Polysulfides species: formation mechanism in acid and basic environment.

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INTRODUCTION

It is well known that polysulfides are formed during copper extraction based on the chalcopyrite ($CuFeS_2$) leaching slowing down the rate of dissolution.[1] During the dissolution process, the chalcopyrite is a source of sulfur in the form of disulfide [2] and sulfur is reduced and polymerized, producing species such as S_n^{2-}, S_n^{-}, S_n and their protonated forms (HS_n, HS_n^{-} and H_2S_n). These species have never been isolated in aqueous solutions, but their existence is proved based on spectroscopic data analysis in solutions under many conditions.[3] The present work has investigated the formation mechanism of different species in different pH of the medium.

METHODS

The S_n (n = 2, 4, 6, 8), S_n^{-} (n = 3, 5, 7, 9, 11), S_n^{2-} (n = 1, 2, … , 8, 10, 12, 14, 16) and their protonated forms (HS_n, HS_n^{-} and H_2S_n) were completely optimized and the thermodynamic properties were estimated based on the harmonic approximation. The PBE exchange/correlation functional with aug-cc-pVTZ basis sets were used as implemented in GAUSSIAN09. The solvent effects were taken into account based on the SMD model. The thermodynamic stability of the polysulfides ions was quantified by the variation of reaction Gibbs free energy ($\Delta_r G$) of the reactions represented in Equations 1-3.

$$S_{n\,(aq)}^{-} + H_3O^{+}_{(aq)} = HS_{n(aq)} + H_2O_{(aq)} \quad (1)$$

$$S_{n\,(aq)}^{2-} + H_3O^{+}_{(aq)} = HS_{n\,(aq)}^{-} + H_2O_{(aq)} \quad (2)$$

$$HS_{n\,(aq)}^{-} + H_3O^{+}_{(aq)} = H_2S_{n(aq)} + H_2O_{(aq)} \quad (3)$$

RESULTS AND DISCUSSION

The protonation reactions were very favorable for the smaller structures (n < 6), as shown in Figure 1. The non-protonated species can only exist in basic environment. Otherwise, non-protonated long chain polysulfides (n > 6) can exist in basic or neutral environmental.

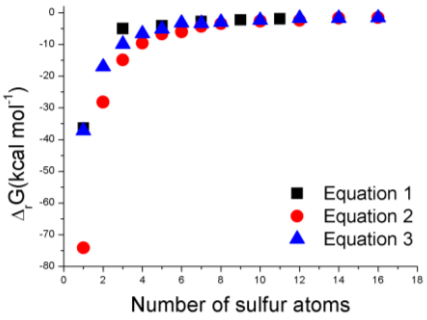

Figure 1. Variation of reaction Gibbs free energy for the chemical reactions in Equations 1-3.

Considering that in basic environment the species S_n^{2-}, S_n^{-} and S_n were prevalent and that in acid environment the protonated or double protonated species were prevalent, three mechanisms were proposed. In basic environment, the reactions indicated the formation of large chains. However, in acid environment the reactions indicated the formation of elemental sulfur.

CONCLUSIONS

The proposed mechanism is coherent with the reality of the system. The elemental sulfur is frequently found during the acid dissolution process of chalcopyrite. The structures of the polysulfides, the thermodynamic data and the formation mechanism will be presented in detail.

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