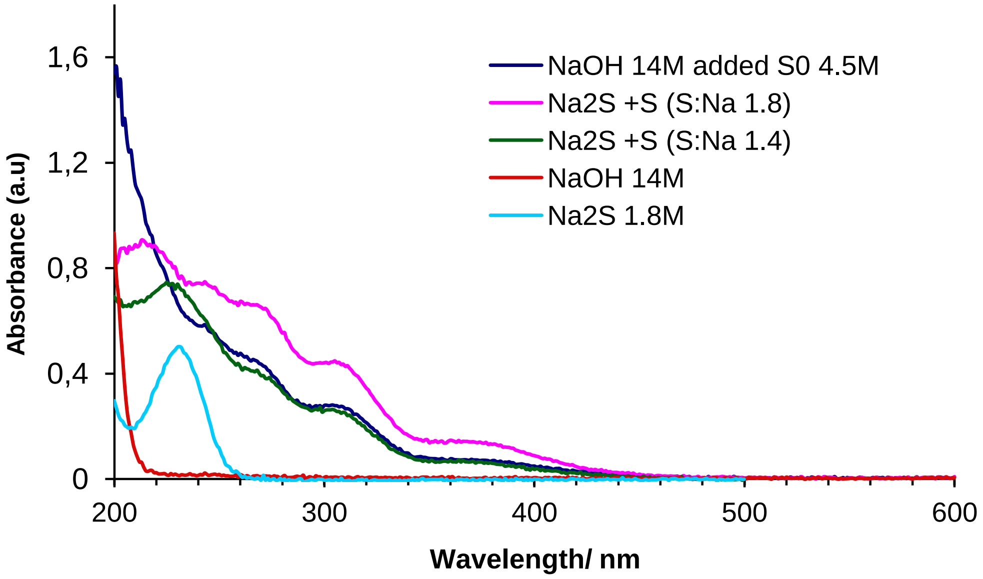

Figure 1. Comparison of UV-ATR spectra of polysulfide species formed in Na_2S and NaOH solution with the addition of sulfur.

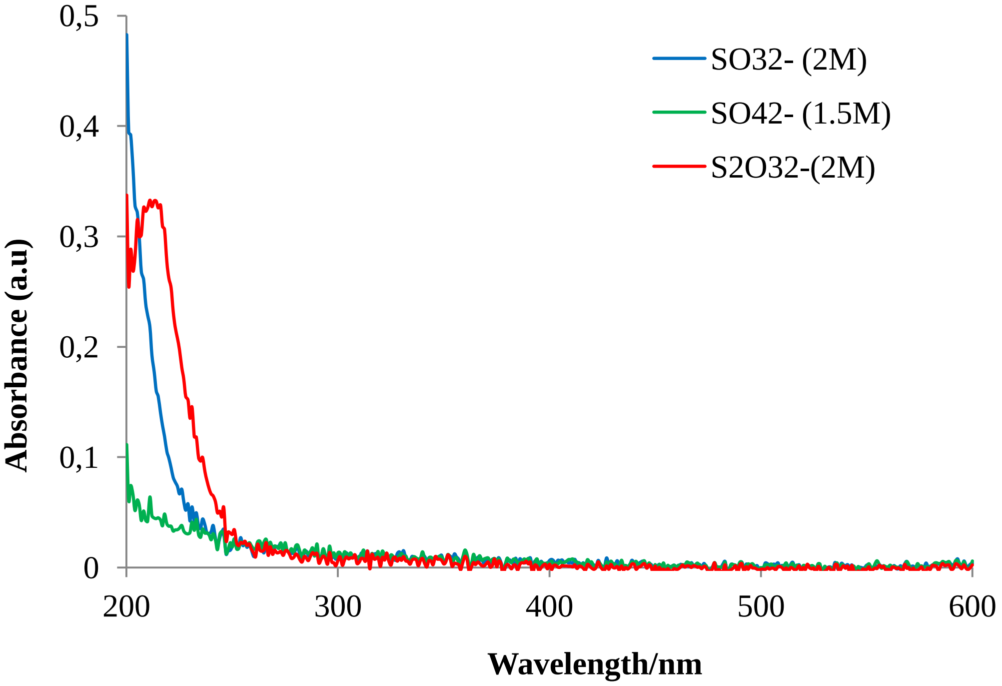

Figure 2. Comparison of UV-ATR spectra of sodium thiosulfate, sodium sulfate and sodium sulfite

The spectra of polysulfide in NaOH also show four similar peaks in the region of 240-400nm but start a sharp increase from 240nm towards 200 nm. On the other hand polysulfide solution in Na_2S

shows a fifth peak at 230nm and shows a sharp increase from 211nm towards 200nm wavelength. The UV-ATR absorption spectra of 2.4 mol dm^{-3} pure sodium sulfide solution (without elemental sulfur) solution also show a strong band at 230nm wavelength. The peak at 230nm is assigned to HS^- species in study and is in good agreement with the literature [4, 16, 17]. The analysis of pure NaOH solution confirms that absorbance in 200-211nm region is due to OH^- ions. Furthermore the possibility of assigning any of the total five peaks to an oxidized sulfide species was also checked in this study. The UV-ATR spectra of pure aqueous solutions of sodium thiosulfate, sulfate and sulfite were recorded as shown in figure 2 in order to compare with the above-mentioned spectra (figure 1) of polysulfide solutions.

The UV-ATR spectra of all three pure aqueous solutions of sodium thiosulfate, sulfate and sulfite show very small absorbance in the 250-450nm region as shown in figure 2. The spectra of pure sodium thiosulfate solutions shows, a sharp increase in absorbance at 250nm having a peak maxima at wavelength of 218nm. Sulfite starts to absorb sharply at 250nm but the exact peak maxima position is not known due to the limitation of the instrument to record spectra below 200nm. It should be noted that the comparison of spectra of two polysulfide solutions having same composition one prepared in the laboratory and other in nitrogen atmosphere shows no difference in this study. The water used for the sample preparation in the nitrogen atmosphere was bubbled with nitrogen gas for three hours in order to remove dissolved oxygen. So the possibility of air oxidation to generate any oxidized sulfur species was ruled out.

4. DISCUSSION

Comparison of spectra for polysulfide solutions having S: Na 1.4 & 1.8 prepared in Na_2S shows that with the increase of S: Na 1.4 to 1.8, the trough between 200-230nm changes into a peak at 218nm. It is believed that species corresponding to this absorbance peak were also present in solution having S: Na 1.4 as well but due to their low concentration in the presence of high HS^- concentration, the spectra were overlapped by the superposition of the HS^- band at 230nm. In solution having S: Na 1.8, with the addition of elemental sulfur and formation of other polysulfide species, the concentration of HS^- decreases and as a result the 230nm peak also decreases respectively. With the decrease the 230nm peak, the shoulder peak for oxidized species at 218 nm becomes more prominent. However the decrease of HS^- species and the increase of shoulder peak for oxidized species may not necessarily happen linearly with added sulfur.

The formation of polysulfide in Na_2S solution via the reaction of elemental sulfur with HS^- ions is generally explained by the equilibrium in equation 2. There are two possible routes for the formation of oxoanions in polysulfide solutions. First elemental sulfur can directly react with OH^- ions to produce oxoanions. From the literature review, [10, 18-19] the formation of polysulfide species by the addition of sulfur in sodium hydroxide solution (in the absence of HS^- ions) is only possible with the formation of oxidised sulfur species as shown by the following possible reactions.

$$4S^0 + 4OH^- \leftrightarrows S_2O_3^{2-} + 2HS^- + H_2O \qquad (6)$$

$$2(n+l)\ S^0 + 6OH^- \rightarrow 2S_n^{2-} + S_2O_3^{2-} + 3H_2O \qquad (7)$$

In this study the UV-ATR spectra of the sulfur solution prepared in aqueous NaOH shows the same processes between the 240-400nm wavelength regions as for those polysulfide solution prepared in aqueous Na_2S, however the solubility of elemental sulfur is much lower in NaOH. Furthermore spectra of the solutions prepared by the dissociation of sulfur in sodium hydroxide solution, also shows a sharp absorbance increase between 200-240nm wavelength region. The sharp absorbance due to OH^- ions was expected only between 200-211 nm, as confirms by UV-ATR spectra of pure NaOH in figure 1 in this study.

In polysulfide solutions prepared by the addition of elemental sulfur in Na_2S, the other possible route described by Giggenbach [20], Licht and Davis [21] for the formation of oxidised sulfur species exist via the disproportionation of polysulfide species as shown by the following equation.

$$4S_nS^{2-} + 4(n-1)OH^- \leftrightarrows nS_2O_3^{2-} + 2(n+2)HS^- \qquad (8)$$

The inter conversion of $S_2O_3^{2-}$ and SO_3^{2-} ions is also possible in polysulfide solutions. Giggenbach [13] extended the study of equilibria between polysulfides at high temperatures as a result of disproportionation. In his studies the author reported that thiosulfate could react with HS^- ions to form sulfite and polysulfide species as shown by the following equation 9.

$$nS_2O_3^{2-} + HS^- + OH^- \leftrightarrows S_nS^{2-} + nSO_3^{2-} + H_2O \qquad (9)$$

Furthermore due to the formation of polysulfide species, the concentration of OH^- and HS^- decreases with the increase of elemental sulfur. The results in this study show, that instead of a decrease in the spectra in 200-211nm regions for OH^- ions a prominent increase was observed as shown in figure 1. This prominent increase indicates the presence of sulfite ions in solution. The increase in the concentration of polysulfide species with a small decrease of thiosulfate will be difficult to see in the spectra as it can be distributed in all species. Further it was also noticed by Ramo et al [22] that thiosulfate has a tendency to oxidize into sulfite in an alkaline medium as shown in the equation 10.

$$S_2O_3^{2-} + S_n^{2-} \leftrightarrows SO_3^{2-} + S_{n+1}^{2-} \qquad (10)$$

Most recently published author own work [23] by using Raman spectroscopy also shows the strong evidence for formation of oxoanion species in these polysulfide electrolytes.

5. CONCLUSIONS

The detailed UV-ATR experiments of this study have uncovered the complexity of the UV spectra mainly reported by standard UV spectrophotometer. In the spectra of polysulfide solutions prepared in Na_2S, the precise locations of peaks in the 200 to 250nm region were complicated by the strong overlap between the other spectra especially at low S: Na ratio with the broad spectra of HS^- at 230nm wavelength where the HS^- concentration is expected to be high. The spectra are comparatively less complicated in the region of 250- 500 nm wavelength regions. The work has also increased the significance of the oxidation of elemental sulfur in sodium sulfide solutions. More problematically oxidized sulfur is only partially visible but a contributor to the UV spectra region. Thus the conclusions in the literature based on equilibrium constants and peak speciation ignoring the possibility for the formation of oxoanions may needs detailed re-examination.

The comparison of two polysulfide samples, one in normal laboratory atmosphere, in deionised water and the other in a nitrogen atmosphere in a gloves box using nitrogen purged water showed no difference in behaviour. It should be emphasized that this is not due to atmospheric oxidation but an implicit part of the process of forming polysulfides.

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