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Yair Avny[a]; Zeev Gur-arieh[a]; Albert Zilkha[a]
[a] Department of Organic Chemistry, The Hebrew University, Jerusalem, Israel

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Adsorption of Silver Nitrate by Cotton Fabrics Containing Polyethylene Sulfide

YAIR AVNY, ZEEV GUR-ARIEH, and ALBERT ZILKHA

Department of Organic Chemistry
The Hebrew University
Jerusalem, Israel

SUMMARY

The adsorption of silver nitrate from aqueous solution by polyethylene sulfide-containing cotton fabrics was investigated. The adsorption could be described by a Freundlich-type isotherm with n = 1. ΔH° was calculated from adsorption isotherms and from the equilibrium constant of complex formation and similar results of -5.6 and -5.4 kcal/mole were obtained, respectively. At low silver nitrate concentrations most of the silver nitrate present in solution could be adsorbed. It was found that adsorption by polyethylene sulfide in the fabric was much higher than that of homopolyethylene sulfide.

INTRODUCTION

It is known [1, 2] that alkyl sulfides form complexes with silver nitrate and other heavy metal salts, leading to complexes of the type $AgNO_3.Et_2S$ [3]. Graft polymers of episulfides on cellulose showed adsorption of silver salts [4]. It was shown [5] that polypropylene sulfide grafted on cellulose membrane adsorbed silver nitrate from aqueous solutions. In a previous paper [6] the preparation of high polyethylene sulfide-containing fabrics was described. The polyethylene sulfide was either present as a

graft polymer or as a homopolymer which was formed inside the fabric. It was found that these fabrics did not contain any terminal mercaptan groups. In the present work adsorption of silver nitrate by these high polyethylene sulfide-containing fabrics was investigated.

EXPERIMENTAL

Cotton fabrics of high polyethylene sulfide content were prepared as previously described [6]. Homopolyethylene sulfide was obtained by polymerizing the monomer with lithium methoxide. Solutions of 0.1 N silver nitrate (BDH) were used. Polyethylene sulfide-containing cotton fabric (0.11 g) was left in standard 0.1 N silver nitrate solution. Adsorption was performed in the dark at constant temperature under constant shaking. The amount of silver nitrate adsorbed was determined by Volhard titration with 0.1 N ammonium thiocyanate (BDH). Adsorption by homopolyethylene sulfide was performed under similar conditions.

RESULTS AND DISCUSSION

The adsorption of silver nitrate by polyethylene sulfide-containing cotton fabrics was carried out in aqueous solution. The amount of silver nitrate adsorbed by the polyethylene sulfide in the fabric was determined from the decrease in silver nitrate concentration in the solution. Control experiments were carried out under similar conditions using swollen cotton fabrics. It was found that adsorption by swollen cotton fabrics was completed within 4 hr, leading to silver nitrate adsorption of 0.25 mmole/g. The adsorption values for the polyethylene sulfide-containing fabrics were corrected according to these control experiments. Adsorption in the presence of molar excess of silver nitrate was almost completed within 4 hr (Table 1). It was found that the adsorption by the polyethylene sulfide-containing fabrics after 48 hr corresponded to 3.47 mmole silver nitrate/g fabric (or 4.48 mmole silver nitrate/g polyethylene sulfide in the fabric). Adsorption by the cellulose in the modified fabric accounted for less than 8% of the total silver nitrate adsorbed. Thus, adsorption could be attributed to complexation of the silver nitrate by the polysulfide. The molar ratio of adsorbed silver nitrate to that of ethylene sulfide units in the polymer was 0.27.

The adsorption of homopolyethylene sulfide was compared under

Table 1. Silver Nitrate Adsorption[a] (Time Dependence)

Time (hr)	Adsorbed silver nitrate[b] (mmole/g)	[Adsorbed silver nitrate][c] / [Ethylene sulfide units]
0.5	2.02	0.15
1.0	2.35	0.18
1.5	2.79	0.21
2.0	2.97	0.23
4.0	3.25	0.25
8.0	3.29	0.25
24.0	3.45	0.26
48.0	3.47	0.27

[a]Cotton fabric (0.12 g) of 77.4% polyethylene sulfide content was left in 0.1 N silver nitrate solution (50 ml) at 25°C.

[b]Determined by titration.

[c]Molar ratio corrected for adsorption by swollen cotton fabric.

similar conditions with that of the polyethylene sulfide in the fabric (Fig. 1). Adsorption was almost completed within 4 hr. It was found that after 48 hr, adsorption by polyethylene sulfide in the fabric was much higher than that of the homopolymer (4.48 and 1.38 mmole silver nitrate/g polyethylene sulfide, respectively). These results may be attributed to the fact that homopolyethylene sulfide is a hydrophobic polymer and its accessibility to the aqueous silver nitrate is therefore limited. Since the polyethylene sulfide in the fabric is dispersed in the hydrophilic cellulose structure, it is more accessible to the silver nitrate solution and that is why higher adsorption was possible.

Determination of the Standard Heat of Adsorption (ΔH°)

Adsorption experiments (Table 2) from aqueous silver nitrate solutions were carried out in the presence of molar excess of ethylene sulfide units in the fabric. Adsorption was determined after the reaction was completed (48 hr) and the results were corrected for silver nitrate adsorption by the cellulose. It was found that decreasing the silver nitrate concentration led to an increase in the relative amount of silver nitrate adsorbed. Adsorption of silver nitrate decreased with increasing temperature. At the temperature

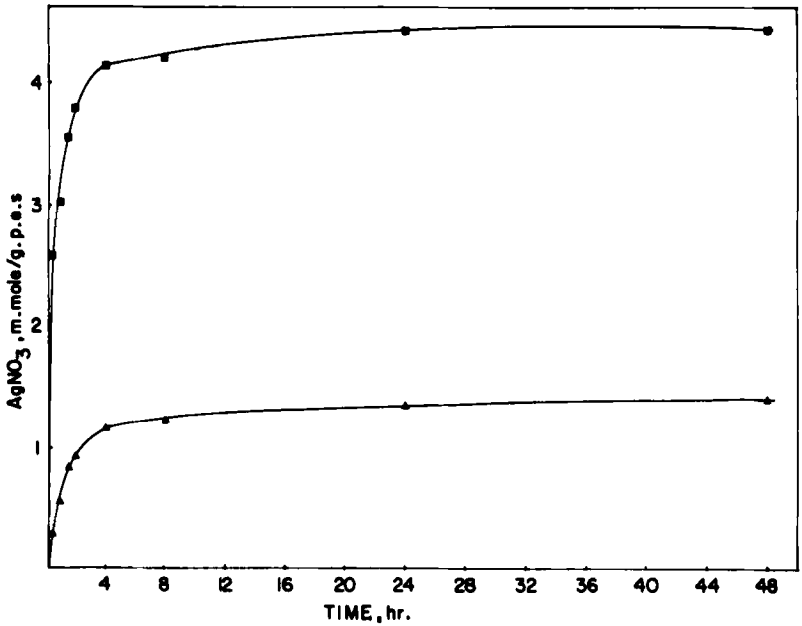

Fig. 1. Time dependence of silver nitrate adsorption by polyethylene sulfide in cotton fabric and in homopolymer. (■) Cotton fabric of 77.4% polyethylene sulfide; (▲) homopolyethylene sulfide.

range investigated, adsorption could be described by Freundlich-type isotherms (Fig. 2), in which n = 1

$$x = kc^{1/n}$$

where x is the mass of adsorbed silver nitrate/kg polyethylene sulfide in fabric, c is the solution concentration at equilibrium, n is the experimental constant, and k is the partition coefficient of silver nitrate between the fabric and solution.

The k values obtained are reported in Table 3.

At equilibrium, substituting concentrations for activities, k can be expressed by

$$\Delta\mu^\circ = RT \ln k$$

where $k = c_1/c_2$. c_1 corresponds to the concentration of silver nitrate in

Table 2. Silver Nitrate Adsorption[a] (Concentration and Temperature Dependence)

	Adsorption temperature (°C)	Silver nitrate solution (N)	Adsorption of silver nitrate	
			mmole/g[b]	%[c]
Series A[d]	5	0.100	6.34	65.0
	5	0.050	3.18	65.6
	5	0.010	0.66	74.0
	5	0.005	0.38	78.0
	5	0.001[e]	0.38	80.0
Series B[f]	23	0.100	4.13	51.0
	23	0.050	2.06	55.2
	23	0.010	0.48	57.5
	23	0.005	0.25	60.0
	23	0.001[e]	0.26	62.0
Series C[d]	40	0.100	3.58	38.0
	40	0.050	1.84	38.4
	40	0.010	6.39	40.0
	40	0.005	0.22	44.0
	40	0.001[e]	0.24	48.0
Series D[g]	60	0.100	2.40	26.0
	60	0.050	1.24	27.2
	60	0.010	0.30	31.0
	60	0.005	0.15	34.0
	60	0.001[e]	0.16	36.0
Series E[g]	80	0.100	1.79	18.0
	80	0.050	0.97	21.6
	80	0.010	0.19	22.0
	80	0.005	0.11	24.0
	80	0.001[e]	0.11	25.0

[a]Cotton fabrics containing polyethylene sulfide were left in silver nitrate solution (10 ml) of the appropriate concentration for 48 hr at the appropriate temperature.

[b]Determined by titration.

[c]% Silver nitrate adsorbed from the original amount of silver nitrate present.

[d]Cotton fabric (0.10 g) of 65.4% polyethylene sulfide content was used.

[e]Volume of silver nitrate (50 ml).

[f]Cotton fabric (0.12 g) of 76.5% polyethylene sulfide content was used.

[g]Cotton fabric (0.11 g) of 65.4% polyethylene sulfide content was used.

Table 3. Thermodynamic Data for Silver Nitrate Adsorption[a]

Temperature (°C)	$1/T \times 10^3$ (1/°K)	k (1/kg)	$-\Delta\mu^\circ$ (Kcal/mole)	$-\Delta\mu^\circ/T$ (cal deg./mole)	$-\Delta S^\circ$ (cal deg./mole)
5	3.60	175.7	2.87	10.33	9.8
23	3.38	82.4	2.61	8.81	10.1
40	3.20	56.7	2.52	8.07	9.8
60	3.00	31.2	2.29	6.87	9.9
80	2.83	19.5	2.09	5.93	9.9

[a]Calculations were made from data given in Table 2.

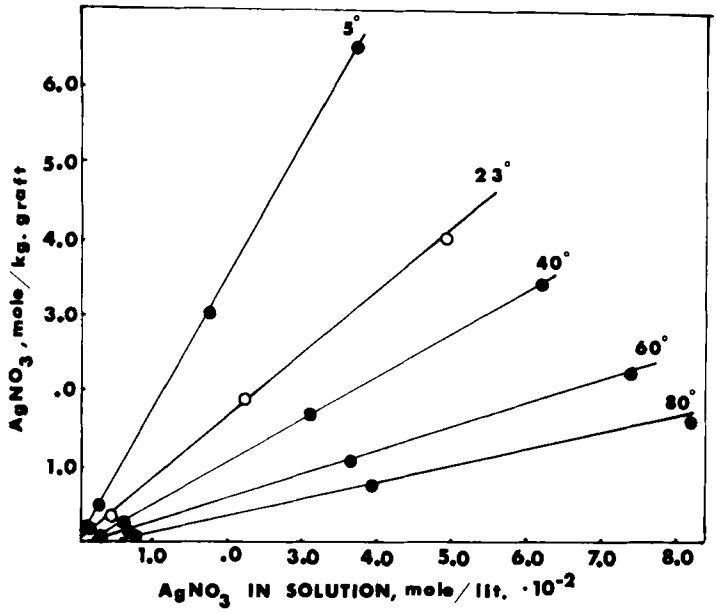

Fig. 2. Silver nitrate adsorption isotherms. Cotton fabrics of the following polyethylene sulfide contents were used: (○) 76.5%, all others 65.4%.

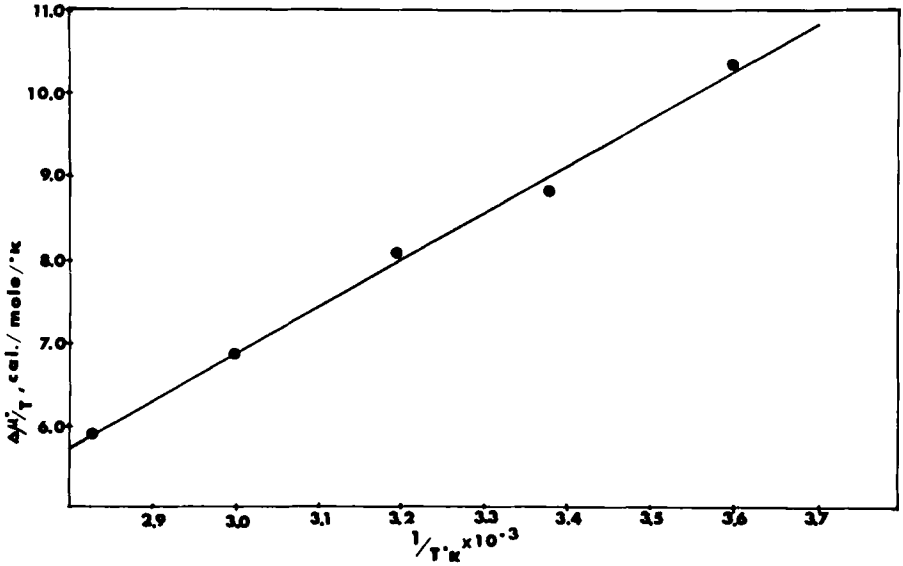

Fig. 3. Silver nitrate adsorption. Plot of $\Delta\mu^\circ/T$ vs. 1/T.

the fabric, and c_2 to the concentration of silver nitrate in the solution. $\Delta\mu^\circ$ is the difference in standard chemical potential of the system. The values of $\Delta\mu^\circ$ were calculated from the k values at each temperature (Table 3). These values were negative and decreased with increasing temperature.

Standard heat of adsorption (ΔH°) is expressed by

$$\frac{d(\Delta\mu^\circ/T)}{d(1/T)} = \Delta H^\circ$$

Assuming that ΔH° remains constant at the temperature range examined, it was calculated by plotting $\Delta\mu^\circ/T$ as a function of 1/T (Fig. 3). ΔH° was found to be -5.6 kcal/mole.

From the values of $\Delta\mu^\circ$ and ΔH° the difference in the standard entropy (ΔS°) was calculated (Table 3) by

$$\Delta\mu^\circ = \Delta H^\circ - T\Delta S^\circ$$

The ΔS° values were negative and were almost constant in the temperature range examined. The negative ΔS° testifies to a greater degree of order of

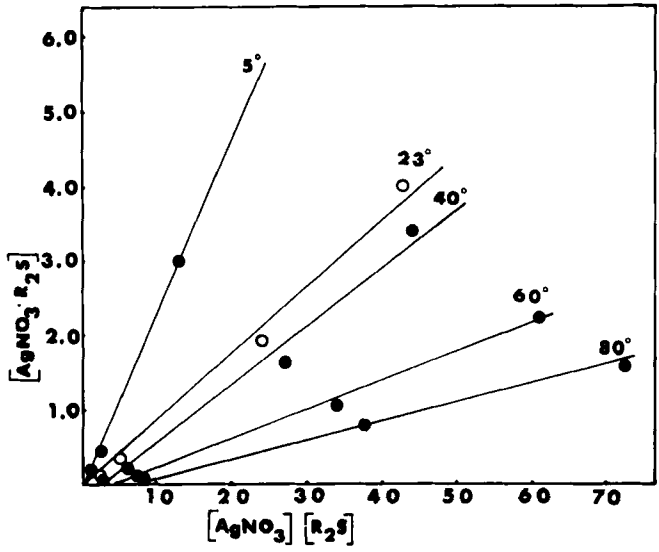

Fig. 4. Complexation of silver nitrate by the polyethylene sulfide in the fabric, concentration and temperature dependence. Cotton fabrics of the following polyethylene sulfide content were used: (○) 76.5%, all others 65.4%.

Table 4. Silver Nitrate Adsorption–Temperature Dependence of Complexation Constant[a]

Temperature (°C)	$1/T \times 10^3$ (1/°K)	K (1/mole)
5	3.60	23.1
23	3.38	8.9
40	3.20	7.8
60	3.00	3.9
80	2.83	2.5

[a]Calculations were made using data given in Table 2.

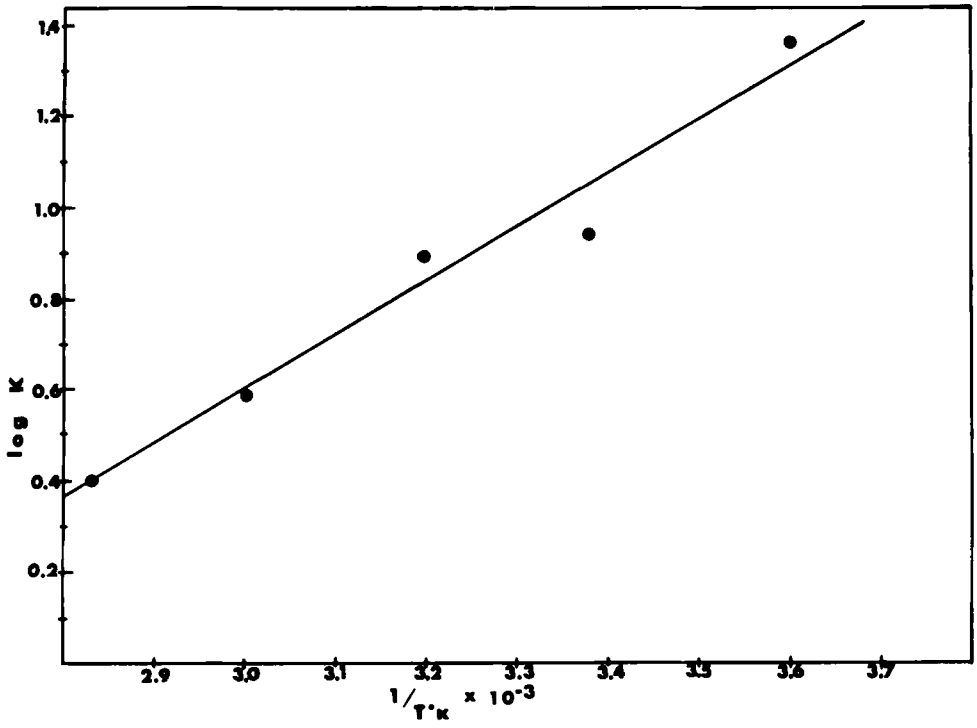

Fig. 5. Silver nitrate adsorption. Plot of log K vs. 1/T.

the adsorbed silver nitrate molecules on the fabric containing polyethylene sulfide compared with their original degree of order in solution.

Since adsorption was achieved by complexation of the silver nitrate with sulfide linkages, then ΔH° can be calculated from the temperature dependence of the equilibrium constant of complex formation (K). Following Kerr's treatment [7] we can assume that a solid phase behaves as if it was solubilized in the solution, and that activity coefficients for the solubilized and unsolubilized material are equal. Such an assumption is accepted in solid ion-exchange materials. In this case K can be defined by the following equation, assuming that all the sulfide bonds are equally reactive and that the ratio of silver nitrate to sulfide in the complex is 1 as reported in the literature [3]

$$K = [AgNO_3.R_2S]/[AgNO_3]\,[R_2S]$$

The K values were calculated from a graphical plot based on this equation (Fig. 4) and are reported in Table 4.

ΔH° was calculated from Van't Hoff's equation by plotting log K vs. 1/T (Fig. 5); the value obtained was -5.4 kcal/mole. The fact that the value of ΔH° obtained was essentially the same in the two methods of calculation shows that a real complex was fomed in the reaction of the polyethylene sulfide in the fabric with silver nitrate.

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