Metal Complexes with Mixed Ligands. 20. A Potentiometric Study of Silver(I) Imidazoles and Silver(I) Hydroxo Imidazoles in 3.0 M (Na)ClO$_4$

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Equilibria between silver(I), imidazole ($C_3H_4N_2$, L) and OH$^-$ have been studied in 3.0 M (Na)ClO$_4$ medium at 25 °C, by means of potentiometric titrations. In the measurements, glass as well as Ag,AgCl electrodes were employed. The total concentrations of silver, B, and imidazole, C, varied through the ranges 0.001−0.020 M and 0.002−0.160 M, respectively. With $C/B > 2$, data could be explained with the complexes AgL$^+$ and AgL$_2^+$ with $\log \beta_1 = 3.336 \pm 0.012$ and $\log \beta_2 = 7.554 \pm 0.003$. At low ratios of C/B a ternary hydroxo-imidazole complex, Ag(OH)L with $\log K(Ag^+ + L + H_2O \rightleftarrows Ag(OH)L + H^+) = -4.78 \pm 0.05$, is formed. Data have been analyzed with the least squares computer program LETAGROPVRID.

Earlier studies of aqueous silver imidazoles have shown the existence of only mononuclear complexes and the species AgL$^+$ and AgL$_2^+$ are reported (L stands for imidazole, $C_3H_4N_2$). The main conclusions drawn from these previous studies are given in Table 1. However, they are based on rather few data with small variations in concentrations and no attempts seem to have been made to try to find any mixed Ag$^+$ − L − OH$^-$ complexes. Investigations in this department of the systems M − L − OH$^-$, where M stands for the metal ions Cu^{2+}, Hg^{2+}, Ni^{2+} and Zn^{2+},[1,2] have shown that besides series of mononuclear complexes ML$_n$, mononuclear as well as polynuclear mixed hydroxo complexes are formed.

The main purpose of the present investigation is to study whether similar complexes exist in the silver imidazole system.

By using glass as well as Ag,AgCl electrodes, free concentrations of Ag$^+$ and H$^+$ can be measured and it is interesting to compare equilibrium constants related to the different electrodes.

EXPERIMENTAL

Chemicals and analysis. Stock solutions of *sodium perchlorate* were prepared by neutralizing concentrated perchloric acid (Merck *p.a.*) with solid Na$_2$CO$_3$ (Merck *p.a.*) according to procedures described earlier.[3] In some cases, detectable amounts of chloride ions were precipitated as AgCl upon

Table 1. Earlier studies on the silver(I) imidazole system, carried out at 25 °C.

Ref.	Medium	Method	$\log K_1$	$\log K_2$	K_2/K_1
15	0.1 M KNO$_3$	pot (gl)	3.17	3.76	3.9
16	0.5 M KNO$_3$	pot (ag)	2.70	4.18	30.2
17	1 M KNO$_3$	pot (gl)	3.11	3.71	4.0
18	1 M KNO$_3$	cal, pot (gl)	3.05	3.83	6.0
20	1 M KNO$_3$	pot (gl)	3.08	3.87	6.2
19	0.5 M (NH$_4$)NO$_3$	pot (Ag)	4.0	2.88	
This work	3 M (Na)ClO$_4$	pot (gl,Ag,AgCl)	3.336	4.218	7.6

adding a slight excess ($\lesssim 0.01$ mM in 3.0 M NaClO$_4$) of AgClO$_4$. In this way no opalescence due to the formation of AgCl was observed in the different Ag$^+$ solutions used. The sodium perchlorate stock was analyzed for NaClO$_4$ by evaporating a known weight of solution at 120 °C and drying to a constant weight. The amount of protolytic impurities (HX) in 3.0 M NaClO$_4$ solutions was detected coulometrically. It was found to be 0.05 ± 0.01 mM, with pK_a(HX) ~ 8. Dilute *perchloric acids* (Merck *p.a.*) were standardized against tris(hydroxymethyl)-aminomethane (TRISMA-base).

Sodium hydroxide solutions were prepared from 50 % aqueous NaOH and standardized against acid or hydrazine sulfate (Merck *p.a.*). The difference in [OH$^-$] obtained by the two methods was less than 0.2 %.

Imidazole (C$_3$H$_4$N$_2$, Merck *p.a.*) was recrystallized twice from benzene and dried at 80 °C.

Stock solutions of C$_3$H$_5$N$_2$$^+$ were prepared by dissolving C$_3$H$_4$N$_2$ in excess of standardized HClO$_4$. This excess, as well as the "C$_3$H$_5$N$_2$$^+$-content", was determined potentiometrically using the Gran extrapolation method.[4] It was found that the titrated amount of imidazole was always about 0.4 % higher than that expected from the amount weighed. The value from titration was assumed to be correct.

Stock solutions of AgClO$_4$ were prepared by dissolving Ag$_2$CO$_3$ in standardized HClO$_4$. Ag$_2$CO$_3$ was precipitated from an AgNO$_3$ solution with Na$_2$CO$_3$. The precipitate was washed repeatedly with H$_2$O until no sodium could be detected with a flame test. The Ag$^+$ content of the stock solutions was determined as AgCl in a potentiometric titration using an Ag,AgCl electrode, the equivalence point being evaluated using the Gran extrapolation method.[4] The H$^+$ concentration was also determined potentiometrically, and the ClO$_4^-$ content was obtained from the sum [H$^+$] + [Ag$^+$].

All solutions were prepared using boiled distilled water.

The different Ag$^+$ and C$_3$H$_5$N$_2$$^+$ solutions used in the titrations were prepared from different stock solutions in order to detect possible systematic errors caused by impurities and analytical errors.

Apparatus. The potentiometric titrations were performed with an automatic system for precise emf-titrations constructed and built at this institute by O. Ginstrup.[5] The measurements were made at 25.00 ± 0.05 °C. The cell arrangement, which was immersed in an oil thermostat, was similar to that described by Forsling *et al.*[6]

During the experiments a stream of nitrogen was bubbled through the solution for stirring and for maintaining an inert atmosphere. Nitrogen from a cylinder was purified from acid and alkaline impurities by bubbling through solutions of 10 % NaOH and 10 % H$_2$SO$_4$. Finally before the gas came into

contact with the equilibrium solution, it was passed through a pure ionic medium.

Electrodes. Ag,AgCl electrodes were prepared according to Brown.[7] For every new titration freshly prepared electrodes were used, and the differences in their measured emf-values did not exceed 0.02 mV. Glass electrodes (Beckman type S41260 and Ingold type 201-NS) were tested against the hydrogen electrode. With log [H$^+$] $\gtrsim -8.5$ they were found to give constant and reproducible potentials within ± 0.2 mV.

In order to check the reliability of the different electrodes during a titration, usually three Ag,AgCl and two glass electrodes were immersed in the equilibrium solution. If a drift in the difference between the measured emf values of the Ag,AgCl as well as the glass electrodes was found to exceed 0.05 and 0.2 mV, respectively, these experimental points were not included in the calculations.

Furthermore, it was found that with $-$log[Ag$^+$] $\gtrsim 4.5$ a slow drift in the measured emf of the Ag,AgCl electrodes was observed. This drift was caused by dissolution of the AgCl layer of the electrode.

METHOD

The present investigation has been carried out through a series of titrations in which both [H$^+$] = h and [Ag$^+$] = b were measured using a glass electrode and an Ag,AgCl electrode, respectively.

The total concentrations of Ag$^+$, B and HL$^+$, C were varied within the limits $0.001 \leq B \leq 0.020$ M, and $0.002 \leq C \leq 0.160$ M. h and b were varied by adding hydroxide or hydrogen ions. Owing to the formation of precipitates, the available $-$log h range was restricted to an upper limit of 8.0. In general, each titration was performed at a constant C/B ratio. The following ratios were studied: 0.5, 0.75, 1.0, 1.5, 2, 3, 4, 8 and 16.

The reproducibility and reversibility of equilibria were tested by performing both forward (increasing $-$log h) and backward (decreasing $-$log h) titrations. As a test of the reversibility dilution experiments at low C/B ratios ($\lesssim 2$) and at constant Z-values were also performed (Z is defined as $(h-H)/B$).

h and b were determined by measuring the emf of the cell

$$- \text{RE} \,|\, \text{equilibrium solution} \,|\, \text{ME} + \qquad (1)$$

where ME denotes the measuring electrode (glass electrode and Ag,AgCl electrode and RE=

Ag,AgCl $|$ 0.01 M Ag$^+$, 3.00 M ClO$_4^-$, 2.99 M Na$^+$ $\|$ 3.00 M NaClO$_4$.

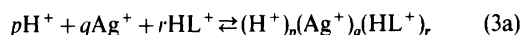Assuming the activity coefficients to be constant, the following expressions are valid for the measured emf:

$$E_H = E_{OH} + 59.157 \log h + E_j \text{ (glass electrode)} \quad (2a)$$
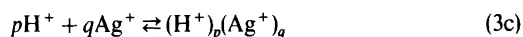
and

$$E_B = E_{OB} + 59.157 \log b + E_j \text{ (Ag,AgCl electrode)} \quad (2b)$$

E_{OH} and E_{OB} are constants determined in acid (H$^+$, Ag$^+$, HL$^+$) solutions of known composition, where complex formation can be neglected ($-\log h \lesssim 3$). For the liquid junction potentials we have used $E_j = -16.7 \ h + 8.0 \ K_w h^{-1}$ mV, where $K_w = 6.03 \times 10^{-15}$ M^2 [8] is the ionic product of water in 3.0 M NaClO$_4$. In most of our titrations the correction for the E_j terms could be neglected.

Data treatment. We will assume the presence of three component equilibria of the general form:

$$pH^+ + qAg^+ + rHL^+ \rightleftarrows (H^+)_p(Ag^+)_q(HL^+)_r \quad (3a)$$

besides the two component equilibria

$$HL^+ \rightleftarrows L + H^+ \quad (3b)$$

$$pH^+ + qAg^+ \rightleftarrows (H^+)_p(Ag^+)_q \quad (3c)$$

The law of mass action and the conditions for the concentrations give:

$$B = b + \Sigma q \beta_{pqr} h^p b^q c^r \quad (4)$$

$$C = c + K_a h^{-1} c + \Sigma r \beta_{pqr} h^p b^q c^r \quad (5)$$

$$H = h - K_a h^{-1} c + \Sigma p \beta_{pqr} h^p b^q c^r - K_{HX}[HX]*/(h+K_{HX}) \quad (6)$$

The summation is taken over all complexes formed. β_{pqr}, K_a and β_{pqo} are the equilibrium constants for the reactions 3a, 3b and 3c, respectively. [HX]* denotes the total concentration of a protolytic impurity with the acidity constant $K_{HX}(K_{HX} \sim 10^{-8}$ M).

For reaction (3b), Sjöberg[3] reported $\log (K_a \pm 3\sigma) = -7.913 \pm 0.002$. Concerning equilibrium (3c) Hietanen and Biedermann[9] found the complex AgOH to predominate at high B(1 M AgNO$_3$) giving

$\log \ \beta_{-110} \lesssim -11.1$. At low B, Antikainen and Dyrssen[10] found (3 M NaClO$_4$) Ag(OH)$_2^-$ to be the main hydrolytic species with $\log \beta_{-210} = -24.84$.

These results on the two component equilibria will, in the following calculations, be considered as known and no attempts will be made to adjust their equilibrium constants. The computational problem now involves determination of sets of pqr-triplets and the corresponding equilibrium constants β_{pqr} that "best" fit the experimental data. In the calculations the least squares computer program LETAGROPVRID[11] (version ETITR[12]) was used.

This program makes it possible to treat E_H and E_B data separately as well as together. In the calculations the error squares sums $U_H = \Sigma(H_{calc} - H)^2$, ($E_H$, $E_H + E_B$ data) and $U_B = \Sigma(B_{calc} - B)^2$, ($E_B$, $E_H + E_B$ data) were minimized.

In the different calculations corrections due to a protolytic impurity (HX) were made according to eqn. 6. This correction is a necessity in evaluating species which are formed in small amounts.

The standard deviations given were defined and calculated according to Sillén.[13] The computations were performed on a CD6600 computer.

Before the LETAGROPVRID calculations were started, experimental data were plotted in the form $\bar{n}(\log[L])$ and η ($\log[L]$). When complexes of the general type Ag$_q$L$_r^{q+}$ are formed, *e.g.* when $-p = r$ in (4a), $\bar{n}$ is given by

$$\bar{n} = (h - H - K_w h^{-1} - [L])/B \quad (7)$$

[L] can be calculated from the relation

$$[L] = K_a h^{-1} c = k_a h^{-1}(C - (h-H)) \quad (8)$$

Furthermore

$$\eta = \log \ (B/b) \quad (9)$$

In cases with $-p \neq r$ it can easily be shown that (8) is no longer valid and apparent values of $\bar{n}$ and [L] are obtained. The $\bar{n}(\log[L])$ and $\eta(\log[L])$ functions are now calculated only to test how poorly a set of experimental data fits a series of complexes Ag$_q$L$_r^{q+}$.

CALCULATIONS AND RESULTS

The analysis of data was started by making $\bar{n}(\log[L])$ and $\eta(\log[L])$ plots which are given in Figs.
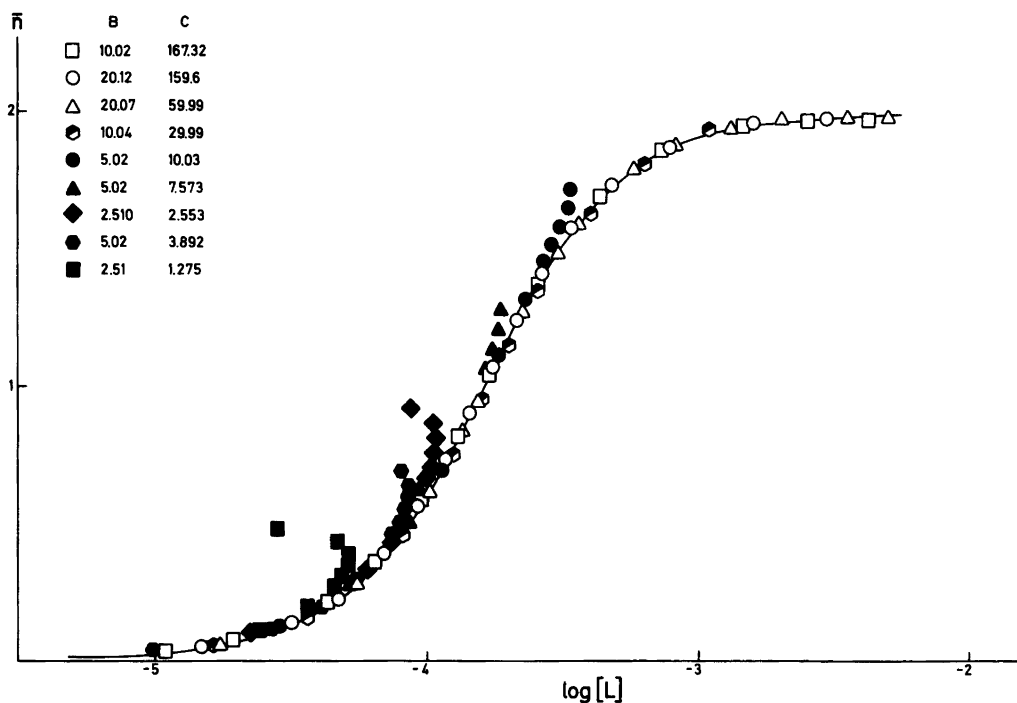
Fig. 1. Experimental data plotted as curves $\bar{n}$ log $[L]$ for C/B ratios 16, 8, 3, 2, 1.5, 1, 0.75, 0.5. Open and filled symbols mark titrations for quotients >2 and ≤2 respectively. Half filled symbols denote a back-titration. In order to make the figure clear only a few titrations have been plotted. The full drawn curve has been calculated with the set of proposed constants for AgL^+ and AgL_2^+.

1 and 2. According to these figures $\bar{n}$ as well as η seems to be independent of B and C for quotients $C/B>2$, thus indicating formation of a series of mononuclear complexes AgL_n^+. Data fulfilling these conditions will in the following be denoted Data 1.

However, at quotients $C/B\leq2$ and $B\leqslant0.010$ M systematic deviations from the mononuclear $\bar{n}$ as well as η curves are observed. This would indicate that additional species are formed. These data will below be denoted as Data 2.

In the LETAGROP calculations different data sets were used (*cf.* Table 2). This will enable us to compare results obtained in the different calculations and thus obtain information of the reliability of the different electrodes as well as of eventual errors in the analytical concentrations.

Data 1. According to Fig. 1 $\bar{n}$ reaches a limiting value of two, thus indicating that at most two imidazole molecules are coordinated to the silver ion. A LETAGROP analysis showed that E_H, E_B as well as $E_H + E_B$ data could very well be explained

with the complexes AgL^+ and AgL_2^+. Details of these calculations are given in Table 2. According to this table the agreement in β_{-111} and β_{-212}, independent of data sets and minimized functions exmployed, is very good, the spread in log β_{-111} and log β_{-212} being less than 0.02 and 0.01 units respectively. This indicates that the different data sets used are in good agreement with each other.

The question now arises of which data set provides the most reliable results. Firstly it must be advantageous to measure both h and b, thus providing data sets h, b, H, C or h, b, B, C. Secondly H was controlled in each titration (Gran extrapolation method with $-\log h\leq3$) while B assumed values determined by the stock solution of $AgClO_4$. Furthermore, as the variation in H is greater than in B, it seems that the equilibrium model deduced from h, b, H, C data should be the most accurate one ($\log\beta_{-111} = -4.577\pm0.012$ and $\log\beta_{-212}= -8.272$ 0.004).

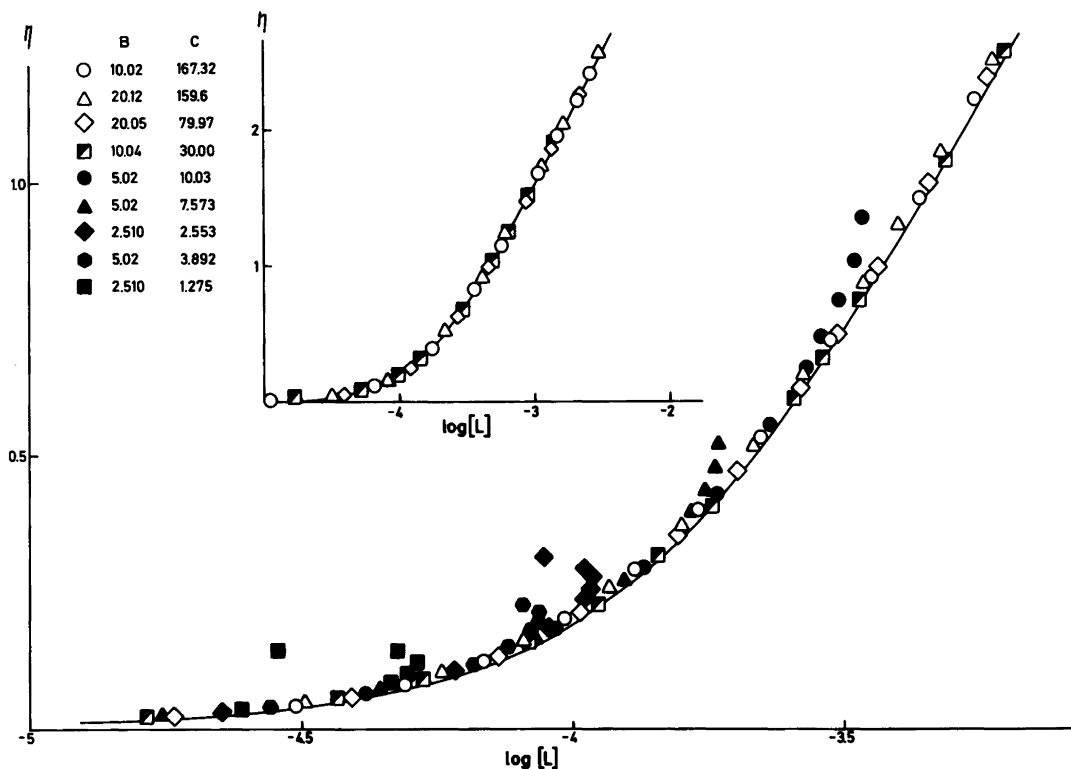*Data 2.* In the search for ternary species it was

Fig. 2. Experimental data plotted as curves η log [L] for C/B ratios 16, 8, 4, 3, 2, 1.5, 1, 0.75, 0.5. Half filled symbols denote a back-titration.

assumed that formation constants for the species AgL^+ and AgL_2^+ had the values proposed above. Furthermore, equilibrium constants for AgOH and $Ag(OH)_2^-$ were those given by Biedermann[9] and Dyrssen,[10] respectively.

The analysis of data 2 was started with a residual calculation, using the results from the calculation on data 1. The residuals clearly indicate that one or more additional complexes, beside those belonging to the series AgL_n^+, must be present. In order to explain these data, we will try the very simple hypothesis that only one additional complex $(H^+)_p(Ag^+)_q(HL^+)_r$ is present. A trial and error procedure with the LETAGROPVRID program was used to determine the composition and equilibrium constant of the additional complex proving the closest fit to data 2. The principal of this method has been that complexes of different pqr compositions have successively been tested one by one, and the complex that gives the lowest value in U_H will be considered as the "best" explanation of

the data. In these calculations experimental $(h, b, H$ and C)-data were used. The error squares sums U_H obtained for the tested combinations are given in Fig. 3. It was found that the lowest value in U_H was obtained for the complex $(H^+)_{-2}(Ag^+)_1$-$(HL^+)_1$, with log $\beta_{-211} = -12.69 \pm 0.05$ giving $\sigma(H) = 0.023$ mM. The residuals $H_{calc} - H_{exp}$, obtained in this calculation show no systematic trends, and the low value in $\sigma(H)$ is an indication that this complex is a good explanation to data 2.

For comparison, calculated values of log β_{-211} from (h, b, B, C), (h, H, B, C) and (b, H, B, C) data are also given in Table 2. As can be seen log β_{-211} varies between -12.69 and -12.77 when E_H and $E_H + E_B$ data were treated. This variation must be considered as acceptable as the constant values lie within their limits of error.

When E_B-data were treated, a rather uncertain determination of β_{-211} was obtained (log $\beta_{-211} = -12.34 \pm 0.19$). One explanation for this is that the $-2,1,1$ complex is formed in small amounts

Table 2. Results of LETAGROP-calculations on different data sets. The formation constants, β_{pqr}, are defined according to the equilibria $pH^+ + qAg^+ + rHL^+ \rightleftarrows H_pAg_q(HL)_r^{(p+q+r)+}$. The errors 3 $\sigma(\log\beta_{pqr})$ are given when the corresponding equilibrium constant has been varied. Results are given from calculations on data 1 (upper half of the table) and data 2 (lower half).

Data	Number of titr/ number of points	AgL$^+$ $\log(\beta_{-1,1,1}$ $\pm 3\sigma)$	AgL$_2^+$ $\log(\beta_{-2,1,2}$ $\pm 3\sigma)$	Ag(OH)L $\log(\beta_{-2,1,1}$ $\pm 3\sigma)$	$\sigma(y)/$ mM	Data set used
E_H		-4.566 ± 0.012	-8.280 ± 0.004		$0.036\,^a$	h, H, B, C
E_B		-4.563 ± 0.001	-8.281 ± 0.001		$0.025\,^b$	b, H, B, C
$E_H + E_B$	12/156	-4.577 ± 0.012	-8.272 ± 0.003		$0.041\,^a$	b, h, H, C
$E_H + E_B$		-4.558 ± 0.005	-8.272 ± 0.004		$0.027\,^b$	b, h, B, C
E_H		-4.577	-8.272	-12.69 ± 0.05	$0.023\,^a$	h, H, B, C
E		-4.577	-8.272	-12.38 ± 0.19	$0.009\,^b$	b, H, B, C
$E_H + E_B$	14/218	-4.577	-8.273	-12.69 $\pm\ 0.05$	$0.024\,^a$	b, h, H, C
$E_H + E_B$		-4.577	-8.272	-12.77 ± 0.06	$0.011\,^b$	b, h, B, C

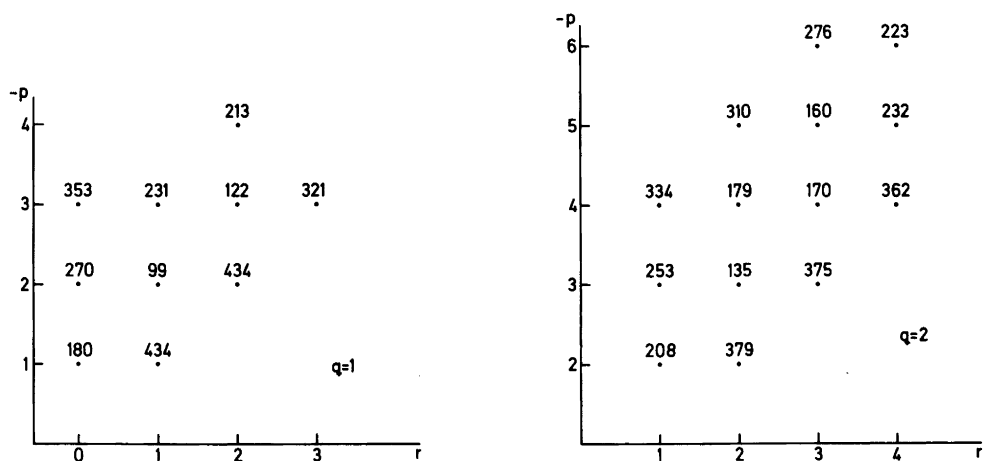^{a} $y = H_{calc} - H_{exp}$. ^{b} $y = B_{calc} - B_{exp}$.

Fig. 3. LETAGROP-search for ternary $H_pAg_q(HL)_r^{(q+p+r)+}$-complexes. The diagrams give error square sums $U_H(pr)_q \times 10^3$ assuming only one complex. In the calculations the species AgOH, $(Ag(OH)_2^-)$ and AgL$_n^+$ $n = 1, 2$ have been assumed to be known. The calculations are based on 109 experimental points, chosen to cover as great concentration ranges as possible.
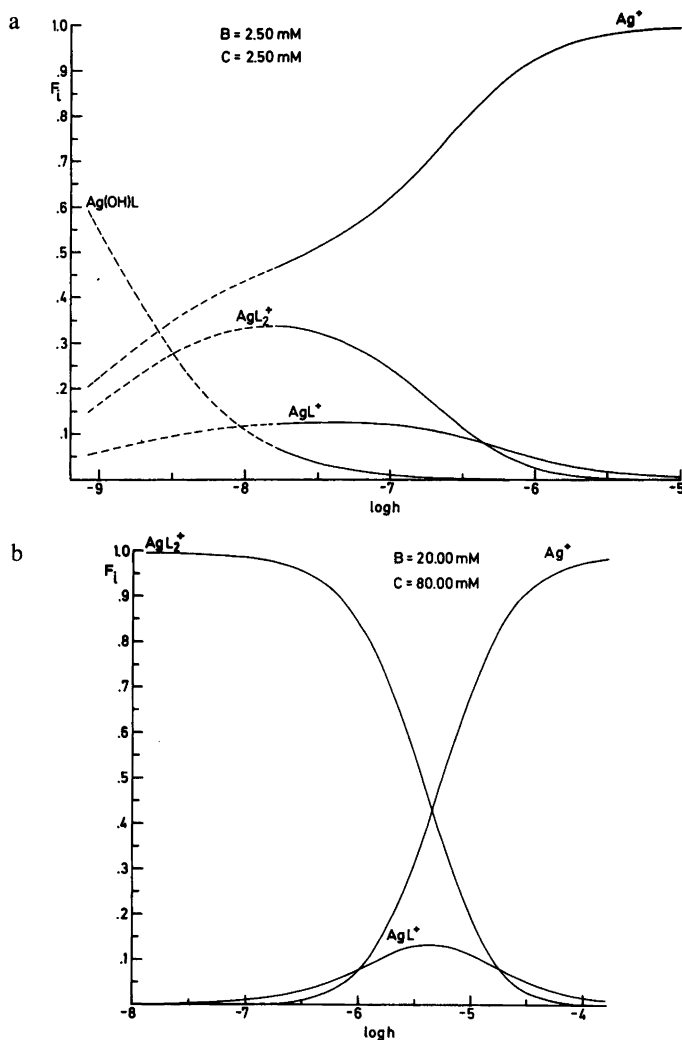
Fig. 4. Distribution diagrams $F_i(\log h)_{B,C}$. F_i is defined as the ratio between silver(I) in a species and the total silver(I). The computer program SOLGASWATER[14] was used for the calculations with the constants given in Table 2. Broken lines denote ranges where no measurements have been performed due to precipitation (extrapolated range).

($\lesssim 10\%$ of B, *cf.* Fig. 4) and that the Ag,AgCl-electrode is not as sensitive as the glass electrode with respect to the formation of this complex. According to the equilibria $Ag^+ + HL^+ \rightleftarrows (H^+)_{-2}$-$(Ag^+)(HL^+) + 2H^+$, the effect in E_H is twice as great as that in E_B.

For the same reasons as discussed under data 1, the most reliable value in $\log \beta_{-211}$ is that evaluated from h, b, H, C-data. Thus $\log \beta_{-211} = -12.69 \pm 0.05$ is proposed.

DISCUSSION

The present investigation of the silver(I) − imidazole system was carried out by measuring two free concentrations, h and b.

In the LETAGROP-calculations, one of the quantities h, b, H or B was excluded, thus yielding four different types of data sets*(*cf.* Table 2). Results

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* A complete list of the experimental data is availabe from this department.

of these calculations have shown that the agreement in the evaluated formation constants was good, which is an indication that systematic or occasional errors in H and B as well as h and b are negligible.

The calculations also showed that with $C/B > 2$, data could very well be explained with the complexes AgL^+ and AgL_2^+.

If we compare the values of the stepwise constants with earlier determinations (see Table 1), we find that the absolute values of K_1 and K_2 are somewhat higher, probably due to medium effects. However, the ratio $K_2/K_1 = 7.6$ is of the same magnitude as values reported by Gold, Gregor[17] and Bauman, Wang.[18]

A diagram showing the distribution of AgL^+ and AgL_2^+ is given in Fig. 4a.

At low ratios $C/B \leq 2$, a ternary complex is formed ($\sim 8\%$ of B, see Fig. 4b). Although it is impossible from potentiometric data to decide whether this is a hydroxoimidazole ($Ag(OH)C_3H_4N_2$) or an imidazolate $Ag(C_3H_3N_2)$ complex, we find the first alternative more probable. This is because two coordinated $Ag(I)$ species, as a rule, are very stable, which favours the hydroxocomplex.

If we assume that a hydroxoimidazolecomplex $Ag(OH)L$ really is formed, the acidity constant of AgL^+ can be calculated to be $\log K_a(AgL^+) = -8.11$. This complex is an acid stronger than Ag^+ and $AgOH$ for which the acidity constants are ≤ -11.1 and ≥ -13.7. Thus the introduction of an imidazole ligand increases the acidity of the silver ion. This has also been found in the nickel(II),[21] copper(II),[3] zinc(II),[22] and mercury(II)[23] imidazole systems investigated by Forsling and Sjöberg. The acidity constants obtained in the Ni^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+} systems are: (pK_a (Me^{2+}), pK_a (MeL^{2+}), ≥ 10.5, 9.30; 8.0, 7.18; 9.25, 8.92; and 3.58, 1.54; respectively.

With L = ethylendiamine (en) and 1,2-propanediamine (pn), Ohtaki and Ito[24] found evidence for $Ag(OH)L$ complexes with the acidity constants $\log K_a(AgL) = -10.72$ (en) and -9.69 (pn). Thus the same trend as in the case with imidazole was observed.

Concerning the different solid phases formed, solubility measurements are in progress in order to determine their solubility products. Attempts are being made to find out whether additional complexes, besides those discussed in the present investigation, are formed in equilibrium with these solid phases. The result of these measurements will be given in a forthcoming paper.

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