Effect of Nonionic Surfactants on the Kinetics of Disproportion of Copper Sulfide Nanoparticles in the Aqueous Sols

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The effect of nonionic surfactants on the disproportion kinetics of copper sulfide nanoparticles (aqueous sols) from the golden brown, copper-rich phase (Q-Cu$_2$S) to the green covellite phase (Q-CuS) has been presented. The transformation follows a first-order rate law. There is a substantial decrease in the rate of transformation in the presence of nonionic surfactants, viz. TX-100, NP-9.5, and NP-40. An attempt has been made to explain the phenomenon based on a surface state catalyzed transformation that is sensitive to the adsorption. The surface coverage (θ), estimated from the dependence of the rate constant on surfactant concentration, fitted the Langmuir adsorption isotherm. From these, the equilibrium constants and standard Gibbs free energy change of adsorption ($\Delta^{\circ}_{ad}G$) have been estimated.

1. Introduction

We report here the effect of surfactants on the transformation kinetics of copper sulfide aqueous sol from its copper-rich (hereafter Cu$_2$S) to sulfur-rich phase (CuS). For more than 3 decades, much of the interest in copper sulfides has been due to their use in CdS/Cu$_{2-x}$S heterojunction[1−3] solar cells—among most extensively studied photovoltaic cells. Recently, their nanoparticles have demonstrated a third-order optical nonlinearity when trapped in the glass/polymer matrixes.[4−8] Its composites with ZnS[9−11] and CdS[12] have been viewed as promising luminescent materials. However, an important shortcoming of this material is the spontaneous disproportion[13] from initial copper(I) to copper(II) phase, which has also been reported in its colloid form.[14] Any progress in retarding this transfor-

mation to a significant extent would be highly beneficial in reviving this material.

The synthesis of copper sulfides' nanoparticles in the form of aqueous[14−16] and nonaqueous sols,[17] microemulsions,[18] thin films,[19−21] and polymer composites[22−25] and by the sol−gel process[26] have been well-documented. Silvester[14] and Drummond et al.[27] have discussed its transformation. However, quantification of the kinetic parameters is needed to understand the mechanism—especially in its nanophase. Keeping this goal in mind, we have undertaken a preliminary investigation of the kinetics of transformation of aqueous sols of copper sulfides. Experimental results obtained suggest that surface state catalyzed electron transfer is involved in its disproportion.

To reveal this, we investigated the transformation in judiciously chosen surfactant solutions. On the basis of

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these experimental findings, a definite role of the empty surface states in mediating the transformation is proposed.

To the best of our knowledge, this is a first report where rate constants have been correlated to the fraction coverage (θ) of the nanoparticles by the surfactant molecules. The data obtained fitted in the Langmuir adsorption isotherm, and from these values, the equilibrium constant and standard Gibbs free energy change ($\Delta_r^\circ G$) in the adsorption were estimated.

2. Experimental Section

2.1. Materials. All the chemicals were of extra-pure grade and used as received without any further purification. All the aqueous solutions were prepared using deaerated double-distilled water (1.8 μS cm^{-1}).

2.2. Preparation of Copper Sulfide Sols. Aqueous sols of copper sulfide were prepared by reacting copper acetate with sodium sulfide in a dilute aqueous solution at room temperature. Sodium sulfide was chosen as a sulfurating agent over H$_2$S gas because its desired concentration can be easily prepared and a known amount could be maintained in the bath.

Typically, 10 mL of 1 mM copper acetate solution was diluted with 39 mL of water in an Erlenmeyer flask. Moist nitrogen was bubbled through it for 15 min. One milliliter of 0.1 M freshly prepared sodium sulfide solution was added dropwise under constant stirring. The golden yellow, transparent sol of copper sulfide so obtained was allowed to age for 5 min prior to its analysis. For its synthesis in the surfactant solutions, the calculated quantity of stock surfactant solution was added to a bath prior to the addition of sodium sulfide. There were no observable differences in the spectral features and kinetics upon addition of surfactants up to 5 min after formation of particles. The pH of the final bath was in the range of 10.5−10.7. No special efforts were taken to maintain the pH. For all the experiments, the concentrations of copper acetate and sodium sulfide in the final bath were maintained at 0.2 and 2 mM, respectively.

To elucidate the kinetics of transformation, UV−vis spectra were recorded on the sols at stipulated time intervals. The characteristic absorbance for Cu$_2$S and CuS phases (at 298 and 900 nm, respectively) were chosen for this purpose. The spectra were recorded using a Shimadzu direct ratio recording spectrophotometer: model UV-204(PC) S with UVPC Spectroscopy software version 3.9. All the measurements were performed in the cuvette holder, thermostated at 28 ± 0.2 °C. For the determination of particle size, a Philips CM12 transmission electron microscope was employed. To image the particles, a droplet of the freshly prepared sol was dried on a carbon-coated copper grid. All the measurements were carried out at 120 kV and a magnification of ×37 000.

3. Results and Discussion

3.1. Characterization of Copper Sulfide Sols. Figure 1a depicts an absorption spectrum recorded for the freshly prepared "golden brown" sol of copper sulfide. The spectral features are comparable with those previously reported[14,15] and are ascribed to the formation of a copper-rich phase of the copper sulfide (Cu$_2$S) by the following scheme:

$$2Cu^{2+}(aq.) + 2S^{2-}(aq.) \rightarrow Cu_2S\cdot S^0(s) \qquad (1)$$
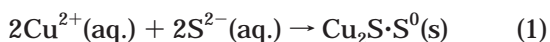
Further comparison of the spectrum with those for bulk[28] and thin films[29] of Cu$_2$S highlights distinct differences; the spectrum reported for the bulk, which onsets at 1022 nm, is blue-shifted to 620 nm, in our case. In addition, a shoulder at 298 nm is also apparent in the spectrum. Hence, the formation of size-quantized particles (Q-Cu$_2$S) is concluded. From the TEM image
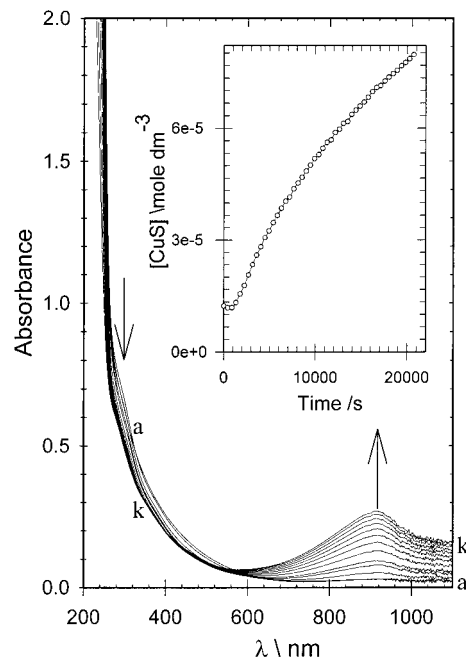

Figure 1. Absorption spectra recorded for copper sulfide sols at various time intervals. The direction of arrows indicates the decrease in [Cu$_2$S] and increase in the [CuS], as a function of time. (a) Recorded ca. 5 min after mixing of the reactants; (k) after ca. 8 h; (b) to (j) are between the time intervals. Please note that not all spectra are shown. The inset depicts a plot of increase [CuS] with time. The induction period of ca. 2000 s is attributed to the incomplete reaction between copper acetate and sodium sulfide.

of freshly prepared sols, the average particle size was estimated to be ca. 7 nm.

3.2. Kinetics of Transformation. In the stipulated time, the golden brown sol was converted gradually to a transparent green sol, which suggests transformation of Cu$_2$S to CuS. The spectra recorded during these intervals are depicted in Figure 1, and as can be seen, the absorbance at 900 nm develops with time. (Refer to Figure 1a−k.) As mentioned earlier, this absorption peak is characteristic of Q-CuS and was absent initially. Concurrently, the Q-Cu$_2$S absorbance peak at 298 nm decreases, having an isosbestic point at around 580 nm. Thus, these changes can be unambiguously attributed to the transformation of Q-Cu$_2$S to Q-CuS. The time-dependent decrease in absorbance at 900 nm enabled systematic investigation of the transformation kinetics. The reported value for the molar absorptivity[14] of CuS at 900 nm (2800 dm^3 mol^{-1} cm^{-1}) was used to express the amount of Q-CuS in terms of mol L^{-1}. An increase in the concentration of Q-CuS in the bath as a function of time is depicted in an inset of Figure 1. The initial induction period up to 2000 s as seen in the inset has also been observed by Silvester et al.[14] They correlated this effect to an autocatalysis by excess of Cu^{2+} ions. However, in our case, sulfide is in excess and thus could simply be attributed to an incomplete reaction between copper acetate and sodium sulfide in the initial period of evolution. As can be seen from the inset of Figure 1, the over all contribution of this deviation is insignificant and was therefore neglected.

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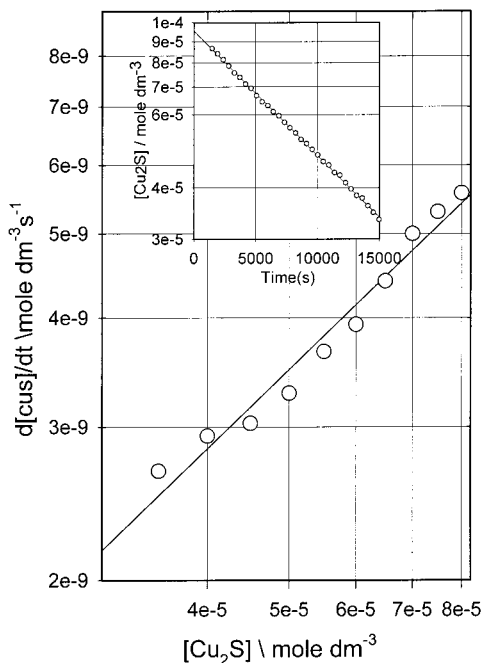(29) Engelken, R. D.; McCloud, H. E. *J. Electrochem. Soc.* **1985**, *132*, 567.

Figure 2. Log−log plot of [d[CuS]/dt] vs [Cu$_2$S] (van't Hoff plot). From the slope, the reaction has been concluded to be first-order. The corresponding semilog first-order fit for the same data is depicted in the inset. From the slope, the rate constant has been estimated.

To determine the kinetic parameters, the data were analyzed by the van't Hoff graphical method[30] as described below.

The rate equation for the transformation can be written as

$$Cu_2S \xrightarrow{k} CuS \cdot Cu^0 \qquad (2)$$
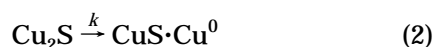
and the corresponding rate law would be

$$\frac{d[CuS]}{dt} = -\frac{d[Cu_2S]}{dt} = k[Cu_2S]^n \qquad (3)$$

where k and n are the rate constant and order of the reaction with respect to Cu$_2$S, respectively. Taking logarithms of both sides yields

$$\ln\left[\frac{d[CuS]}{dt}\right] = \ln k + n \ln[Cu_2S] \qquad (4)$$

Thus, a plot of (d[CuS]/dt) vs ln[Cu$_2$S] should yield a straight line having the slope and intercept equal to "n" and ln(k), respectively. As depicted in Figure 2, the data fitted very well in eq 4 with a correlation coefficient (r^2) = 0.94 and having slope and intercept equal to 0.936 ≈ 1 and −4.429, respectively. From the analysis, the first-order rate constant obtained was 3.72×10^{-5} s^{-1}. This is further supported by the linear fit ($r^2 = 0.99$) of the semilog plot for Q-Cu$_2$S concentration vs time, as depicted in the inset of Figure 2. From the slope, the value of the rate constant was estimated to be 6.54×10^{-5} s^{-1}. The comparatively large deviation in the van't Hoff fit ($r^2 = 0.94$) was attributed to additional error introduced while measuring the slope of the tangent
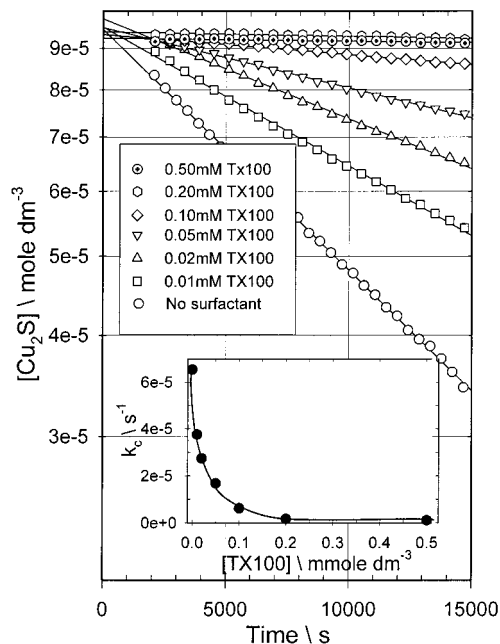
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Figure 3. First-order fits for the transformation of Q-Cu$_2$S for various concentrations of TX-100. The rate constants (k_c) obtained from the slopes, as a function of [TX-100], are plotted in the inset.

(rate of the reaction at various time intervals) on the concentration−time curve. In conclusion, the semilog plot method appears to be more reliable for the determination of kinetic parameters and thus was used in future analysis.

3.2.1. Effect of Surfactants on the Transformation Kinetics. While stabilizing the copper sulfide nanoparticles against the flocculation with the aid of nonionic surfactants, we observed that its presence plays a significant role in transformation kinetics. To understand this phenomenon, the transformation was investigated in the presence of polyoxyethelene-based (POE-based) surfactants. Its choice was dictated by the availability of various POE chain lengths in relatively pure form. Figure 3 depicts semilog plots for the concentration of Q-Cu$_2$S vs time in the presence of various TX-100 concentrations. All the plots fit in the linear regression ($r^2 \geq 0.94$), indicating the first-order kinetics as observed in the previous case. However, there is a decrease in the slope of the plots and thus in the rate constant (k_c), as a function of [TX-100]. These changes are plotted in the inset of Figure 3. k_c decreased from 6.54×10^{-5} s^{-1} in the control experiment ([TX-100] = 0) to a limiting value (k_L) of 7.4×10^{-7} s^{-1} in 0.2 mM TX-100. Further increases in the concentration of TX-100 did not induce any measurable changes in k_L. These experiments clearly indicate a correlation between the transformation kinetics and adsorption of surfactants on the particles. This adsorption is believed to have an overlap of electronic states of a lone pair of electrons from the POE chain with empty available surface states of the Q-Cu$_2$S surface. This presumably makes the surface states occupied and inaccessible for the transformation reaction. Upon increasing of the surfactant concentration, more and more surface states become occupied and are manifested as a decrease in the value of k_c. Upon saturation, further increasing in the concentration of TX-100 does not have any effect
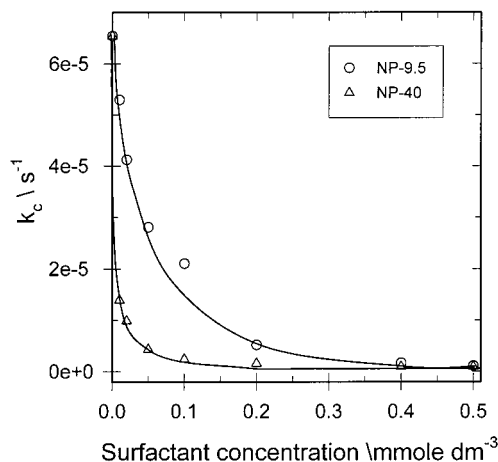
Figure 4. Plot of rate constant (k_c) vs concentrations of NP-9.5 and NP-40.

on k_c. Thus, experimental results suggest the involvement of the surface states in the transformation mechanism.

3.2.2. Effect of POE Chain Length on the Transformation Kinetics. To ascertain the role of the POE chain on k_c, the kinetics have been investigated in the nonyl phenyl ether based surfactants, viz. NP-9.5 and NP-40 having average length POE moieties equal to 9.5 and 40, respectively. Both surfactants have identical structure except for the POE chain length. The values of k_c at various concentrations of these surfactants have been determined using the first-order fit, as described above. These are plotted as a function of respective concentrations in Figure 4. From these plots, k_L for NP9.5 and NP40 were found to be 4.85×10^{-7} and 4.14×10^{-7} s^{-1}, respectively. These are similar to those obtained for TX-100. It indicates that k_c, which is a function of surfactant concentration, is a manifestation of the surface properties of Q-Cu$_2$S and not the nature of the nonionic surfactant. Interestingly, the limit $k_c \rightarrow k_L$ has been attained at different surfactant concentrations, depending on the length of the POE chain. In NP-9.5 and NP-40, it reaches concentrations of 0.4 and 0.1 mM, respectively. It could possibly be attributed to the difference in POE content of the surfactants.

3.2.3. Model for the Transformation. The transformation of Cu$_2$S to CuS involves disproportion of two Cu^{1+} moieties to Cu^0 and Cu^{2+} due to an electron transfer between them.[14] Our experiments suggest that the electron transfer is mediated by empty surface states. It is illustrated in Figure 5. In this, case (a) represents the transformation mechanism without any surfactant adsorbed. The electron will be transferred to empty available surface states, as shown in eq 5. where

$$Cu_2S \equiv Cu^{1+}Cu^{1+}S^{2-} + (\,) \rightleftharpoons Cu^{1+}Cu^{2+}S^{2-}...(e^-) \quad (5)$$
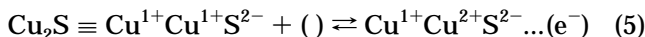
an empty bracket indicates the unfilled surface states. It is obvious that not all the electrons transferred in the surface states will induce the disproportion reaction. Thus, this step is represented as a type of pre-equilibrium case. Some of these attempts acquire sufficient energy and reduce Cu^{1+} to Cu^0 as shown below,

$$Cu^{1+}Cu^{2+}S^{2-}...(e^-) \xrightarrow{k_0} Cu^0Cu^{2+}S^{2-} \equiv Cu^0CuS + (\,)$$
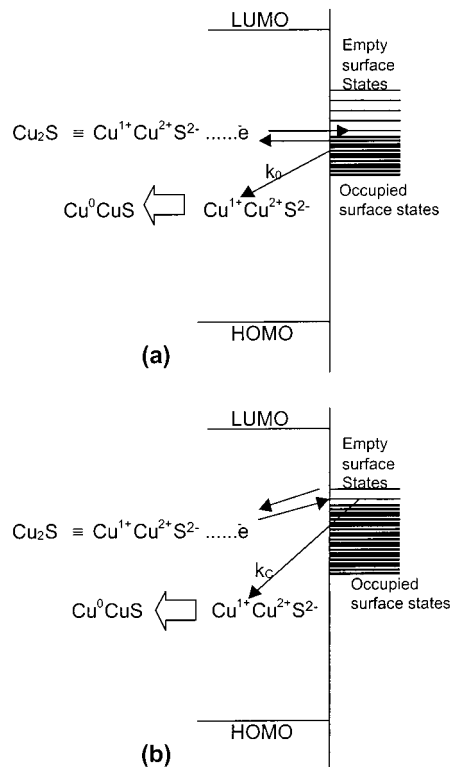$$(6)$$

Figure 5. Schematics for the surface state assisted transformation reaction. (a) No surfactant is adsorbed on the surface. The empty surface states are shown to be available for the transformation. (b) Some of the surface states shown to be preoccupied due to adsorption, which leads to a decrease in the rate constant from k_o to k_c.

where $k_0 = 6.54 \times 10^{-5}$ s^{-1} is the rate constant observed in the sol without any surfactant. The empty surface states so released will be available for the next electron transfer and effectively catalyze the transformation.

In the presence of surfactant, depending on its concentration, a part of the surface state will be preoccupied and thus not available for the electron transfer. Therefore, in eq 6, k_0 will be replaced by k_c where $k_c \leq k_0$. It is illustrated in Figure 5b. At higher concentrations of surfactant, it is expected to saturate the entire surface. As a result, the transformation should stop completely after a critical concentration of the surfactant. The value of k_c does saturate to "k_L", irrespective of the nature of the surfactant. However, it does not become zero. This could be explained in two ways. (1) An additional path could be available for the transformation other than the one mediated by surface states; the same path is responsible for the observed disproportion in the bulk copper sulfide where the surface-to-volume ratio is negligible and unlikely to have enough surface states to catalyze the reaction. (2) Saturation may simply be the limited level of coupling and not necessarily all surface states would be occupied even at very high surfactant concentration. Those surface states are presumably responsible for k_L.

4. Adsorption Isotherms

An attempt has been made to estimate the fraction of surface covered (θ) as a function of a surfactant (adsorbate) concentration. As the plots of k_c vs surfactant concentration are hyperbolic in nature (refer to

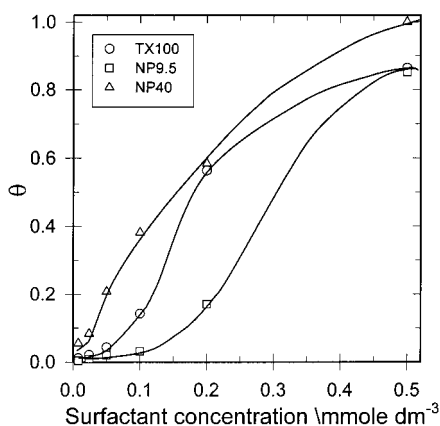**Figure 6.** Adsorption isotherm for the adsorption of TX-100, NP-9.5, and NP-40 on Q-Cu$_2$S.

Figure 3 inset and Figure 4), these can be fitted empirically to the following relation:

$$\frac{1}{k_c} = \frac{1}{k_0} + \xi \cdot \theta \qquad (7)$$

Thus,

$$\theta = \frac{k_0 - k_c}{\xi \cdot k_c \cdot k_0} \qquad (8)$$

where "ξ" is an arbitrarily chosen constant that is always greater than zero.

The value of ξ can be estimated by using boundary conditions as follows: $k_c \rightarrow k_L$ upon saturation of the surface, that is, when $\theta \rightarrow 1$; imposing this condition on eq 8 leads to

$$\frac{k_0 - k_L}{\xi \cdot k_L \cdot k_0} = 1$$

or

$$\xi = \left(\frac{k_0 - k_L}{k_L \cdot k_0} \right) \qquad (9)$$

Substituting eq 9 into eq 8,

$$\theta = \left(\frac{k_L \cdot k_0}{k_0 - k_L} \right) \times \left(\frac{1}{k_c} - \frac{1}{k_0} \right) \qquad (10)$$

The values of k_0 and k_L are obtained experimentally and thus θ can be estimated.

Equation 10 can be tested by re-imposing the boundary conditions. In the absence of any surfactant, $k_c = k_0$, and substituting this in eq 10, θ does become equal to 0. At the other extreme, upon saturation, $k_c = k_L$, and upon substituting this into the main equation, $\theta = 1$. Thus, it satisfies both the extremes.

Using eq 10, the value of θ is calculated at various surfactant concentrations. The corresponding adsorption isotherms for NP-9.5, NP-40, and TX-100 are depicted in Figure 6. The "S"-shaped isotherms, which are more pronounced in NP-9.5 and TX-100, indicate that the enthalpy of adsorption is not constant and decreases
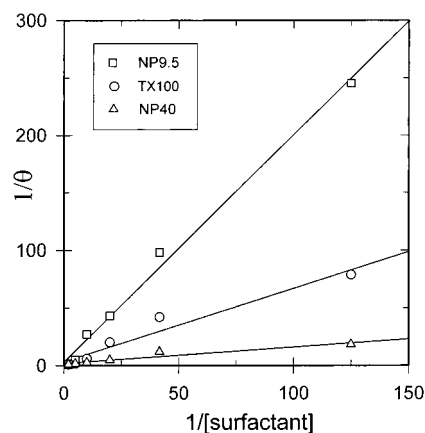

Figure 7. Fitting of adsorption of TX-100, NP-9.5, and NP-40 on Q-Cu$_2$S to the Langmuir adsorption isotherms.

Table 1

surfactants	equilibrium constant "K"	$\Delta_{ad}^{\circ}G$/kJ mol^{-1}
TX-100	1.357	−0.755
NP-9.5	0.431	2.077
NP-40	7.097	−4.847

with increasing θ. The corresponding fits to the Langmuir adsorption isotherm are given in Figure 7, where the r^2 values better than 0.9 were obtained. From the slopes, equilibrium constants "K" and the corresponding standard free energy changes in adsorption "$\Delta_{ad}^{\circ}G$" were calculated and as listed in Table 1. As can be seen $\Delta_{ad}^{\circ}G$ for NP-40 is greater than that obtained for NP-9.5 and TX-100. This can be attributed to the longer length of the POE chain. The magnitude of $\Delta_{ad}^{\circ}G$, suggests the adsorption is physical in nature, though it was expected to be chemisorption based on involvement of surface states. The reason for this is not yet known.

Conclusions

A systematic investigation on the disproportion kinetics of size-quantized particles of copper sulfide from its Cu$_2$S to CuS phase was carried out. A hundred-fold decrease in the rate constants was observed in the presence of nonionic surfactants and this was related to the catalytic role of empty surface states in the transformation reaction. For the first time, the rate constant was related to the fractional surface coverage (θ) by the surfactants. Data obtained fitted well to the Langmuir adsorption isotherms. The corresponding equilibrium constants and standard Gibbs free energy change involved in the adsorption were estimated.

Supporting Information Available: Figures of plotted rate constants k_c estimated from the plots of first-order fits for the kinetics of transformation of Q-Cu$_2$S in the presence of NP9.5 and NP40 at various concentrations, as a function of surfactant concentration (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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