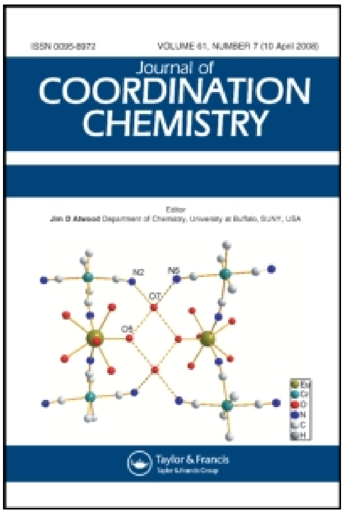

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COMPLEX FORMATION OF SILVER ION WITH ETHYLENEDIAMINE AND 1,2-PROPANEDIAMINE

Hitoshi Ohtaki[a]; Yoshiakiito[b]
[a] Department of Electrochemistry, Tokyo Institute of Technology, Meguro, Tokyo, Japan [b] Laboratory of Analytical Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya, Japan

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COMPLEX FORMATION OF SILVER ION WITH ETHYLENEDIAMINE AND 1,2-PROPANEDIAMINE

HITOSHI OHTAKI

Department of Electrochemistry, Tokyo Institute of Technology, O-okayama, Meguro, Tokyo, 152, Japan.

and

YOSHIAKI ITO†

Laboratory of Analytical Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya, 464, Japan.

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Complex formation of silver ion with ethylenediamine and 1,2-propanediamine has been studied potentiometrically at 25°C in 3M $LiClO_4$ aqueous solution. In the range of the total silver concentration of 0.0025 to 0.020 M and of pH up to 10.4, the emf data obtained could be explained in terms of the formation of the following complexes: $AgHL^{2+}$, $\log \beta_{111} = 13.56 \pm 0.02$; $AgH_2L_2{}^{3+}$, $\log \beta_{122} = 27.37 \pm 0.02$; AgL^+, $\log \beta_{101} = 6.13 \pm 0.02$; Ag_2L^{2+}, $\log \beta_{201} = 7.67 \pm 0.05$; $Ag_2L_2{}^{2+}$, $\log \beta_{202} = 14.53 \pm 0.07$; Ag(OH)L, $\log \beta_{1-11} = -4.59 \pm 0.05$ in the system of ethylenediamine solution and $\log \beta_{111} = 12.72 \pm 0.02$, $\log \beta_{122} = 25.84 \pm 0.02$, $\log \beta_{101} = 5.52 \pm 0.02$, $\log \beta_{201} = 7.60 \pm 0.02$, $\log \beta_{202} = 13.47 \pm 0.07$ and $\log \beta_{1-11} = -4.17 \pm 0.05$ in the system of 1,2-propanediamine solution, where $\beta_{pqr} = [Ag_pH_qL_r{}^{(p+q)+}]/[Ag^+]^p[H^+]^q[L]^r$ and $\beta_{p-qr} = [Ag_p(OH)_qL_r{}^{(p-q)+}] \times [H^+]^q/[Ag^+]^p[L]^r$, and L denotes the neutral molecule of the diamines. Dissociation constants of protonated ethylenediamine and 1,2-propanediamine were found to be $pK_1 = 8.04_4 \pm 0.01$ and $pK_2 = 10.65_0 \pm 0.01$ for the former and $pK_1 = 7.63_5 \pm 0.01$ and $pK_2 = 9.98_7 \pm 0.01$ for the latter.

INTRODUCTION

Reactions of metal ions with multidentate ligands have widely been studied by numerous workers. Nevertheless, a relatively few attentions have been focused on the formation of mixed complexes containing protons and hydroxyl groups and even polynuclear complexes. Development of high speed electronic computers helps us analyze data of complicated systems containing polynuclear and mixed complexes.[1-4]

An earlier but noticeable work has been demonstrated by Schwarzenbach *et al.*[5,6] for systems of silver ion with diamines and they reported the formation of polynuclear complexes and some mixed silver-ethylenediamine complexes containing protons as well as usual mononuclear complexes. The formation of mixed complexes may not be exceptional in these cases but it may appear in many metal-multidentate ligand systems in which previous workers might sometimes miss to detect these complexes.

As the first step of investigation of complex formation of metal ions with multidentate ligands, we tried to examine the system of silver ion with ethylenediamine and 1,2-propanediamine in a 3M $LiClO_4$ aqueous medium and compared the results obtained with those reported by Schwarzenbach *et al.*[5,6]

EXPERIMENTAL

Reagents

Ethylenediamine diperchlorate and 1,2-propanediamine diperchlorate. Each base (reagent grade, Wako Pure Chemicals Co., Osaka, Japan) was dissolved in water and then treated with dilute perchloric acid at low temperature. The solution was concentrated under a reduced pressure at 30–40°C. Diamine diperchlorates thus prepared were recrystallized three times from aqueous ethanol and crystals were dried *in vacuo.*

Silver perchlorate solution was prepared from $HClO_4$ and Ag_2CO_3 which was precipitated from $AgNO_3$ solution with Na_2CO_3. The silver carbonate precipitates were washed repeatedly by decantation until no sodium ions were detected with a flame test. The concentration of silver ion in the silver perchlorate solution was determined gravimetrically, silver chloride being dried at about 120°C.

Lithium perchlorate was prepared according to Biedermann and Ciavatta.[7]

Lithium hydroxide solution was prepared by electrolysis of lithium perchlorate solution. About 3 M

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† To whom correspondence should be addressed.

lithium perchlorate aqueous solution with a slight amount of perchloric acid was taken in a polyethylene bottle and electrolyzed at about 30 mA with platinum foil electrodes. The polyethylene bottle was connected with an anode chamber through a bridge containing $LiClO_4$ solution. Nitrogen gas was bubbled continuously in the solution during electrolysis.

The concentration of hydroxide ion was determined by means of titration with a standard perchloric acid using a brom cresol green-methyl red mixed indicator. The concentration of lithium ion in the solution was determined by adding H_2SO_4 to the lithium hydroxide–lithium perchlorate solution, fuming off $HClO_4$, and weighing as the sulfate. The difference of the total lithium and $[OH^-]$ was estimated as $[ClO_4^-]$.

The total concentration of perchlorate ions in the solution was adjusted to 3 M by the addition of some $LiClO_4$ crystals or by dilution with distilled water free from carbon dioxide. The solution was filtered through a G4 glass filter under an atmosphere of nitrogen and kept in a polyethylene bottle filled with nitrogen gas. Finally, the concentration of lithium hydroxide in the solution was standardized against a standard perchloric acid by means of titration. The concentration of hydroxide ion was around 0.07 M.

Perchloric acid (E. Merck Co., reagent grade) was used without further purification.

Apparatus

Glass electrodes. Beckman (No. 40498) glass electrodes were used.

Silver electrodes were prepared according to Brown.[8]

The "Wilhelm" type of the half-cell described by Forsling, Hietanen and Sillén[9] was set for emf measurements.

An Orion Digital pH Meter Model 801 was used in combination with a *Manual Electrode Switch Model 605.* Potentials at each point of measurements were determined with an accuracy of ±0.1 *mV*. The pH of a solution never exceeded 10.4 in the course of measurements in all systems.

The Method of Measurements

During a potentiometric measurement, the total concentration of silver ion C_M, was kept constant; the studied range of C_M values was from 0.0025 to 0.020 M.

Lithium perchlorate was used as an ionic medium in order to keep constant the total concentration of perchlorate ion (3M).

The potentiometric titration was performed in the following manner. Thus, into a solution S_1, equal volumes of solutions T_1 and T_2 were added, the compositions of these solutions were; $S_1 = C_M$ $AgClO_4$, C_L $H_2NCH_2CH_2NH_2 \cdot 2HClO_4$ (*or* $H_2NCH(CH_3)CH_2NH_2 \cdot 2HClO_4$), $(3 - C_M - 2C_L - H_0)$ $LiClO_4$, H_0 $HClO_4$; $T_1 = A$ LiOH, $(3 - A)$ $LiClO_4$; $T_2 = 2C_M$ $AgClO_4$, $(3 - 2C_M - X)$ $LiClO_4$, X $HClO_4$. Values of H_0, the initial concentration of the acid in the solution taken in a titration vessel were controlled to be about 0.01 M. The concentration of the added hydroxide ion was calculated from the difference between A and X.

Similar titrations have been performed with solutions S_1 at $C_M = 0$ and T_1 in order to determine dissociation constants of protonated diamines.

The hydrogen ion concentration was measured by means of the cell

$$\text{Ref} \mid \text{Solution} \mid \text{GE} \qquad \text{(A)}$$

where GE denotes a glass electrode and Ref the reference half-cell (B);

3.00 M $LiClO_4$ aqueous solution	2.99 M $LiClO_4$ 0.01 M $AgClO_4$ aqueous solution	Ag	(B)

The emf of the cell (A) can be written as, at 25°C,

$$E_H = E_H^{0\prime} + 59.15 \log [H^+] + 59.15 \log f_H + E_j(H, Ag) \qquad (1)$$

where $E_H^{0\prime}$ is a constant and parentheses denote the concentration of the relevant ion. f_H represents the activity coefficient of H^+. $E_j(H, Ag)$ denotes the liquid junction potential at the junction, Solution | 3M $LiClO_4$ aqueous solution, given as a function of concentrations of hydrogen and silver ions. At $C_M = 0$, the liquid junction potential, $E_j(H, 0)$, has been estimated to be $-16[H^+]$ mV/M[10]. The liquid junction potential caused by migration of silver ions through the interface of Solution|3M $LiClO_4$ aqueous solution is assumed to be negligible in the course of potentiometric measurements in which the total concentration of silver ion is relatively low and constant.

In a solution of a constant ionic medium a constant f_H may reasonably be assumed. Then Eq. (1) may be written as

$$E_H = E_H^0 + 59.15 \log [H^+] + E_j(H) \qquad (2)$$

where $E_H^0 = E_H^{0\prime} + 59.15 \log f_H$. The value of E_H^0 was estimated experimentally by means of a Gran plot[11] in each titration procedure.

The concentration of silver ion was measured by means of the cell

$$\text{Ref} \mid \text{Solution} \mid \text{Ag} \qquad \text{(C)}$$

with the same reference half-cell used in (A). The emf of the cell (C) is given as

$$E_{Ag} = E_{Ag}^{0\prime} + 59.15 \log [Ag^+] + 59.15 \log f_{Ag} + E_j(H, Ag) \qquad (3)$$

Constant f_{Ag} and negligible $E_j(Ag)$ being assumed in the constant ionic medium with a relatively low concentration of silver ion, Eq. (3) may be written as

$$E_{Ag} = E_{Ag}^0 + 59.15 \log [Ag^+] + E_j(H) \qquad (4)$$

where

$$E_{Ag}^0 = E_{Ag}^{0\prime} + 59.15 \log f_{Ag}$$

In the pH range where the solution is so acid that no silver-diamine complex forms, E_H can be determined by means of a Gran plot, while E_{Ag}^0 can be determined by the use of eq. (4) with replacement of $[Ag^+]$ with C_M. With these values of E_H^0 and E_{Ag}^0, concentrations of hydrogen ion and free silver ion at any pH can be determined by Eqs. (2) and (4), respectively.

All titrations were performed in the ionic medium of 3 M $LiClO_4$ at 25.00 ± 0.01°C in a paraffin oil thermostat, which was placed in a room thermostated at 25 ± 1°C. Titrations were carried out under an atmosphere of nitrogen gas, which was free from carbon dioxide and was preequilibrated with 3 M $LiClO_4$ aqueous solution.

RESULTS

Table I gives experimental values of concentrations of the total ligand C_L, the degree of neutralization X, $-\log [H^+]$ and $-\log [Ag^+]$.

Silver-ethylenediamine complexes

Acid dissociation constants of protonated ethylenediamine in 3M $LiClO_4$ aqueous solution were determined from data of the formation function. A generalizes least squares method was applied in order to make the error square sum ($U = \Sigma(\bar{n} - \bar{n}_{calc})^2$) a minimum for the set of dissociation constants K_1 and K_2 with the help of an electronic computer HITAC 8700. $\bar{n}_{calc}$ denotes the value $\bar{n}_{calc} = ([H^+]\ K_2^{-1} + 2[H^+]^2 K_1^{-1} K_2^{-1}/(1 + [H^+] K_2^{-1} + [H^+]^2 K_1^{-1} K_2^{-1})$ for a particular set of the constants K_1 and K_2. Dissociation constants thus obtained were

$$pK_1 = 8.04_4 \pm 0.01$$
$$pK_2 = 10.65_0 \pm 0.01$$

Titration curves of silver-ethylenediamine solutions are shown in Fig. 1.

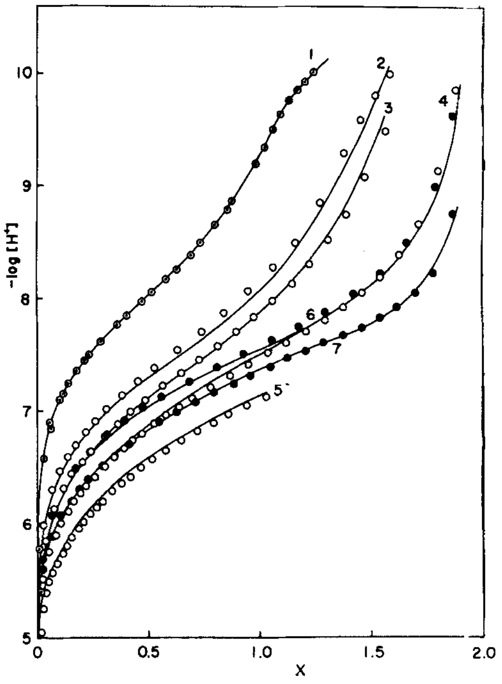

FIGURE 1 Titration curves of ethylenediamine and silver-ethylenediamine solutions. Curve 1; C_M = 0.0 M, $C_{L,0}$ = 0.01000 M and C_M = 0.0 M, $C_{L,0}$ = 0.01486 M, where $C_{L,0}$ represents the initial concentration of ethylenediamine in solution: 2; C_M = 0.002504, $C_{L,0}$ = 0.01002 M; 3; C_M = 0.005007 M, $C_{L,0}$ = 0.02005 M: 4; C_M = 0.01001 M, $C_{L,0}$ = 0.04006 M: 5; C_M = 0.02001 M, $C_{L,0}$ = 0.08004 M: 6; C_M = 0.005007 M, $C_{L,0}$ = 0.01000 M: 7; C_M = 0.009991 M, $C_{L,0}$ = 0.02006 M. Solid lines are calculated titration curves by the use of the formation constants finally proposed in Table 1.

Evaluation of the composition and formation constants of complexes

If we assume that no mixed complex forms, the concentration of free ethylenediamine [L] and the formation function of silver-ethylenediamine complexes $\bar{n}$ may readily be calculated with the following equations:

TABLE I
Survey of data

(1) Silver-ethylenediamine solutions

$C_M = 2.504 \times 10^{-3}$ M
$C_{L,0} = 1.002 \times 10^{-2}$ M

$C_L \times 10^3$	X	$-\log [H^+]$	$-\log [Ag^+]$
8.672	0.03542	5.990	2.632
8.589	0.07368	6.313	2.664
8.528	0.1063	6.473	2.697
8.459	0.1416	6.596	2.725
8.389	0.1771	6.703	2.759
8.294	0.2267	6.828	2.805
8.217	0.2677	6.921	2.845
8.126	0.3174	7.023	2.896
7.999	0.3882	7.151	2.972
7.877	0.4591	7.273	3.060
7.758	0.5299	7.385	3.143
7.586	0.6362	7.550	3.275
7.422	0.7410	7.719	3.437
7.265	0.8474	7.865	3.623
7.115	0.9521	8.083	3.831
6.972	1.057	8.292	4.069
6.833	1.162	8.536	4.340
6.700	1.268	8.859	4.693
6.572	1.373	9.298	5.150
6.490	1.442	9.603	5.461
6.409	1.512	9.833	5.687
6.331	1.583	10.005	5.843
6.253	1.653	10.135	5.956
6.177	1.724	10.233	6.036

$C_M = 5.007 \times 10^{-3}$ M
$C_{L,0} = 2.005 \times 10^{-2}$ M

$C_L \times 10^3$	X	$-\log [H^+]$	$-\log [Ag^+]$
16.05	0.04022	5.846	2.338
15.77	0.08047	6.127	2.375
15.49	0.1215	6.311	2.414
15.22	0.1626	6.446	2.451
14.96	0.2037	6.553	2.487
14.71	0.2447	6.648	2.528
14.36	0.3054	6.776	2.585
14.02	0.3669	6.889	2.642
13.69	0.4285	6.998	2.705
13.38	0.4893	7.097	2.766
12.99	0.5697	7.224	2.854
12.62	0.6517	7.347	2.947
12.27	0.7331	7.473	3.053
11.94	0.8137	7.594	3.163
11.62	0.8959	7.718	3.288
11.32	0.9779	7.853	3.427
11.04	1.060	8.002	3.593
10.77	1.142	8.156	3.768
10.51	1.225	8.325	3.961
10.26	1.307	8.526	4.186
10.03	1.388	8.763	4.446
9.806	1.471	9.092	4.798
9.593	1.551	9.498	5.205

$C_M = 5.007 \times 10^{-3}$ M
$C_{L,0} = 1.000 \times 10^{-2}$ M

$C_L \times 10^3$	X	$-\log [H^+]$	$-\log [Ag^+]$
8.464	0.07094	6.091	2.336
8.367	0.1205	6.333	2.363
8.260	0.1782	6.507	2.391
8.151	0.2359	6.642	2.419
8.001	0.3183	6.793	2.458
7.861	0.3992	6.920	2.499
7.722	0.4816	7.003	2.538
7.589	0.5642	7.134	2.577
7.397	0.6878	7.273	2.693
7.215	0.8116	7.400	2.703
7.042	0.9337	7.523	2.771
6.877	1.057	7.645	2.845
6.720	1.179	7.770	2.932
6.570	1.347	7.900	3.026
6.427	1.424	8.015	3.145
6.290	1.546	8.237	3.295
6.159	1.668	8.507	3.522
6.032	1.790	8.989	3.936
5.951	1.872	9.633	4.500

$C_M = 1.001 \times 10^{-2}$ M,
$C_{L,0} = 4.006 \times 10^{-2}$ M

$C_L \times 10^3$	X	$-\log [H^+]$	$-\log [Ag^+]$
30.52	0.03198	5.513	2.034
29.81	0.06005	5.757	2.061
29.14	0.08751	5.907	2.088
28.49	0.1155	6.022	2.113
27.87	0.1436	6.113	2.135
27.27	0.1717	6.198	2.161
26.70	0.1997	6.276	2.184
26.16	0.2278	6.343	2.206
25.38	0.2693	6.431	2.235
24.65	0.3113	6.516	2.272
23.96	0.3528	6.593	2.304
23.31	0.3943	6.666	2.335
22.69	0.4360	6.735	2.367
22.11	0.4772	6.801	2.397
21.37	0.5330	6.891	2.440
20.68	0.5885	6.970	2.480
20.03	0.6445	7.048	2.519
19.42	0.7008	7.124	2.561
18.57	0.7846	7.231	2.622
17.78	0.8695	7.336	2.685
17.07	0.9531	7.432	2.746
16.41	1.037	7.530	2.812
15.80	1.121	7.626	2.879
15.24	1.205	7.724	2.954
14.71	1.290	7.831	3.038
14.22	1.373	7.946	3.133

continued

TABLE I (*continued*)

$C_L \times 10^3$	X	$-\log [H^+]$	$-\log [Ag^+]$	$C_L \times 10^3$	X	$-\log [H^+]$	$-\log [Ag^+]$
13.77	1.457	8.071	3.238	9.004	1.695	8.079	2.622
13.34	1.540	8.215	3.366	8.825	1.776	8.247	2.649
12.93	1.625	8.402	3.532	8.653	1.857	8.568	2.676
12.55	1.708	8.676	3.782				
12.19	1.792	9.148	4.216	$C_M = 2.001 \times 10^{-2}$ M			
11.86	1.874	9.875	4.823	$C_{L,0} = 8.004 \times 10^{-2}$ M			
$C_M = 9.991 \times 10^{-3}$ M				60.60	0.02023	5.065	1.721
$C_{L,0} = 2.006 \times 10^{-2}$ M				59.15	0.03500	5.263	1.735
				57.80	0.04882	5.390	1.748
15.23	0.07479	5.897	2.039	56.48	0.06294	5.491	1.762
14.97	0.1154	6.081	2.057	55.24	0.07705	5.572	1.773
14.72	0.1560	6.210	2.074	53.45	0.09822	5.674	1.790
14.48	0.1967	6.314	2.095	51.78	0.1194	5.757	1.806
14.24	0.2367	6.404	2.113	50.22	0.1403	5.828	1.821
13.91	0.2902	6.524	2.139	48.75	0.1614	5.890	1.834
13.59	0.3577	6.622	2.162	46.92	0.1894	5.966	1.853
13.28	0.4180	6.715	2.188	45.22	0.2171	6.037	1.870
12.99	0.4781	6.798	2.210	43.65	0.2449	6.100	1.887
12.62	0.5586	6.904	2.243	42.18	0.2729	6.157	1.902
12.27	0.6391	7.003	2.274	40.80	0.3010	6.211	1.915
11.94	0.7197	7.087	2.301	38.87	0.3432	6.291	1.937
11.62	0.8011	7.172	2.328	37.12	0.3855	6.365	1.956
11.32	0.8825	7.251	2.357	35.52	0.4279	6.433	1.975
11.04	0.9638	7.327	2.384	34.05	0.4702	6.499	1.992
10.77	1.045	7.400	2.411	32.28	0.5266	6.582	2.012
10.51	1.127	7.473	2.438	30.68	0.5828	6.656	2.030
10.26	1.208	7.547	2.465	28.90	0.6533	6.749	2.052
10.03	1.288	7.618	2.490	27.32	0.7240	6.835	2.073
9.805	1.370	7.689	2.516	25.81	0.7958	6.911	2.088
9.592	1.450	7.768	2.541	24.62	0.8647	6.984	2.103
9,387	1.532	7.856	2.566	23.25	0.9480	7.067	2.118
9.192	1.613	7.958	2.595	22.02	1.032	7.145	2.132

(2) Silver-1,3-propanediamine solutions

$C_L \times 10^3$	X	$-\log [H^+]$	$-\log [Ag^+]$	$C_L \times 10^3$	X	$-\log [H^+]$	$-\log [Ag^+]$
$C_M = 2.492 \times 10^{-3}$ M				$C_M = 4.979 \times 10^{-3}$ M			
$C_{L,0} = 1.000 \times 10^{-2}$ M				$C_{L,0} = 1.993 \times 10^{-2}$ M			
				14.53	0.01328	5.130	2.314
7.002	0.08062	6.064	2.657	14.22	0.06548	5.765	2.351
6.954	0.1161	6.228	2.684	14.06	0.09509	5.931	2.378
6.859	0.1871	6.463	2.739	13.43	0.2137	6.310	2.476
6.736	0.2816	6.665	2.809	12.99	0.3016	6.498	2.549
6.619	0.3738	6.840	2.888	12.51	0.4082	6.705	2.653
6.505	0.4683	6.993	2.969	12.01	0.5257	6.895	2.763
6.369	0.5864	7.165	3.081	11.49	0.6608	7.103	2.895
6.211	0.7284	7.364	3.225	11.01	0.7960	7.301	3.044
6.026	0.9033	7.620	3.438	10.53	0.9434	7.515	3.227
5.853	1.078	7.872	3.695	10.15	1.072	7.715	3.419
5.688	1.256	8.171	4.019	9.627	1.268	8.034	3.751
5.534	1.430	8.585	4.472	9.196	1.435	8.430	4.178
5.433	1.549	8.969	4.885	8.869	1.577	8.896	4.675
5.340	1.665	9.408	5.341	8.650	1.680	9.346	5.144
5.247	1.783	9.713	5.632	8.408	1.798	9.755	5.521
5.159	1.899	9.921	5.808	8.293	1.858	9.896	5.642

continued

TABLE I (*continued*)

$C_L \times 10^3$	X	$-\log [H^+]$	$-\log [Ag^+]$	$C_L \times 10^3$	X	$-\log [H^+]$	$-\log [Ag^+]$
$C_M = 9.963 \times 10^{-3}$M $C_{L,0} = 3.983 \times 10^{-2}$M				$C_M = 1.992 \times 10^{-2}$M $C_{L,0} = 7.969 \times 10^{-2}$M			
26.90	0.06465	5.535	2.058	50.13	0.07969	5.297	1.762
24.36	0.2028	6.029	2.168	46.47	0.1346	5.520	1.804
22.78	0.3040	6.242	2.243	42.66	0.2008	5.721	1.855
21.13	0.4266	6.455	2.329	38.80	0.2816	5.895	1.902
19.49	0.5681	6.671	2.425	34.63	0.3892	6.088	1.948
18.10	0.7092	6.869	2.518	30.54	0.5238	6.277	1.994
16.72	0.8719	7.080	2.626	26.74	0.6854	6.492	2.043
15.38	1.057	7.300	2.752	22.92	0.9005	6.742	2.088
14.13	1.230	7.535	2.902	20.37	1.089	6.935	2.122
13.58	1.364	7.652	2.981	18.08	1.305	7.118	2.146
12.88	1.507	7.829	3.113	15.67	1.601	7.359	2.169
12.13	1.647	8.125	3.348	14.26	1.816	7.574	2.176
11.61	1.808	8.333	3.522	13.38	1.978	7.816	2.186
11.24	1.909	8.642	3.786				
10.96	1.989	9.045	4.133				

$$[L] = \frac{2C_L + H - [H^+] + [OH^-]}{[H^+]K_2^{-1} + 2[H^+]^2 K_1^{-1} K_2^{-1}} \qquad (5)$$

$$\bar{n} = \frac{C_L - [L](1 + [H^+]K_2^{-1} + [H^+]^2 K_1^{-1} K_2^{-1})}{C_M} \qquad (6)$$

where C_M and C_L denote the total concentrations of silver and ethylenediamine in the solution, respectively, H represents the analytical excesss of the hydrogen ion, which is given by the difference between concentrations of free perchloric acid present in the solution and lithium hydroxide added. However, $\bar{n}$ *vs.* log [L] curves thus calculated could not be explained with any reasonable assumption of complex formation and showed that the assumption of no mixed complex was unreasonable; formation of mixed complexes must be taken consideration.

(1) Low pH range

In the pH range lower than about 6.3, only a few per cent of H_2L^{2+} dissociate to HL^+ and H^+. Therefore, as the first step of approximation, we assume that the following reaction is the main one; thus,

$$pAg^+ + rH_2L^{2+} = Ag_pH_qL_r^{(p+q)^+} + (2r-q)H^+ \qquad (7)$$

and the equilibrium constant of the reaction is defined as

$$\kappa_{pqr} = \frac{[Ag_pH_qL_r^{(p+q)^+}][H^+]^{(2r-q)}}{[Ag^+]^p[H_2L^{2+}]^r} = \beta_{pqr}K_1{}^rK_2{}^r \qquad (8)$$

where β_{pqr} denotes the overall formation constant of the complex $Ag_pH_qL_r^{(p+q)^+}$;

$$\beta_{pqr} = \frac{[Ag_pH_qL_r^{(p+q)^+}]}{[Ag^+]^p[H^+]^q[L]^r} \qquad (9)$$

The total concentration of silver ion is thus given as

$$\begin{aligned} C_M &= [Ag^+] + \sum_{pqr}\sum\sum p[Ag_pH_qL_r^{(p+q)^+}] \\ &= [Ag^+] + \sum_{pqr}\sum\sum p\kappa_{pqr}[Ag^+]^p[H^+]^{-(2r-q)}[H_2L^{2+}]^r \end{aligned} \qquad (10)$$

Rearrangement of Eq. (10) leads to

$$\begin{aligned} \frac{C_M - [Ag^+]}{[Ag^+]} = \phi - 1 &= \sum_{pqr}\sum\sum p\kappa_{pqr}[Ag^+]^{p-1} \\ &\quad \times [H^+]^{-(2r-q)}[H_2L^{2+}]^r \end{aligned} \qquad (11)$$

If we, as the first approximation, assume that only one complex is formed in this range of pH, Eq. (11) may be reduced to Eq. (12).

$$\phi - 1 = p\kappa_{pqr}[Ag^+]^{p-1}[H^+]^{-(2r-q)}[H_2L^{2+}]^r \qquad (12)$$

or

$$\begin{aligned} \log(\phi - 1) &= \log p\kappa_{pqr} + (p-1)\log[Ag^+] \\ &\quad - (2r-q)\log[H^+] + r\log[H_2H^{2+}] \end{aligned} \qquad (13)$$

Since we can put $C_M \cong [Ag^+]$ and $C_L \cong [H_2L^{2+}]$, and moreover, $[H_2L^{2+}]$ is kept practically constant in the relatively narrow range of pH examined, plots of $\log(\phi - 1)$ against $\log[H^+]$ should give a set of straight lines with a slope of $-(2r - q)$ provided that the assumptions made here are reasonable. Figure 2 shows the relationship between $\log(\phi - 1)$ and $\log[H^+]$. All points fell on straight lines with a slope of about -1 and these lines were dependent on the concentration of ethylenediamine but almost independent of that of silver ion. If these points were plotted on $\log(\phi - 1) - \log C_L$ as the ordinate and $\log[H^+]$ as the abscissa, they gathered closely and fell almost on a single straight line. Thus, we concluded that $r = 1$, $p - 1 = 0$ and $2r - q = 1$, or $p = 1$ and $r = 1$ in Eq. (13). Therefore, the composition of the main complex formed was given as $AgHL^{2+}$ in this range of pH.

However, small systematic shifts of points were observed in the plot of $\log(\phi - 1) - \log C_L$ *vs.* $\log[H^+]$ and the slope of these lines were slightly steeper than -1. Thus, the formation of another complex, $Ag_{p'}H_{q'}L_{r'}{}^{(p'+q')+}$, was also expected. If we assume the formation of these two complexes $AgHL^{2+}$ and $Ag_p{}' H_q{}'^{(p'+q')+}$, Eq. (11) is rewritten as follows;

$$\phi - 1 = \kappa_{111}[H^+]^{-1}[H_2L^{2+}] + p'\kappa_{p'q'r'}[Ag^+]^{p'-1} \times [H^+]^{-(2r'-q')}[H_2L^{2+}]^{r'} = \kappa_{111}[H^+]^{-1}[H_2L^{2+}] \times \left(1 + p'\frac{\kappa_{p'q'r'}}{\kappa_{111}}[Ag^+]^{p'-1}[H^+]^{-(2r'-q'-1)}[H_2L^{2+}]^{r'-1}\right) \quad (14)$$

Plots of $\log(\phi - 1) - \log C_L + \log[H^+]$ are dependent on C_L but independent of C_M; thus, $p' = 1$. Since the points fitted on to a family of normalized curve, $y = \log(1 + x^{-1}) = f(\log x)$, $2r' - q' - 1$ must be unity. From the position of the best fit of the normalized curve to experimental points, we found values of $\log \kappa_{111}$ and $\log(\kappa_{p'q'r'}[H_2L^{2+}]^{r'-1}/\kappa_{111})$. Plots of the $\log(\kappa_{p'q'r'}[H_2L^{2+}]^{r'-1}/\kappa_{111})$ values against $\log C_L$ gave a straight line with a slope of unity. Thus, it was concluded that $r' - 1 = 1$ and then $q' = 2$.

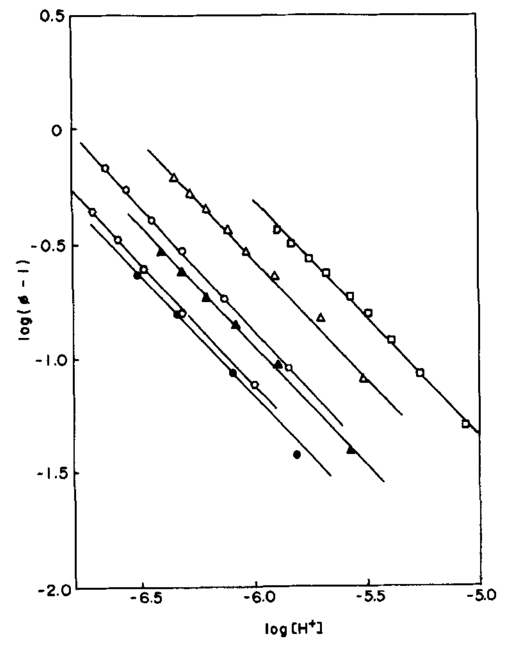

FIGURE 2 Relationships between $\log(\phi - 1)$ and $\log[H^+]$.
◯; $C_M = 0.002504$ M, $C_{L,0} = 0.01002$ M.
○; $C_M = 0.005007$ M, $C_{L,0} = 0.02005$ M.
△; $C_M = 0.01001$ M, $C_{L,0} = 0.04006$ M.
□; $C_M = 0.02001$ M, $C_{L,0} = 0.08004$ M.
●; $C_M = 0.005007$ M, $C_{L,0} = 0.01000$ M.
▲; $C_M = 0.009991$ M, $C_{L,0} = 0.02006$ M.

Above considerations lead to a conclusion that complexes formed in the pH range lower than about 6.3 are $AgHL^{2+}$ and $AgH_2L_2{}^{3+}$. If we accept this conclusion for compositions of complexes formed, we can refine the results by means of successive approximations as follows. Since the concentration of free ethylenediamine is negligible in this pH range, the total concentration of ethylenediamine is given, taking into account the dissociation of H_2L^{2+} into HL^+ and H^+, as

$$C_L = [HL^+] + [H_2L^{2+}] + [AgHL^{2+}] + 2[AgH_2L_2{}^{3+}] = [HL^+] + K_1^{-1}[HL^+][H^+] + \beta_{111}K_2[Ag^+][HL^+] + 2\beta_{122}K_2{}^2[Ag^+][HL^+]^2 \quad (15)$$

Eq. (15) can be solved with respect to [HL] as follows;

$$[HL^+] = [\{(1 + K_1[H^+] + \beta_{111}K_2[Ag^+])^2 + 8\beta_{122}K_2{}^2[Ag^+]C_L\}^{1/2} - (1 + K_1^{-1}[H^+] + \beta_{111}K_2[Ag^+])]/4\beta_{122}K_2{}^2[Ag^+] \quad (16)$$

The first set of β_{111} and β_{122} found from reading off by means of the curve fitting was inserted into Eq. (16) together with experimental data of $[Ag^+]$, $[H^+]$ and C_L. $[HL^+]$ thus calculated was turned back to Eq. (17);

$$\frac{C_M - [Ag^+]}{[Ag^+]} = \phi - 1 = \beta_{111}K_2[HL^+] + \beta_{122}K_2{}^2[HL^+]^2 \quad (17)$$

The method of curve fitting may be a convenient way of determining values of β_{111} and β_{122} from the plot of log $(\phi - 1) - \log\ [HL^+]$ *vs.* log $[HL^+]$. Successive approximations were carried out until β_{111} and β_{122} converged to certain values. Final values of β_{111} and β_{122} were found to be

$$\log \beta_{111} = 13.58$$
$$\log \beta_{122} = 27.30$$

(2) Intermediate range of pH

Since we have found complexes $AgHL^{2+}$, and $AgH_2L_2{}^{3+}$, the total concentrations of silver and ethylenediamine, respectively, are given as follows:

$$C_M = [Ag^+] + \beta_{111}[Ag^+][H^+][L] + \beta_{122}[Ag^+][H^+]^2[L]^2 + \sum_{pqr}\sum\sum p\beta_{pqr}[Ag^+]^p[H^+]^q[L]^r \quad (18)$$

and

$$C_L = [L] + K_2{}^{-1}[H^+][L] + K_1{}^{-1}K_2{}^{-1}[H^+][L] + \beta_{111}[Ag^+][H^+][L] + 2\beta_{122}[Ag^+][H^+]^2[L]^2 + \sum_{pqr}\sum\sum r\beta_{pqr}[Ag^+]^p[H^+]^q[L]^r \quad (19)$$

From the material balance for hydrogen atoms, we obtain

$$2C_L + H = [H^+] + K_2{}^{-1}[H^+][L] + 2K_1{}^{-1}K_2{}^{-1}[H^+]^2[L] + \beta_{111}[Ag^+][H^+][L] + 2\beta_{122}[Ag^+][H^+]^2[L]^2 + \sum_{pqr}\sum\sum q\beta_{pqr}[Ag^+]^p[H^+]^q[L]^r - K_W[H^+]^{-1} \quad (20)$$

where K_W denotes the autoprotolysis constant of water in 3M $LiClO_4$ aqueous solution. Although the value has not been determined, it may be assumed $K_W = 10^{-14.22}$ (the value found in 3M $NaClO_4$[12]) without introduction of any serious error in calculation of Eq. (20) at log $[H^+] > -10.4$.

If we assume that there is no more mixed complex than $AgHL^{2+}$ and $AgH_2L_2{}^{3+}$ in the pH range studied, we can put $q = 0$ in Eqs. (18) through (20). Eq. (20) is thus simplified as follows:

$$2C_L + H = [H^+] + K_2{}^{-1}[H^+][L] + 2K_1{}^{-1}K_2{}^{-1}[H^+]^2[L] + \beta_{111}[Ag^+][H^+][L] + 2\beta_{122}[Ag^+][H^+]^2[L]^2 - K_W[H^+]^{-1} \quad (21)$$

and [L] is obtained as a unique solution of Eq. (21), thus,

$$[L] = \frac{(B^2 + 2AC)^{1/2} - B}{4A} \quad (22)$$

where $A = \beta_{122}[Ag^+][H^+]^2$, $B = K_2{}^{-1}[H^+] + 2K_1{}^{-1}K_2{}^{-1}[H^+]^2 + \beta_{111}[Ag^+][H^+]$ and $C = 2C_L + H - [H^+] + K_W[H^+]^{-1}$. A function $\bar{n}_c$ is defined as

$$\bar{n}_c = \frac{\sum_{pr}\sum r[Ag_pL_r{}^{p+}]}{[Ag^+] + \sum_{pr}\sum p[Ag_pL_r{}^{p+}]}$$

$$= \frac{\sum_{pr}\sum r\beta_{p0r}[Ag^+]^{p-1}[L]^r}{1 + \sum_{pr}\sum p\beta_{p0r}[Ag^+]^{p-1}[L]^r}$$

$$= \{C_L - ([L] + K_2{}^{-1}[H^+][L] + K_1{}^{-1}K_2{}^{-1}[H^+]^2[L] + \beta_{111}[Ag^+][H^+][L] + 2\beta_{122}[Ag^+][H^+]^2[L]^2)\}/C_{M,c} \quad (23)$$

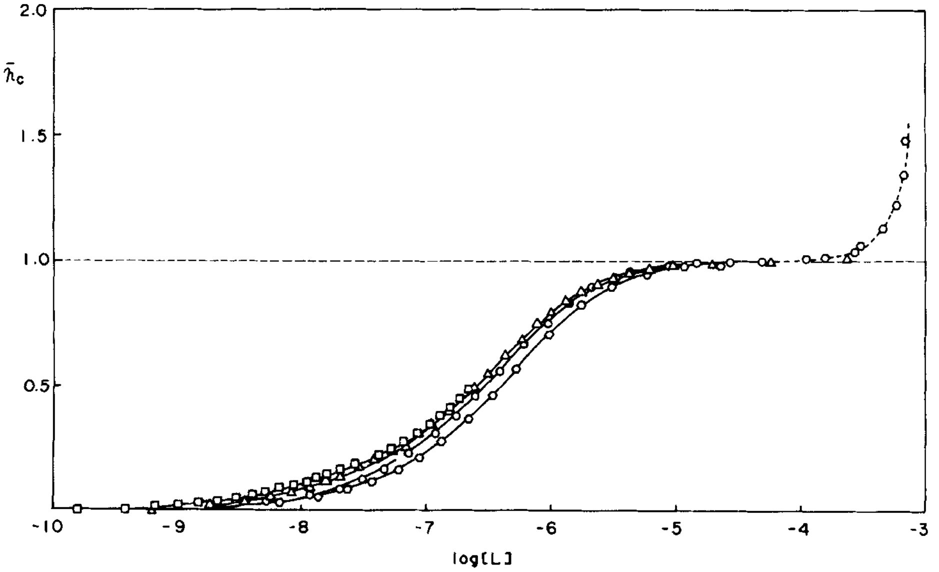

FIGURE 3 $\bar{n}_c$ *vs.* log [L] calculated by Eqs. (22) through (24).

where

$$C_{M,c} = C_M - \beta_{111}[Ag^+][H^+][L] - \beta_{122}[Ag^+][H^+]^2[L]^2$$
$$= [Ag^+] + \sum_{pr}\sum p\beta_{p0r}[Ag^+]^p[L]^r \qquad (24)$$

Plots of $\bar{n}_c$ against log [L] thus calculated are shown in Figure 3. In the range $-10 < \log\,[L] < -4$, the $\bar{n}_c$ increased with increasing log [L] and approached 1. $\bar{n}_c$ was a function of the concentration of silver ion as well as that of ethylenediamine, the family of curves in Figure 3 showed the formation of polynuclear complexes in the solution.

Rearrangement of Eq. (24) leads to

$$\frac{C_{M,c} - [Ag^+]}{[Ag^+][L]} = \sum_{pr}\sum p\beta_{p0r}[Ag^+]^{p-1}[L]^{r-1} \qquad (25)$$

In the range of $\log\,[Ag^+] \leqslant -2.5$, plots of $\log\,\{(C_{M,c} - [Ag^+])/[Ag^+][L]\}$ against $\log\,[Ag^+]$ fell on a single curve and were independent of the concentration of ethylenediamine. Moreover, the curve fitted well to the normalized curve, $y = \log(1 + x) = f(\log x)$. Therefore, it was concluded that the species formed in this range was AgL^+ and Ag_2L^{2+}, because $r - 1 = 0$ and $p - 1 = 0$ and 1. At the higher concentration range of silver ion, scattering of points was observed, which suggested the formation of some other species. If we neglect the formation of higher complexes than Ag_2L^{2+}, Eq. (24) is rewritten as

$$C_{M,c} = [Ag^+] + \beta_{101}[Ag^+][L] + 2\beta_{201}[Ag^+]^2[L] \qquad (26)$$

Formation constants of the complexes AgL^+ and Ag_2L^{2+} were evaluated as follows;

$$\log\beta_{101} = 6.28$$
$$\log\beta_{201} = 8.39$$

Informations for other complexes will be obtained by computer calculations which will be discussed later.

(3) The range of pH higher than 9

In the pH range higher than 9 where values of log [L] were larger than -4 in this study, the $\bar{n}_c$ values steeply increased with the concentration of free ethylenediamine. The $\bar{n}_c$ curve of this part could not be explained in terms of formation of a series of complexes AgL_m ($m \geqslant 2$). This anomalous increase in $\bar{n}_c$ may possibly be due to the wrong assumption of no proton complex formation even in this pH range (a hydroxo complex can be regarded as a kind of proton complex with a negative number of protons). The emf data obtained in this pH range were reasonably interpreted in terms of formation of a hydroxo complexes as described in the following.

As seen from Figure 3, the $\bar{n}_c$ curve reached a plateau at $\bar{n}_c = 1$ and thus, all silver ions were regarded as in the form of AgL^+ at $pH \cong 9$. If the AgL^+ complex hydrolyzes at the higher pH range, the reaction may be written as

$$AgL^+ + H_2O = Ag(OH)L + H^+ \qquad (27)$$

The formation constant of the complex, Ag(OH)L, is given as

$$\beta_{1-11} = \frac{[Ag(OH)L][H^+]}{[Ag^+][L]} \qquad (28)$$

Since the concentration of free silver ion in the solution is negligible compared with those of the complexes in this pH range, the total concentrations of silver and ethylenediamine are given as follows;

$$C_M = [AgL^+] + [Ag(OH)L]$$
$$= [Ag^+][L]\beta_{101}(1 + \beta_{1-11}\beta_{101}^{-1}[H^+]^{-1}) \qquad (29)$$

and

$$C_L = [L] + [HL^+] + [H_2L^{2+}] + [AgL^+] + [Ag(OH)L]$$
$$= [L](1 + K_2^{-1}[H^+] + K_1^{-1}K_2^{-1}[H^+]^2) + C_M \qquad (30)$$

Then, the concentration of free ethylenediamine [L] is obtained by Eq. (31);

$$[L] = \frac{C_L - C_M}{1 + K_2^{-1}[H^+] + K_1^{-1}K_2^{-1}[H^+]^2} \qquad (31)$$

Inserting Eq. (31) into Eq. (29) and rearranging, we derive

$$\log(C_M/[Ag^+][L])$$
$$= \log\beta_{101} + \log(1 + \beta_{1-11}\beta_{101}^{-1}[H^+]^{-1}) \qquad (32)$$

and the value of the left hand side in Eq. (32) can be calculated from experimental data.

Plots of $\log(C_M/[Ag^+][L])$ *vs.* $\log\,[H^+]$ fitted well to a normalized curve, $y = \log(1 + x^{-1}) = f(\log x)$ and thus, we obtained values of $\log\beta_{101}$ and $\log\beta_{1-11}$ from the plot.

$$\log\beta_{101} = 6.35$$
$$\log\beta_{1-11} = -4.60$$

The value of β_{101} found by the present calculation was in good agreement with the β_{101} value obtained in the previous section, and this supports the assumption and the calculation examined in this section.

Silver-1,2-propanediamine complexes The essentially similar procedure has been used for determination of dissociation constants of protonated 1,2-propanediamine and of formation constants of silver-1,2-propanediamine complexes.

Dissociation constants of 1,2-propanediamine were determined to be

$$pK_1 = 7.63_5 \pm 0.01$$
$$pK_2 = 9.98_7 \pm 0.01$$

Titration curves of silver-1,2-propanediamine solutions are shown in Figure 4.

The entirely same method of analysis of data as that described in the previous sections has been employed for determination of formation constants of silver-1,2-propanediamine complexes.

In the acid region, complexes $AgHL^{2+}$ and $AgH_2L_2{}^{3+}$ were found. The $\bar{n}_c$ curves were calculated on the basis of Eq. (23) in the intermediate range of pH and they are shown in Figure 5. The formation constants of AgL^+ and Ag_2L^{2+} complexes were determined from the plot of log $\{(C_{M,c} - [Ag^+])/[Ag^+][L]\}$ drawn by the use of Eq. (25). The $\bar{n}_c$ curves cross at $\bar{n}_c = 1$ and then diverge. Thus, the formation of AgL_m complexes ($m \geqslant 2$) is not the main reaction in this range of pH, as has already been discussed in the previous system. If we adopt the same assumption examined in the preceding system that the Ag(OH)L complex forms in this range of pH, Eq. (32) can be used for determination

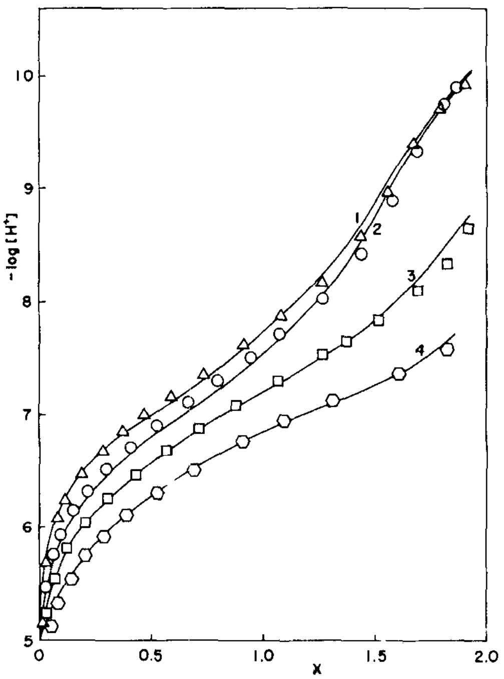

FIGURE 4 Titration curves of silver-1,2-propanediamine solutions. Curve 1; C_M = 0.002492 M, $C_{L,0}$ = 0.01000 M: 2; C_M = 0.004979 M, $C_{L,0}$ = 0.01993 M: 3; C_M = 0.009963 M, $C_{L,0}$ = 0.03983 M: 4; C_M = 0.01991 M, $C_{L,0}$ = 0.07969 M. Solid lines are calculated titration curves by the use of the formation constants finally proposed in Table 2.

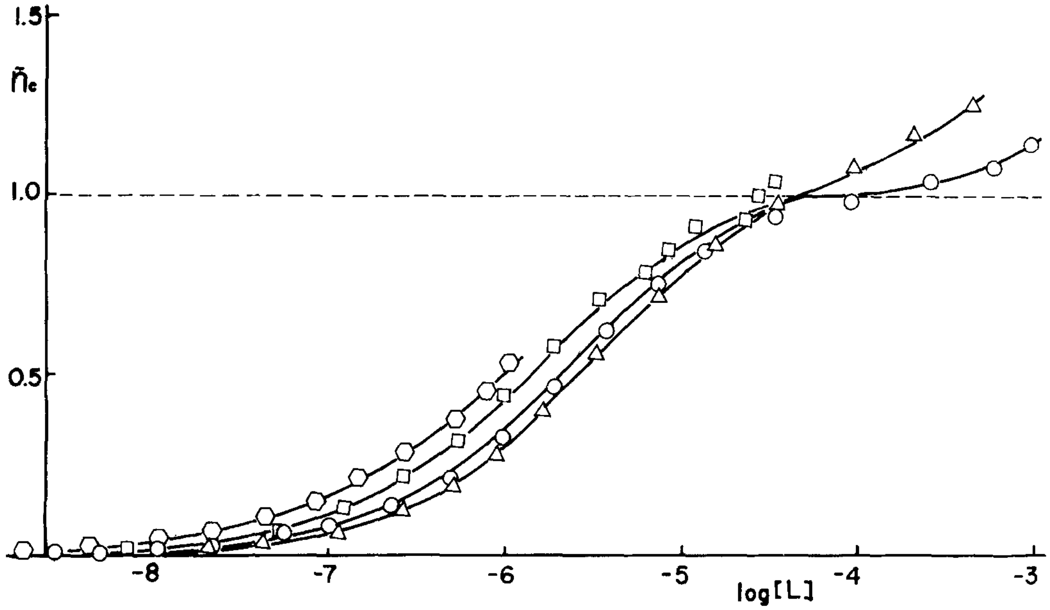

FIGURE 5 $\bar{n}_c$ *vs.* log [L] in the silver-1,2-propanediamine system. Symbols are the same as those used in Figure 4.

of β_{1-11}. Plots of log $(C_M/[Ag^+][L])$ *vs.* $-\log[H^+]$ fitted satisfactorily with the normalized curve, $y = \log(1 + x^{-1}) = f(\log x)$, and the plot was independent of the concentration of silver ion, and thus the formation of the Ag(OH)L complex is confirmed.

Refinement of the results by computer calculations

The data in each system were finally treated by a generalized least squares method with an electronic computer HITAC 5020E in order to make the error square sum $U = \Sigma(X - X_{calc})^2|$ a minimum for the set of formation constants β_{pqr}, where X denotes the ratio of the concentration of hydroxide ions added and the total concentration of a diamine in the solution.

If we assume the formation of the complexes which have been estimated by the mathematical treatments in the previous section, some descrepancies of data from calculated titration curves were observed (case 1). If we add a complex $Ag_2L_2^{2+}$ which has been suggested by Schwarzenbach *et al.*[5] and is very probable to form under the present experimental conditions, the error square sum decreased to about a half of that calculated under the previous assumption (case 2). Addition of other complexes such as $AgHL_2^{2+}$ and AgL_2^+, instead of $Ag_2L_2^{2+}$, to the complexes in the case 1 did not improve the results (cases 3 and 4). Although we tested a limited number of assumptions for complex formation, it seemed sufficient to add only the $Ag_2L_2^{2+}$ complex to the complexes found by the mathematical treatments in order to interprete the experimental data. The compositions and formation constants of the complexes finally accepted are summarized together with uncertainties of each constant in the last columns of Tables II and III for silver-ethylenediamine and 1,2-propanediamine systems, respectively.

TABLE II
Formation constants of silver-ethylenediamine complexes calculated under various assumptions (log β_{pqr})

$pK_1 = 8.04_4 \pm 0.01$; $pK_2 = 10.65_0 \pm 0.01$

Complex	case 1	case 2	case 3	case 4	final value
AgL^+	6.32	6.13	6.34	6.34	6.13 ± 0.02
Ag_2L^{2+}	7.77	7.67	7.54	7.54	7.67 ± 0.05
$AgHL^{2+}$	13.55	13.56	13.55	13.55	13.56 ± 0.02
$AgH_2L_2^{3+}$	27.33	27.37	27.34	27.33	27.37 ± 0.02
Ag(OH)L	−4.63	−4.59	−4.43	−4.41	−4.59 ± 0.05
$Ag_2L_2^{2+}$	–	14.53	–	–	14.53 ± 0.07
$AgHL_2^{2+}$	–	–	$14._5$	–	–
AgL_2^+	–	–	–	$7._1$	–
U	*1.374*	*0.5737*	*1.355*	*1.354*	

TABLE III
Formation constants of silver-1,2-propanediamine complexes calculated under various assumptions (log β_{pqr})

$pK_1 = 7.63_5 \pm 0.01$; $pK_2 = 9.98_7 \pm 0.01$

Complex	case 1	case 2	case 3	case 4	final value
AgL^+	5.77	5.52	5.76	5.72	5.52 ± 0.02
Ag_2L^{2+}	7.62	7.60	7.66	7.72	7.60 ± 0.05
$AgHL^{2+}$	12.74	12.72	12.73	12.73	12.72 ± 0.02
$AgH_2L_2^{3+}$	25.69	25.84	25.73	25.73	25.84 ± 0.02
Ag(OH)L	−4.15	−4.17	−4.13	−4.43	−4.17 ± 0.05
$Ag_2L_2^{2+}$	–	13.47	–	–	13.47 ± 0.07
$AgHL_2^{2+}$	–	–	$14._3$	–	–
AgL_2^+	–	–	–	$9._1$	–
U	*0.5725*	*0.2644*	*0.5915*	*0.4777*	

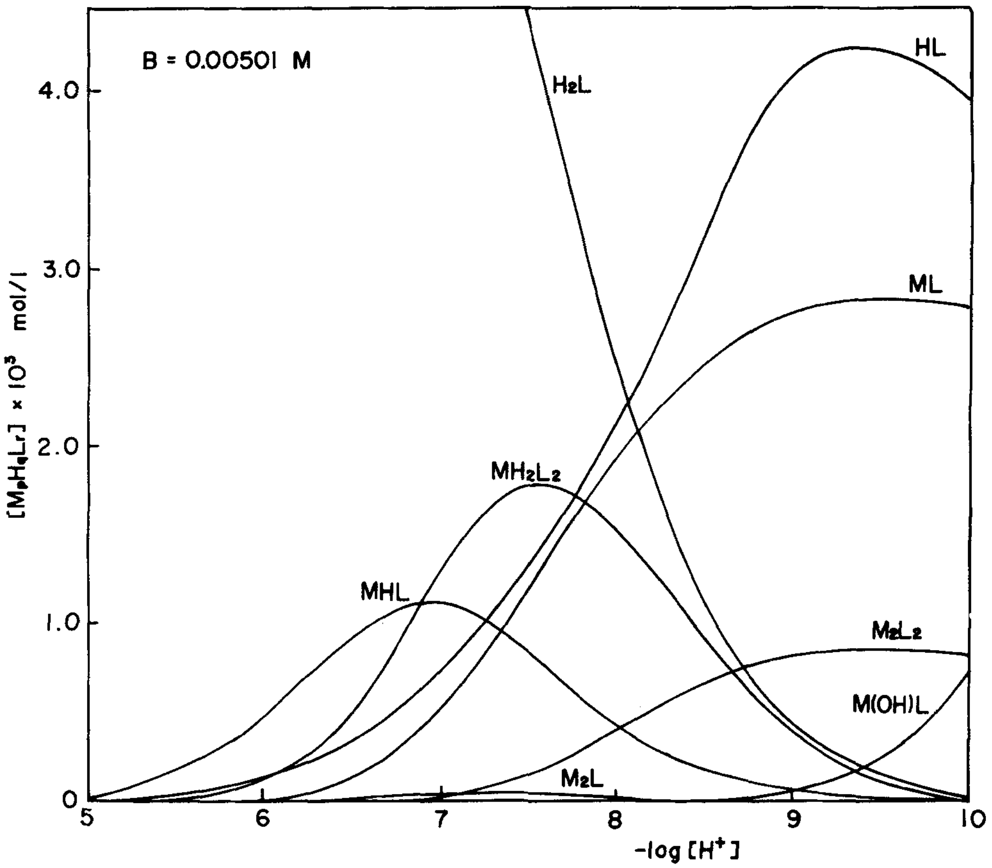

FIGURE 6 The distribution of the silver-ethylenediamine complexes at $B = 0.005007$ M.

Formation constants estimated by the mathematical treatments under relatively simple assumptions are generally in good agreement with those calculated by an electronic computer by means of the least square sum method except for that of Ag_2L^{2+}; in the course of the mathematical treatment for estimation of this complex, the formation of any higher complexes such as $Ag_2L_2{}^{2+}$ was not carefully taken into consideration. The distribution of the complexes in the silver-ethylenediamine system is graphically represented in Figure 6.

DISCUSSION

The fact that protonated 1,2-propanediamine is a stronger acid than the corresponding ethylenediamine is not explained in terms of the inductive effect of the substituted methyl group. The stability of an acid depends upon not only the interaction between the proton and the conjugate base group but also the interaction between the acid and solvent molecules. The former interaction may weaken the acidity of protonated 1,2-propanediamine by the inductive effect of the substituted methyl group. However, introduction of a methyl group into an ethylenediamine molecule may enhance the structure-making effect of the aliphatic chain and then, 1,2-propanediamine may be a stronger structure-maker than ethylenediamine. On the other hand, a protonated amino group is known as a structure-breaker. Therefore, in order to form a stable acid molecule in an aqueous solution, water structure should be distorted around the protonated amino groups. In protonated 1,2-propanediamine the methyl group prevents structure breaking of solvent water molecules by the adjacent amino group, and then the protonated amino group becomes less stable than an amino group which is connected with a primary carbon atom. This consideration leads to a conclusion that protonated 1,2-propanediamine is a stronger acid than the corresponding ethylenediamine and moreover, the protonated amino group attached to the secondary carbon atom first releases a proton. The above conclusion is supported by the fact that protonated *meso*-2,3-butanediamine is a stronger acid than the protonated ethylenediamine and 1,2-propanediamine†.

Stepwise formation constants of $AgHL^{2+}$ and $AgH_2L_2{}^{3+}$ complexes are calculated from values in Tables II and III.

$$Ag^+ + HL^+ = AgHL^{2+}; \log K^{HL}_{AgHL} = 2.91 \ (L = en), \quad 2.73 \ (L = pn)$$

$$AgHL^{2+} + HL^+ = AgH_2L_2{}^{3+}; \log K^{HL}_{AgH_2L_2} = 3.16 \ (en), \ 3.13 \ (pn)$$

The second formation constant $K^{HL}_{AgH_2L_2}$ is larger than the first K^{HL}_{AgHL} in both cases. In the formation reactions of silver-ammine complexes,[13] formation constants of the complexes are in the same order:

$$Ag^+ + NH_3 = AgNH_3^+; \log K^{NH_3}_{AgNH_3} = 3.20$$

$$AgNH_3{}^+ + NH_3 = Ag(NH_3)_2{}^+; \ \log K^{NH_3}_{Ag(NH_3)_2} = 3.83$$

Since an HL^+ molecule is regarded as a monodentate ligand, the silver ion has the coordination number of 2 in the complexes and the $AgH_2L_2{}^{3+}$ complex is in the linear form.

The dissociation constant of the $AgHL^{2+}$ complex to AgL^+ and H^+ is readily obtained from the data in the tables:

$$AgHL^{2+} = H^+ + AgL^+$$
$$pK_{AgHL} = 7.43 \ (en), \ 7.20 \ (pn) \qquad (35)$$

The $AgHL^{2+}$ complex is stabilized by only 0.5–0.6 p*K* unit by releasing a proton compared with the dissociation reaction of the corresponding free acid H_2L^{2+} ($pK_1 = 8.04$ (en), 7.64 (pn)). Therefore, the free energy change in the reaction (35) may not be sufficient to form a stable silver-diamine chelate. Although the formation constant of the AgL^+ complex is much larger than β_1 of the $AgNH_3{}^+$ complex, it is slightly smaller than β_2 and the stabilization of the AgL^+ complex by the chelate effect is not observed. These results suggest that the diamine L reacts with the silver ion as a weak bidentate ligand rather than a monodentate one and an amino group from which a proton has been released is weakly bound with the silver ion. Since the methylene chain of these diamines is not long enough to form a stable chelate ring with the silver ion, the ring formed by the ligand molecule may be distorted so that the chelate complex is rather unstable and tends to form a dimerized species such as $Ag_2L_2{}^{2+}$.

It is not so simple to conclude which amino group is combined with a silver ion when a protonated silver-1,2-propanediamine complex $AgHL^{2+}$ is formed. However, a conclusion derived in the previous discussion that the amino group attached to the secondary carbon atom first releases a proton may help the present argument. As seen from Figure 6, the formation of complexes $AgHL^{2+}$ and $AgH_2L_2{}^{3+}$ becomes maximum at the relatively low pH where the concentration of HL^+ is far less than the maximum value. This suggests that the amino group which dissociates a proton at the first step coordinates to a silver ion when the protonated silver-diamine complexes are formed and thus, the silver ion combines with the amino group attached to the secondary carbon atom. This consideration may be supported by the fact that the dimerization constant $K_d = [Ag_2L_2{}^{2+}]/[AgL^+]^2$ is almost independent of diamines, $\log K_d = 2.2_9 \pm 0.1_1$ for ethylenediamine and $2.4_3 \pm 0.1_1$ for 1,2-propanediamine systems, since it is expected that the free energy changes in combination of silver with an amino group attached to a primary carbon atom to form ten membered ring[6] in the dimerization reaction may not appreciably differ in both diamines.

The Ag(OH)L complex is formed by hydrolysis of the AgL^+ complex at the higher pH region. The hydrolysis constant of AgL^+ complex is in the same order of magnitude with that of Ag^+, but the former complex is a slightly stronger acid than the latter.

$$AgL^+ + H_2O = Ag(OH)L + H^+; \log K_{Ag(OH)L} = -10.7_2 \ (en), \ -9.6_9 \ (pn)$$

$$Ag^+ + H_2O = AgOH + H^+; \qquad \log K_{AgOH} \cong -11.1^{14} \ (\text{in 1M } AgNO_3)$$

The $AgL_2{}^+$ complex has not been detected under the present experimental conditions. Hydrolysis of the AgL^+ complex starts at $pH \cong 9$ where the concentration of free ligand is approximately 10^{-4}M. Therefore, the formation constant of the $AgL_2{}^+$

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†The p*K* values of these diamines are listed in the "Stability Constants" edited by L. G. Sillén and A. E. Martell [Chemical Society, London (1964, 1971)]. The values determined under the same experimental conditions are given by Basolo and his co-workers: ethylenediamine[a], $pK_1 = 7.47$, $pK_2 = 10.18$; 1,2-propanediamine[b], $pK_1 = 7.13$, $pK_2 = 10.00$; *m*-2,3-butanediamine[c], $pK_1 = 6.92$, $pK_2 = 9.97$ in 0.5 M KNO_3 at 25°C.
[(a) F. Basolo and R. K. Murmann, *J. Am. Chem. Soc.*, **74**, 5243 (1952), (b) F. Basolo, R. K. Murmann and Y. T. Chen, *ibid.*, **75**, 1478 (1953), (c) F. Basolo, Y. T. Chen and R. K. Murmann, *ibid.*, **76**, 956 (1954)].

complex must be much smaller than 10^9. According to Schwarzenbach *et al.*,[6] the overall formation constant of the AgL_2^+ complex for ethylenediamine was $10^{7.7}$, which supports our consideration.

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