

# Metal Ammine Formation in Solution. XVIII. On the Silver(I) Complexes of Ethylenediamine. A Solubility Study of the Polymerization of the Mono-ethylenediamine Complex

JANNIK BJERRUM and EVA BANG

Chemistry Department I, Inorganic Chemistry, H. C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen Ø, Denmark

It has been found by one of the present authors (E.B.) that the mono(ethylenediamine)silver cation in the salt  $[\text{Ag en}]\text{ClO}_4$  is polymerized in infinite chains. In order to examine whether such extensive polymerization also takes place in solution, the polymerization equilibria:  $x\text{Ag en}^+ \rightleftharpoons \text{Ag}_x\text{en}_x^{x+}$  have been studied by means of solubility measurements with  $\text{Ag en ClO}_4$  in a 1 M  $\text{Na}(\text{ClO}_4, \text{NO}_3)$  medium of varying perchlorate concentration. These measurements confirm that the polymerization does not stop at the dimer stage as assumed by Schwarzenbach. A model embodying one equilibrium constant  $K_{1,2}$  for the dimerization and another constant  $K_{av}$  for all the subsequent polymerization steps ( $K_{x-1,x}$ ) rationalizes our experimental data satisfactorily. The following values were obtained for the constants at 20 and 25 °C:  $K_{1,2} = 93 \pm 13$ , and  $51 \pm 16 \text{ M}^{-1}$ ,  $K_{av} = 32.5 \pm 1.6$ , and  $19.7 \pm 2.7 \text{ M}^{-1}$ .

Ethylenediamine binds to the 3d-transition metal(II) cations with a considerable chelate effect,<sup>1,2</sup> so that only half as many diamine molecules are bound as there are  $\text{NH}_3$ -molecules coordinated in the corresponding metal-ion ammonia systems. The silver cation behaves differently. This was first shown by P. Job,<sup>3</sup> who found that this cation, which cannot bind more than two ammonia molecules, nevertheless binds two molecules of the diamine, and furthermore that the stability constants  $\beta_2$  of  $\text{Ag}(\text{NH}_3)_2^+$  and  $\text{Ag en}_2^+$  are almost equal. Job also found, in contrast to findings for the silver cation with monodentate ligands, that  $K_1$  is much larger than  $K_2$ . These results were confirmed and discussed by one of the present authors<sup>4</sup> and are not surprising in view of the linear arrangement

N–Ag–N in the diamminesilver complex. However, when only one of the amino group in the diamine is coordinated, the other amino group must be able to bind to a proton or to a silver ion forming the adducts  $\text{Ag enH}^{2+}$  and  $\text{Ag}_2\text{en}^{2+}$ . The existence of these species was confirmed by Schwarzenbach *et al.*,<sup>5</sup> who also found the presence of a dimeric species  $\text{Ag}_2\text{en}_2^{2+}$ . Further evidence for the formation of a dimer was also provided by salt-crystoscopic measurements.<sup>6</sup> The dimeric species has also been postulated in more recent investigations,<sup>7,8</sup> in which it was found that the reproduction of the experimental data by the use of the computed stability constants was improved when the formation of  $\text{Ag}_2\text{en}_2^{2+}$  was taken into account.

Schwarzenbach and coworkers<sup>5</sup> consider the dimer to be the only polymerization product present, and they suggest from its comparatively high stability that it has a 10-membered ring structure. Such a ring structure does not appear in  $\text{Ag en ClO}_4$  in the crystalline state. A recent determination of the structure of this salt by one of the present authors<sup>9</sup> showed that  $\text{Ag en}^+$  forms infinite chains with each diamine molecule bridging two silver atoms. In order to examine whether such extensive polymerization also takes place in solution, the polymerization equilibria:  $x\text{Ag en}^+ \rightleftharpoons \text{Ag}_x\text{en}_x^{x+}$  have been studied by means of solubility measurements employing the moderately soluble complex salt  $\text{Ag enClO}_4$  at varying concentrations of perchlorate.

## THE SOLUBILITY DATA

The solubility measurements were made using a 1 M Na(ClO<sub>4</sub>,NO<sub>3</sub>) medium in which the solubility of Ag en ClO<sub>4</sub> ( $S_{Ag}$ ) varied from  $\sim 2 \times 10^{-3}$  M in 1 M NaClO<sub>4</sub> to  $\sim 0.1$  M in 1 M NaNO<sub>3</sub>. Equilibrium was established in a few hours. The saturated solutions were analyzed by silver titration and the results obtained for 20 and 25 °C are shown in Table 1. The residual amounts of undissolved silver salt were slightly discoloured, but were shown to give X-ray powder diagrams identical with that of the pure salt (for further details, see Experimental).

The various mono(ethylenediamine)silver species dominate in solutions of Ag en ClO<sub>4</sub>, but in order to decrease pH and further stabilize these species, enH<sup>+</sup> was added up to a concentration of 30 % of

the silver concentration. The addition of enH<sup>+</sup> was not of great consequence, as preliminary experiments without this addition yielded the same values for the solubilities within the uncertainty of the measurements.

The hydrogen ion concentration and aqua silver ion concentrations in some of the solutions were measured at 20 °C, and the values of the products [Ag<sup>+</sup>][OH<sup>-</sup>] given in the last column of Table 1 are calculated assuming [H<sup>+</sup>][OH<sup>-</sup>] =  $10^{-13.94}$ . The solubility product for Ag<sub>2</sub>O,  $K_s \sim 10^{-7.4}$  (in 1 M NaClO<sub>4</sub> at 20 °C) is in all cases larger than the actual values of [Ag<sup>+</sup>][OH<sup>-</sup>], showing that all the solutions are unsaturated with respect to silver oxide.

In order to estimate the influence of replacement of ClO<sub>4</sub><sup>-</sup> by NO<sub>3</sub><sup>-</sup> in the 1 M Na(ClO<sub>4</sub>,NO<sub>3</sub>)

Table 1. Solubility measurements with Ag en ClO<sub>4</sub>.

No.	[ClO <sub>4</sub> <sup>-</sup> ]	$C_{enH^+}$	$S_{Ag}$	$S'_{Ag}$	$-\log[H^+]$	$-\log[Ag^+]$	$-\log[Ag^+][OH^-]$
In 1 M Na(ClO <sub>4</sub> ,NO <sub>3</sub> ) at 20 °C							
1	1.007	0.00002	0.001720	0.001720	—	—	—
2	1.007	0.00060	0.001725	0.001725	8.77	3.72	8.89
3	0.9064	0.00060	0.001928	0.001901	8.84	3.73	8.83
4	0.7762	0.00060	0.002456	0.002373	8.85	3.74	8.83
5	0.6331	0.00016	0.003024	0.00286	9.24	—	—
6	0.4296	0.00026	0.00546	0.00500	9.28	3.40	8.06
7	0.3282	0.00042	0.0086	0.00773	9.19	3.38	8.13
8	0.2530	0.00070	0.0138	0.01225	9.15	3.32	8.11
9	0.2011	0.00104	0.0212	0.01865	9.17	3.37	8.14
10	0.1557	0.00162	0.0351	0.03084	9.12	3.38	8.20
11	0.1441	0.0022	0.0436	0.0380	9.01	3.39	8.32
12	0.1269	0.0028	0.0565	0.0490	9.04	—	—
13	0.1176	0.0034	0.0674	0.0585	9.10	—	—
14	0.1080	0.0040	0.0830	0.0719	9.03	—	—
15	0.1033	0.0046	0.0933	0.0807	8.97	—	—
16	0.1038	0.0050	0.1038	0.0898	8.93	—	—
In 1 M Na(ClO <sub>4</sub> ,NO <sub>3</sub> ) at 25 °C							
17	1.006	0.00001	0.00294	0.00294	—	—	—
18	1.006	0	0.00312	0.00312	—	—	—
19	0.906	0.00002	0.00337	0.00332	—	—	—
20	0.6277	0.00003	0.00585	0.00552	—	—	—
21	0.4116	0.00025	0.01046	0.00954	—	—	—
22	0.3181	0.0006	0.0172	0.01544	—	—	—
23	0.2613	0.0012	0.0206	0.01832	—	—	—
24	0.2309	0.0014	0.0303	0.02680	—	—	—
25	0.1631	0.002	0.0627	0.0548	—	—	—
26	0.1356	0.004	0.1055	0.0918	—	—	—
27	0.1311	0.004	0.1111	0.0966	—	—	—
28	0.1207	0.005	0.1107	0.0961	—	—	—
29	0.1187	0.005	0.1187	0.1028	—	—	—

Table 2. Solubility of  $\text{AgBrO}_3$  in some 1 molar salt media at 25 °C, and  $\gamma^\pm$  of some electrolytes in 1 molal solution.

	1 M $\text{NaClO}_4$	1 M $\text{NaNO}_3$	1 M $\text{KNO}_3$
$S_{\text{AgBrO}_3}$	0.0120	0.0146	0.0161
	0.5 M $\text{NaClO}_4$ 0.5 M $\text{NaNO}_3$	1.10 M $\text{NaNO}_3$	
$S_{\text{AgBrO}_3}$	0.0132	0.0152	
$\gamma^\pm$	1 m $\text{NaClO}_4$ 0.629	1 m $\text{NaNO}_3$ 0.548	1 m $\text{KNO}_3$ 0.443

medium on the solubility of the silver salt, some solubility measurements were performed with  $\text{AgBrO}_3$ , which has a suitable solubility and no ions in common with the medium. The data are shown in Table 2, together with the mean activity coefficients  $\gamma^\pm$  of 1 molal solutions of  $\text{NaClO}_4$ ,  $\text{NaNO}_3$  and  $\text{KNO}_3$  taken from data in the literature.<sup>10</sup> The solubility of  $\text{AgBrO}_3$  in 1 M  $\text{NaNO}_3$  is higher than that in 1 M  $\text{NaClO}_4$ , and in agreement with Harned's rule the solubility of  $\text{AgBrO}_3$  can be corrected for the influence of the replacement of  $\text{ClO}_4^-$  by  $\text{NO}_3^-$  by means of the expression:

$$S'_{\text{AgBrO}_3} = S_{\text{AgBrO}_3} (1 - \alpha C_{\text{NaNO}_3})$$

with  $\alpha = 0.18$ . The value for  $\alpha$  is not necessarily the same as for the influence of the change in medium on the solubility of the complex silver salt. Thus  $\alpha$  is found to be 0.126 from the values for  $\gamma^\pm$  in 1 molal  $\text{NaClO}_4$  and  $\text{NaNO}_3$ , and as a kind of average we have chosen to correct the solubilities of  $\text{Ag enClO}_4$  by use of an expression with  $\alpha = 0.15$ . The concentration of perchlorate is given by

$$[\text{ClO}_4^-] = C_{\text{NaClO}_4} + S_{\text{Ag}}$$

$$S'_{\text{Ag}} = S_{\text{Ag}} \{1 - 0.15(1 - [\text{ClO}_4^-])\}$$

$$\sim S_{\text{Ag}}(1 - 0.15C_{\text{NaNO}_3})$$

#### TREATMENT OF THE DATA

The solubility of  $\text{Ag enClO}_4$  increases greatly with decreasing perchlorate concentration and an analysis of the data shows that polymerization continues beyond the dimer stage. In our treatment of the data the following abbreviations are

used for the concentration of the various species, and for the consecutive polymerization constants:

$$m = [\text{Ag en}^+], m_2 = [\text{Ag}_2 \text{en}_2^{2+}] \dots \dots \dots$$

$$m_x = [\text{Ag}_x \text{en}_x^{x+}] \quad (1)$$

$$K_{1,2} = \frac{m_2}{m^2}, K_{2,3} = \frac{m_3}{m_2 m} \dots \dots \dots$$

$$K_{x-1,x} = \frac{m_x}{m_{x-1} m} \quad (2)$$

The symbol

$$\beta_{1,x} = K_{1,2} K_{2,3} \dots \dots K_{x-1,x} \quad (3)$$

is used for the cumulative constants and  $K_s = m[\text{ClO}_4^-]$  for the solubility product of  $[\text{Ag en}]\text{ClO}_4$ . The solubility can then be expressed as follows:

$$S_{\text{Ag}} = m + 2K_{1,2}m^2 + 3\beta_{1,3}m^3 + \dots x\beta_{1,x}m^x \quad (4)$$

where  $m$  can be calculated when  $K_s$  is known. This equation can be transformed to:

$$\frac{S_{\text{Ag}} - m}{m} = 2K_{1,2} + 3\beta_{1,3}m + \dots x\beta_{1,x}m^{x-1} \quad (5)$$

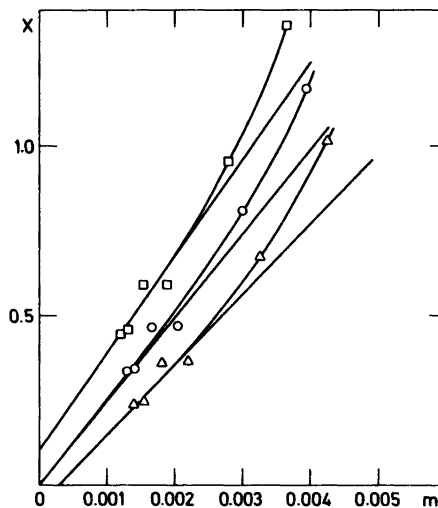


Fig. 1. Values of the function  $X = (S_{\text{Ag}} - m)/m$  plotted versus  $m = [\text{Ag en}^+]$  [calculated with  $K_s = [\text{Ag en}^+][\text{ClO}_4^-] = 1.2 \times 10^{-3}$  ( $\square$ ),  $1.3 \times 10^{-3}$  ( $\circ$ ),  $1.4 \times 10^{-3}$  ( $\triangle$ )].

A preliminary estimate of  $K_{1,2}$  and  $K_s$  from the uncorrected solubilities at 20 °C was obtained by plotting  $X = (S_{Ag} - m)/m$  versus  $m = K_s/[\text{ClO}_4^-]$ . In this calculation  $K_s$  was obtained by systematic approximation until the curve through the calculated  $X, m$ -points passed through the origin, and  $2K_{1,2}$  was then determined as the slope of the tangent at this point (see Fig. 1). Using this procedure the following constants were obtained:  $K_{1,2} = 124 \text{ M}^{-1}$  and  $K_s = 1.3 \times 10^{-3} \text{ M}^2$  (compare with the computer calculated values in Table 3), and the graph gives evidence for further polymerization.

More complete calculations were made with different models employing  $K_s = m[\text{ClO}_4^-]$  as one of the parameters. In model I it was assumed that the polymerization continues towards infinity and that the consecutive constants  $K_{x-1,x}$  for polymerization beyond the dimerization stage all have the same value,  $K_{av}$ . With this assumption it can be shown that the solubility is given by the expression:

$$S_{Ag} = \sum_1^{\infty} x \beta_{1,x} m^x = m(1 - K_{1,2} K_{av}^{-1}) + K_{1,2} K_{av}^{-1} m(1 - K_{av} m)^{-2} \quad (6)$$

Model II takes account only of  $K_{1,2}$  and  $K_{2,3}$  and assumes that the polymerization stops with the formation of the trimer. Model III is a further refinement of model I with an individual value for  $K_{2,3}$ . Finally, a model which assumes that the polymerization stops at the dimer (Schwarzenbach's model) was also examined.

Ole Mønsted of this department has assisted us with the computer calculations based on these models, and Table 3 and Fig. 2 show the results of the calculations made using his program. In all cases the parameters were estimated by minimization of the quantity:

$$\sum [S(\text{obs}) - S(\text{calc})]^2 / (\sigma_s^2 + \left(\frac{\partial S}{\partial C}\right)^2 \sigma_c^2)$$

where  $S(\text{obs})$  and  $S(\text{calc})$  are the experimental and calculated solubilities, and  $\sigma_s^2$  and  $\sigma_c^2$  are the variances of the solubility of  $\text{Ag en ClO}_4$  ( $S = S_{Ag}$ ) and the perchlorate concentration ( $C = [\text{ClO}_4^-]$ ), respectively. The calculations were performed using all the corresponding values of  $[\text{ClO}_4^-]$  and  $S_{Ag}$ , and were carried out in some cases with both the directly measured solubilities  $S_{Ag}$  and the solubilities  $S'_{Ag}$

Table 3. Results of calculations of the constants at 20 °C under different assumptions.

	$0.9S_{Ag}$	$S_{Ag}$	$S'_{Ag}$
Authors' model I			
$K_s \times 10^3$	1.2	$1.26 \pm 0.05$	$1.33 \pm 0.05$
$K_{1,2}$	110	$134 \pm 18$	$93 \pm 13$
$K_{av}$	$\sim 33$	$32 \pm 1.4$	$32.5 \pm 1.6$
$K_s \times 10^3$ <sup>a</sup>			
		$2.10 \pm 0.27$	$2.38 \pm 0.18$
$K_{1,2}$ <sup>a</sup>		$82 \pm 34$	$51 \pm 16$
$K_{av}$ <sup>a</sup>		$22 \pm 2.8$	$19.7 \pm 2.7$
Authors' model II			
$K_s \times 10^3$		—	$1.51 \pm 0.07$
$K_{1,2}$		—	$33 \pm 14$
$K_{2,3}$		—	$175 \pm 67$
Authors' model III			
$K_s \times 10^3$		$1.28 \pm 0.11$	—
$K_{1,2}$		$122 \pm 48$	—
$K_{2,3}$		$39 \pm 28$	—
$K_{av}$		$26 \pm 18$	—
Schwarzenbach's model			
$K_s$		$0.73 \pm 0.14$	$0.85 \pm 0.13$
$K_{1,2}$		$745 \pm 310$	$451 \pm 159$

<sup>a</sup> At 25 °C.

corrected for the medium influence. The uncertainty in the solubilities was assumed to be 2 % at 20 °C, 3 % at 25 °C and 1 % in the perchlorate concentrations.

The calculations summarized in Table 3 were made ignoring the fact that species other than the  $\text{Ag}_{x\text{en}_x}$  polymers are present in nonnegligible concentrations. The most important species besides the  $\text{Ag}_{x\text{en}_x}$  polymers are  $\text{Ag}^+$ ,  $\text{AgH en}^{2+}$  and  $\text{Ag}_2\text{en}^{2+}$ , and in order to estimate the error introduced by this omission, the fractions of these species were estimated (Table 4) for some of the solutions referred to in Table 1 (Nos. 2, 6 and 11). The frac-

Table 4. Estimated fractions of species other than  $\text{Ag}_{x\text{en}_x}^{z+}$  in solutions saturated with  $\text{Ag en ClO}_4$ .

Soln. No.	$\alpha_{\text{Ag}^+}$	$\alpha_{\text{Ag en}^{\ddagger}}$	$\alpha_{\text{AgH en}^{2+}}$	$\alpha_{\text{Ag}_2\text{en}^{2+}}$
2	0.11	0	$\sim 0.04$	$< 0.01$
6	0.07	0	$< 0.01$	$< 0.01$
11	0.01	0	$< 0.01$	$< 0.01$

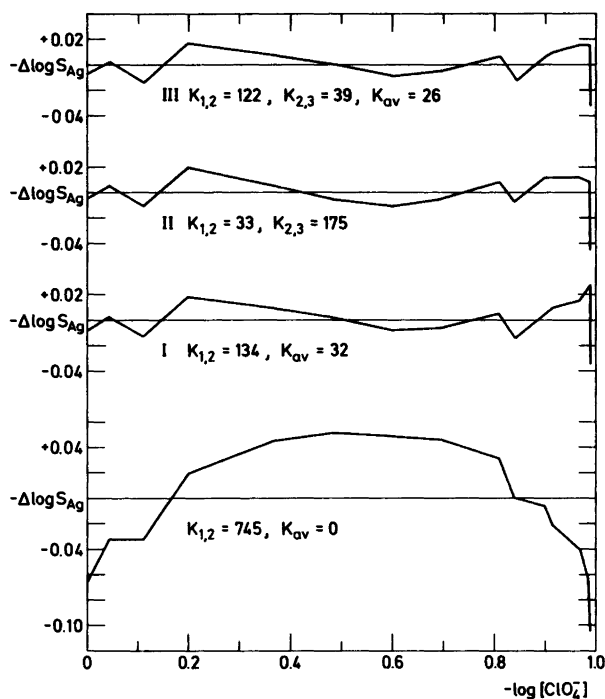


Fig. 2. Diagram showing  $-\Delta \log S_{Ag} = \log S_{Ag}(\text{exp}) - \log S_{Ag}(\text{calc})$  versus  $-\log[\text{ClO}_4^-]$  for the different models considered. In ascending order: Schwarzenbach's followed by the authors' models I, II and III. The polymerization constants at 20 °C corresponding to the uncorrected solubilities are used except in the case of model II.

tions of aqua silver ion  $\alpha_{Ag^+} = [\text{Ag}^+]/S_{Ag}$  were calculated directly from the data given in the table, and those of  $\text{AgH en}^{2+}$  and  $\text{Ag}_2\text{en}^{2+}$  were estimated using the constants reported by Schwarzenbach<sup>5</sup> and by Ohtaki *et al.*<sup>7</sup> for the species in question.

The result of a preliminary calculation of  $K_s$  and  $K_{1,2}$  (as in Fig. 1) made with the assumption that only 90% of the silver is present as mono(ethylenediamine) silver species is shown in Table 3. However, this may give a somewhat distorted picture as it is only in the solutions with the lowest silver concentrations (see Table 4) that the concentrations of other species, especially aqua silver ion, are significant. A correction taking this fact into account would decrease  $K_s$  by about 10%, but would also counteract the influence of the medium correction on  $K_{1,2}$ : with a decreased solubility for  $[\text{ClO}_4^-] \sim 1 \text{ M}$  and a corrected lower solubility in 1 M  $\text{NaNO}_3$  the factor by which the solubility increases on going from 1 M  $\text{NaClO}_4$  to  $\sim 1 \text{ M}$

$\text{NaNO}_3$  would not be much lower than if no correction was applied.

## DISCUSSION OF RESULTS

Fig. 2 shows diagrammatically, in the form of plots of  $\log S_{Ag}(\text{exp}) - \log S_{Ag}(\text{calc})$  versus  $-\log[\text{ClO}_4^-]$ , the extent to which the parameters calculated by the various models satisfy the data. It is clear that all of our models reproduce the experimental data fairly well and much better than Schwarzenbach's model, which gives rise to large systematic deviations. It is especially surprising that model I and model II satisfy the data almost equally well, and that model III with an extra parameter does not improve the result further. However, it should be noticed that model II yields a suspiciously low value for  $K_{1,2}$ , while models I and III give more reasonable values which are in fair agreement with the value obtained for  $K_{1,2}$  by

the graphical extrapolation of the data for the lowest silver concentrations.

That polymerization does not stop at the dimer stage is still more evident when the average polymerization factor

$$\bar{f} = \sum x m_x / \sum m_x \quad (7)$$

is calculated from the data. Denoting the total osmotic concentration of the polymeric species with  $\sigma$ , the following equation applies:

$$\sigma = m + K_{1,2} m^2 + \beta_{1,3} m^3 + \dots + \beta_{1,x} m^x \quad (8)$$

Differentiating this with respect to  $m$  and comparing with (4), the following relationship is obtained for solutions saturated with  $\text{Ag enClO}_4$ <sup>11</sup>

$$\frac{d\sigma}{dm} = \frac{S_{\text{Ag}}}{m} \quad (9)$$

By means of this relationship,  $\sigma$  can be obtained from the data in Table 1 by numerical integration

$$\sigma = \int_{m=0}^m \frac{S_{\text{Ag}}}{m} dm \quad (10)$$

The corrected solubilities  $S'_{\text{Ag}}$  at 20 °C (with  $K_s = 0.00133$ ) were used in the calculations, and the numerical integration results for solns. Nos. 1 to 16 are shown in Table 5. The average polymerization factor  $\bar{f} = S'_{\text{Ag}}/\sigma$  is given in the last column of the table, and Fig. 3 shows a plot of  $\bar{f}$  versus  $m = [\text{Ag en}^+]$ . The osmotic concentration of the

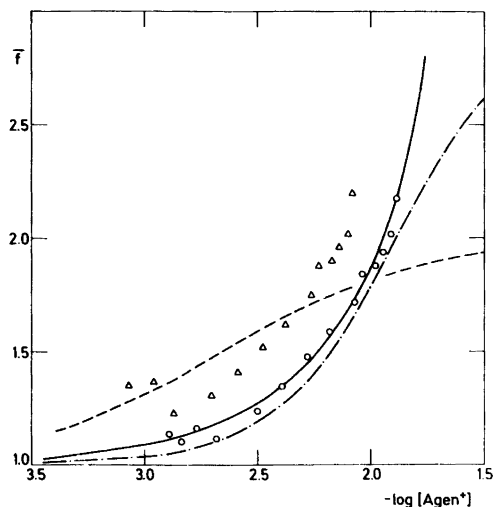


Fig. 3. The average polymerization factor  $\bar{f}$  as a function of  $-\log [\text{Ag en}^+]$  at 20 °C. The curves are calculated on the basis of model I (—), model II (---) and Schwarzenbach's model (- · -) with the polymerization constants corresponding to  $S'_{\text{Ag}}$ . The (O) points for model I and the ( $\Delta$ ) points for Schwarzenbach's model indicate the values obtained by numerical integration using the corresponding values for  $K_s$ , viz. 0.00133 and 0.00085  $\text{M}^2$ , respectively.

species (8) for model I with  $x \rightarrow \infty$  is given by the expression

$$\sigma = (m + (K_{1,2} - K_{\text{av}})m^2)(1 - K_{\text{av}}m)^{-1} \quad (11)$$

Table 5. Calculation of the average polymerization factor  $\bar{f} = S'_{\text{Ag}}/\sigma$  by numerical integration using the corrected solubilities at 20 °C.  $K_s = m[\text{ClO}_4^-] = 0.00133$ .

No.	$[\text{ClO}_4^-]$	$m$	$S'_{\text{Ag}}$	$\Delta\sigma$	$\sigma$	$\bar{f}$
1, 2	1.007	0.001321	0.001725	0.001523	0.001523	1.133
3	0.9064	0.001467	0.001901	0.000190	0.001713	1.110
4	0.7762	0.001713	0.002373	0.000329	0.002042	1.162
5	0.6331	0.002101	0.00286	0.000533	0.002575	1.111
6	0.4296	0.003096	0.00500	0.001481	0.004056	1.232
7	0.3282	0.004052	0.00773	0.001684	0.005740	1.347
8	0.2530	0.005257	0.01225	0.002553	0.008293	1.477
9	0.2011	0.006614	0.01865	0.003494	0.01179	1.582
10	0.1557	0.008542	0.03084	0.006199	0.01799	1.714
11	0.1441	0.009230	0.0380	0.002658	0.02064	1.840
12	0.1269	0.01048	0.0490	0.005499	0.02614	1.875
13	0.1176	0.01131	0.0585	0.004082	0.03023	1.935
14	0.1080	0.01231	0.0719	0.005507	0.03573	2.012
15, 16	0.1035	0.01284	0.0853	0.003521	0.03925	2.173

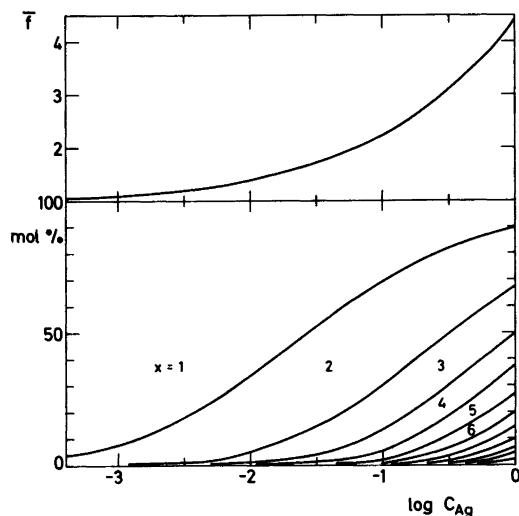


Fig. 4. The lower part of the figure shows the ranges of existence of the polymers  $\text{Ag}_x\text{en}_x^{x+}$  and the upper part the polymerization factor  $\bar{f}$  for solutions of mono(ethylenediamine) silver salts as a function of the formal silver concentration. The ordinate in the lower part of the figure gives the mol percentages of the various polymers ( $x=1, 2, 3 \dots$ ) and the abscissa gives the logarithm of the formal silver concentration. The figure is based on model I and the corrected polymerization constants at 20 °C.

and when this expression is combined with (6),  $\bar{f} = S'_{\text{Ag}}/\sigma$  can be calculated for arbitrary values of  $m$  using the known values of  $K_{1,2}$  and  $K_{\text{av}}$ . Fig. 3 shows how well the calculated curve (solid line) approximates the integrated experimental values from Table 5 (○).

Fig. 3 also shows the calculated curves for model II (— · —) and for Schwarzenbach's model (— — —). For model II the integrated values obtained by means of relation (10) and  $K_s = 0.00151$  agree well with the calculated but this is not so for the values obtained with Schwarzenbach's model. For practical reasons the integrated values for model II are not shown in the figure.

It is clear from Figs. 2 and 3 that Schwarzenbach's model is inconsistent with our measurements, whereas satisfactory experimental agreement is obtained using models I and II. In choosing between the latter two models most speaks for model I. Thus, as already mentioned, model II gives a value for  $K_{1,2}$  which is much too low and which does not agree with the graphically determined value. It is

Table 6. Results of some viscosity measurements at 25 °C. Relative viscosities (water = 1.00).

$\text{AgNO}_3$ (1 M), en (1 M)	1.33
$\text{NaNO}_3$ (1 M), en (1 M)	1.23
$\text{Cu}(\text{NO}_3)_2$ (1 M), en (2 M)	1.29
$\text{NaNO}_3$ (2 M), en (2 M)	1.71
$\text{AgNO}_3$ (1 M)	1.06 <sup>a</sup>
$\text{NaNO}_3$ (1 M)	1.07 <sup>a</sup>
$\text{Cu}(\text{NO}_3)_2$ (0.5 M)	1.18 <sup>a</sup>

<sup>a</sup> Taken from Landolt-Börnstein Tabellen, 5. Ed. (1923) 154.

also difficult to believe that polymerization should stop at the trimer stage when it continues beyond the dimer. It is much more likely that higher polymers are formed by linear polymerization, which would be consistent with the X-ray structure of  $\text{Ag enClO}_4$ . For this reason model I has been chosen as our working hypothesis.

It is, of course, possible that  $K_{\text{av}}$  decreases strongly with polymer chain length, but it should be noticed that our model predicts that  $\bar{f} \rightarrow \infty$  for a maximum value of the monomer concentration given by  $m = K_{\text{av}}^{-1}$ . The fractions  $\alpha_x = K_{1,2} K_{\text{av}}^{x-2} m^x / \sigma$  are also accessible for calculation, and Fig. 4 shows the ranges of existence of the polymers  $\text{Ag}_x\text{en}_x$  as a function of the formal silver concentration.

Parissakis and Schwarzenbach<sup>6</sup> have shown by salt-cryoscopy on  $[\text{Ag en}]_2\text{SO}_4$  dissolved in molten Glauber's salt that  $\text{Ag en}^+$  has a nuclearity close to two in the concentration range 0.02–0.06 M, and Magyar has recently confirmed this result by an ebullioscopic method<sup>12</sup> with aqueous solutions of  $\text{Ag en NO}_3$  of concentration up to 0.4 M.\* It is obvious that these results are incompatible with the conclusions drawn from our solubility measurements. According to our model I it would be expected that the higher polymers, even though they are present only in low concentrations (see Fig. 4), would cause an increased viscosity of the solutions. Some viscosity measurements were therefore made with an Ubbelohde Viscosimeter at 25 °C. The results are shown in Table 6, and it can be seen that a 1 M solution of  $\text{Ag en NO}_3$  actually has a higher viscosity than a 1 M solution of  $\text{NaNO}_3$  made 1 M with respect to ethylenediamine. On the other hand a 1 M solution of the complex

\* Personal communication from Professor Schwarzenbach.

salt  $[\text{Cu en}_2](\text{NO}_3)_2$  was found to have a considerably lower viscosity than 2 M  $\text{NaNO}_3$  made 2 M with respect to the diamine. This lends some support to our assumptions, although the magnitude of the effect is not sufficiently large to be convincing and it must be concluded that further experiments are necessary to explain the discrepancy between the results of Schwarzenbach and coworkers and our results.

## EXPERIMENTAL

*Chemicals.* All reagents were *pro analysi* or of good commercial quality.

*Ag en ClO<sub>4</sub>* was prepared as follows: A solution of  $\text{AgClO}_4 \cdot \text{H}_2\text{O}$  (1.5 g, 0.0067 mol) in 5 ml water was added with stirring to a solution of anhydrous ethylenediamine (0.40 g, 0.0067 mol) in 45 ml water. The white crystalline precipitate of *Ag en ClO<sub>4</sub>* was filtered off, washed with ice-cold water and air-dried. It can be recrystallized from water, but this was not considered to be necessary. Yield ~1.1 g (60%). *Anal.* Calc. for *Ag en ClO<sub>4</sub>*: Ag 40.33. Found:  $40.2 \pm 0.05$ . The salt is potentially explosive and was for this reason prepared in individual, small portions.

*AgBrO<sub>3</sub>* was precipitated by slowly adding a solution of  $\text{NaBrO}_3$  (16 g, ~0.1 mol) in 200 ml water to a solution of  $\text{AgNO}_3$  (17 g, 0.1 mol) in 500 ml water. The precipitate was filtered off, washed with water and dried at 100 °C. *Anal.* Calc. for *AgBrO<sub>3</sub>*: Ag 45.75, Br 33.90. Found: Ag 45.0, Br 33.7.

*Solubility measurements* with the silver salts were performed as follows: 1 M  $\text{Na}(\text{ClO}_4, \text{NO}_3)$  media were made up in 100 ml volumetric flasks from 2 M stock solutions of  $\text{NaClO}_4$  and  $\text{NaNO}_3$ . The perchlorate concentration in the stock solution was checked by analysis (cation exchange with Dowex 50 WX 8 and titration of the perchloric acid). In the final experiments with *Ag en ClO<sub>4</sub>*, an amount of  $\text{enHNO}_3$  equal to 5% of the expected solubility of the silver salt was also added from a stock solution of the diamine which had been titrated to the calculated pH. After addition of the necessary amount of silver salt (0.3–3 g) the solutions were transferred to pyrex flasks with tightly fitting stoppers and set to rotate in a thermostatted water bath. After equilibration, which was achieved within a few hours, the saturated solutions were separated from undissolved silver salt by filtration through cotton.

*The total silver concentration* in the most dilute (<0.01 M) *Ag en ClO<sub>4</sub>* solutions was determined by potentiometric titration with iodide, in the more concentrated *Ag en ClO<sub>4</sub>* solutions by Volhard

titration and in the *AgBrO<sub>3</sub>* solutions by Mohr titration (titrating the silver solution into standardized chloride solution).

*The free silver ion concentrations* were measured relative to  $10^{-3}$ – $10^{-2}$  M solutions of  $\text{AgNO}_3$  in the salt medium in question. An ignited rod of pure silver was used as silver electrode. A 1 M  $\text{NH}_4\text{NO}_3$  solution served as salt-bridge between the 1 M KCl-calomel electrode and the silver perchlorate solutions.

*The hydrogen ion concentrations* were measured relative to  $10^{-3}$ – $10^{-2}$  M solutions of  $\text{HNO}_3$  or  $\text{HClO}_4$ . The measurements were performed as described by Ilcheva and Bjerrum.<sup>13</sup> Owing to the insolubility of  $\text{KClO}_4$  a 1 M  $\text{NH}_4\text{NO}_3$  solution was employed as salt-bridge between the 1 M KCl calomel electrode and the perchlorate solution.

*Acknowledgements.* Our thanks are due to the late Professor Schwarzenbach, who suggested the structure investigation and followed this work with interest and criticism, and to lektor Ole Mønsted for his advice and for carrying out the computer calculations. Morten Jannik Bjerrum carried out the solubility measurements with *AgBrO<sub>3</sub>*, and Mrs. Gerda Nielsen performed the viscosity measurements. The authors also thank Dr. Martin Hancock for correcting the English manuscript.

## REFERENCES

1. Bjerrum, J. and Nielsen, E. J. *Acta Chem. Scand.* 2 (1948) 297.
2. Schwarzenbach, G. *Helv. Chim. Acta* 35 (1952) 2344.
3. Job, P. *Ann. Chim. (Paris)* [10] 9 (1928) 166.
4. Bjerrum, J. *Chem. Rev.* 40 (1950) 381.
5. Schwarzenbach, G., Ackermann, H., Maissen, G. and Anderegg, G. *Helv. Chim. Acta* 35 (1952) 2337.
6. Parissakis, G. and Schwarzenbach, G. *Helv. Chim. Acta* 41 (1958) 2042, 2431.
7. Ohtaki, H. and Ito, Y. *J. Coord. Chem.* 3 (1973) 131.
8. Poucke, L. C. van *Talanta* 23 (1976) 161.
9. Bang, E. *Acta Chem. Scand.* A 32 (1978) 555.
10. Robinson, R. A. and Stokes, R. H. *Trans. Faraday Soc.* 45 (1949) 620.
11. Bjerrum, J. *Kemisk Maanedssblad og Nordisk Handelsblad for kemisk Industri* 24 (1943) 21.
12. Magyar, B. *Structure Bonding (Berlin)* 14 (1973) 111.
13. Ilcheva, L. and Bjerrum, J. *Acta Chem. Scand.* A 30 (1976) 343.

Received November 3, 1978.