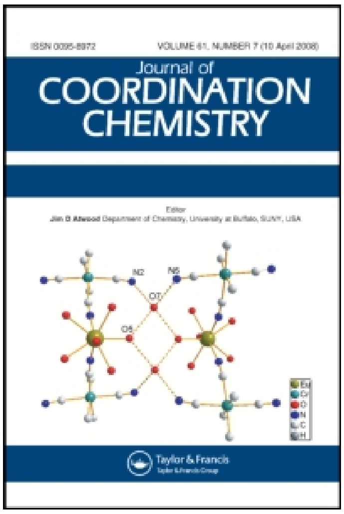

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A POTENTIOMETRIC STUDY OF THE COMPLEXATION OF ALIPHATIC ACYCLIC MONOAMINES WITH Ag(I) IN 1 M NITRATE

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Complexation of 12 aliphatic monoamines with Ag(I) has been studied in 1M KNO_3 at 25°C using a potentiometric titration technique, performing pH and pAg measurements. To study these ternary systems, the binary systems (Ag-OH, L-H, H-OH) were first investigated. The model used for background Ag(I) hydrolysis is consistent with the literature. Graphical techniques were used for the calculation of formation constants of silver-amine complexes. The estimates were further refined using the Superquad program. Evidence has been found for the formation of mixed Ag(I)-hydroxo ligand complexes only with aliphatic primary monoamines.

KEYWORDS: aliphatic monoamines, silver, complexes, hydrolysis, mixed complexes, stability constants

INTRODUCTION

Complex formation of silver with nitrogen-donor ligands such as aliphatic monoamines has been studied quite extensively in aqueous[1-5] as well as non-aqueous solutions[6] and mixtures.[7] Primary monoamines have received by far the most attention. Values for secondary and tertiary monoamines, on the other hand, are difficult to find. This is probably due to the fact that formation curves are steep. Consequently, difficulties are encountered in calculating accurate stability constants.[8]

The characteristic coordination number of Ag^+ with monodentate amines and ammonia is 2, resulting in a linear structure. The stepwise formation of the 1:1 and 1:2 silver-amine (L) complexes are usually expressed by the equations below, where charges have been omitted for simplicity.

$$K_1 = \beta_1 = [AgL]/([Ag][L])$$
$$K_2 = [AgL_2]/([AgL][L])$$
$$\beta_2 = [AgL_2]/([Ag][L]^2) \quad \text{with } \beta_2 = K_1.K_2$$

An interesting aspect of complex formation is that for primary and secondary amines the first stepwise stability constant K_1 is usually smaller than the second

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constant K_2.[1-5] For tertiary aliphatic monoamines this sequence is reported to be reversed but data on these products are rather too scarce to generalise.[5,6] The peculiar tendancy of silver with primary and secondary monoamines is in apparent defiance of the statistical probability for the addition of a ligand to a complex. A conclusive explanation of this phenomenon has yet to be formulated. Most investigators use the self medium technique[27] to study these amines in order to avoid silver hydrolysis in basic medium due to the high pK_A values of the amines and the relatively weak complexes formed. This technique is however not ideal if one wishes to compare complexation models and pK_A values with other data derived from the more common ratio technique in aqueous solution at high ionic strength.

The study aimed to investigate the systematic effects of a methyl and ethyl substituent on the donating power of the N-atom towards Ag(I) using the ratio technique, while correcting for possible Ag(I)-hydrolysis. The following amines were investigated: ammonia, methylamine, ethylamine, propylamine, butylamine, dimethylamine*, methylethylamine*, diethylamine, trimethylamine*, dimethylethylamine*, diethylmethylamine* and triethylamine. The amines marked with an asterisk have no stability constants for silver complexes in the literature, at 25°C.

Because of parallels drawn earlier between alcohol amines and aliphatic amines[8] and the fact that mixed Ag(I)-hydroxo ligand complexes have been detected with alcohol amines such as THAM[9] and with aliphatic polyamines such as diethylenetriamines[10,11] and ethylene and propylene diamines,[12,13] we believed it might be worthwhile to measure the missing stability constants and at the same time test new models, besides AgL and AgL_2 complexes, for aliphatic monoamines.

In this work, the following terminology is used: C_{Ag} = total concentration of silver, C_L = total concentration of ligand (L), C_H = total proton concentration, β_{pqr} = stability constant of the general species $[M_pL_qH_r]$ defined by the equations

$$pM + qL + rH \rightleftharpoons M_pL_qH_r \text{ and}$$

$$\beta_{pqr} = \frac{[M_pL_qH_r]}{[M]^p[L]^q[H]^r}$$

(for $r < 0$ hydroxo complexes and $r > 0$ protonated complexes are formed), k = protonation constant of the weak acid

$$L + H^+ \rightleftharpoons LH^+ \qquad k = [LH^+]/([H^+][L]).$$

The terms $\bar{n}_H$ and $H\bar{n}$ are calculated from the following equations:[30]

$$\bar{n}_H = \frac{[H^+]\cdot k}{1 + [H^+]\cdot k} \qquad \bar{n} = \frac{C_L - (C_H - ([H^+] - [OH^-]))/\bar{n}_H}{C_{Ag}},$$

where $\beta_{00-1} = K_w$ = the auto-dissocation constant of water.
The hydrolysis constants β_{p0-r} and β^*_{p0-r} refer, respectively, to the reactions

$$p\,Ag^+ + rH_2O \rightleftharpoons Ag_p(OH)_r^{(p-r)} + rH^+,$$
$$p\,Ag^+ + r\,OH^- \rightleftharpoons Ag_p(OH)_r^{(p-r)},$$

with $\beta_{p0-r} = (\beta_{00-1})^r.\beta^*_{p0-r}$.

EXPERIMENTAL

Reagents

The nitrate salts of all amines were prepared, purified and analyzed as mentioned earlier.[14] $AgNO_3$ (Merck p.a.), KNO_3 (Merck p.a.) and NH_4NO_3 (Fluka p.a.) were used without further purification. KOH and HNO_3 solutions were prepared from Titrisol ampoules (Merck p.a.). KOH solutions were prepared under a N_2 atmosphere with freshly boiled, doubly distilled, deionized water and kept under a CO_2-free atmosphere in a polyethylene bottle (used within two weeks of preparation). The ionic strength of all solutions was kept constant with KNO_3 at 1M $[NO_3^-]$.

Stock solutions of ligand consisted of (0.01 M $LHNO_3$ + 0.001 M HNO_3 + 0.989 M KNO_3). The Ag(I) stock solutions were either (0.01 M $AgNO_3$ + 0.99 M KNO_3) or (0.001 M $AgNO_3$ + 0.999 M KNO_3). The volume of each stock solution added into the titration vessel has been varied in order to obtain an appropriate C_{Ag}/C_L - ratio.

Apparatus

The pH measurements were performed with a Radiometer PHM-64-or-84 instrument with a resolution of 0.1 mV. The following electrodes were used: an Ingold glass electrode (pH 0-14, U262-S7), an Ingold Argental reference electrode (363-S7) in a saltbridge (Schott-Geräte B511 with ceramic plug) filled with 1.5 M KNO_3. The pAg measurements were performed with an Orion 94-16 Ag/Ag_2S electrode. Due to the low resistance of this electrode ($< 1\ M\Omega$) the potential can be measured with a resolution of 0.01 mV without the assistance of an operational amplifier using a Keithley voltmeter model 190 or 197; (input resistance $> 1\ G\Omega$). The experimental setup is as described for the glass electrode[15] but for the Ag/Ag_2S electrode the equilibrium cycle has been repeated until the difference in averages was less than 0.02 mV/min.

TITRATIONS

Calibration

The calibration of the glass electrode and determination of its characteristics, the determination of pK_w (13.775 ± 0.003) and the pK_A values of the monoamines has been described in previous papers.[14-15] The Ag/Ag_2S electrode was calibrated with 10 different silver solutions varying in concentration between 10^{-2} and 5×10^{-6}M. The electrode responds in a Nernstian fashion in this range.

The formation of $AgNO_3$ ion pairs is neglected. These ion pairs are outer sphere complexes with a low association constant.[16,17]

$$Ag^+ + NO_3^- \rightleftharpoons AgNO_3 \quad \beta_{AgNO_3} = [AgNO_3]/([Ag^+][NO_3^-])$$

Published values for β_{AgNO_3} vary between 0.56^{16} to 0.09^{17} (non-potentiometric measurement techniques). We expect that ion pair formation involving nitrate with silver-amine complexes is also possible. It is assumed that these ion pairs are not in competition with ligands for the complexation of silver.

Silver hydrolysis titrations

The optimum titration area was first determined using the titration simulation programs Spe and Speplot[18] with estimates obtained from the literature.[19-23] It is necessary to find the best experimental conditions because Ag_2O rapidly precipitates in basic medium (the lower the silver concentration the larger the pH region that can be explored without precipitation) and the fact that the Ag/Ag_2S electrode needs a minimum total silver concentration of 10^{-6} M to respond ideally[19] and avoid measurable adsorbtion of Ag^+ on the glass vessel.[20]

Solutions of 0.002 M HNO_3 + (10^{-5}; 2 × 10^{-5}; 3 × 10^{-5}; 5 × 10^{-5}M $[Ag^+]$) + 0.998 M KNO_3 were titrated with 0.1 M KOH until the Ag/Ag_2S electrode became unstable or precipitation was visible. The first points of the titrations can be used for interenal calibration of the Ag/Ag_2S electrode. The published pK_S values of Ag_2O[21] at 1 M ionic strength vary between 7.18 (1 M KNO_3) and 7.27 (1 M $NaClO_4$). To keep a safe margin, the slightly larger pK_S value of 7.3 was used as a cut-off value so that titration points with an ionic product $[Ag^+][OH^-] > 10^{-7.3}$ were excluded from the calculations.

Silver-amine complexation titrations

The primary monoamines ammonia, methylamine, ethylamine, propylamine and butylamine were titrated with KOH using a 1/2, 1/3, 1/4 and 1/5 C_{Ag}/C_L ratio. Precipitation generally occurred during the 1/2 and 1/3 ratio titrations. For the secondary amines, titrations with ratio's greater than 1/5 did not produce any good experimental points due to precipitation. The ratios were therefore lowered to 1/10, 1/15, 1/20, 1/30. The tertiary amines need even lower C_{Ag}/C_L ratio's: 1/50, 1/75, 1/100.

N_2 was purged for 15 min through the solution before the titration was started. Just before the potential jump, from strong acid to amine-buffer region, the vessel was manually sealed so that a slight N_2 pressure was allowed to build up in the cell. The N_2 flow was then stopped. We continued to titrate until one of the electrodes became unstable (usually Ag/Ag_2S), until precipitation was visible or until pH = 12 was reached. The titrations were performed at least in duplicate and the first titration points were used for internal calibration of the Ag/Ag_2S electrode. The glass electrode characteristics were checked in 0.005 M HNO_3 before and after each titration, as described previously.[14-15]

Calculations

The programs used were written in Fortran 77 and run in double precision. Spe and Speplot were slightly modified for our use. Plots were made using the Disspla drawing package. Listings of all programs, including those used for the graphical analysis, are available from the authors.

RESULTS

Silver hydrolysis

[AgOH] and $[Ag(OH)_2^-]$ are the predominant species in alkaline solutions of $AgNO_3$

below 0.5 M $[OH^-]^{21}$, if no precipitation occurs. The mass balance equations can be written as follows:

$$C_{Ag} = [Ag^+] + \beta^*_{10-1}[Ag^+][OH^-] + \beta^*_{10-2}[Ag^+][OH^-]^2$$
$$C_H = [H^+] - [OH^-] - \beta^*_{10-1}[Ag^+][OH^-] - 2\,\beta^*_{10-2}[Ag^+]\,[OH^-]^2$$

In principle, if pH and pAg measurements are performed, the system is completely determined so each titration point can yield 2 constants.

If we suppose that only [AgOH] is present under our experimental conditions, the Leden function, F_0, can be used to calculate the formation constant.

$$F_0([OH^-]) = \frac{(C_{Ag} - [Ag^+])}{[Ag^+]} = \beta^*_{10-1}[OH^-]$$

A plot of F_0 *vs* $[OH^-]$ yields β^*_{10-1} as its slope (Figure 1a). It is clear from the figure that no linear relationship is found. The shape of the curve suggests the presence of a higher hydroxo species like $Ag(OH)_2^-$.

Therefore, if [AgOH] and $[Ag(OH)_2^-]$ are present, F_0 becomes:

$$F_0([OH^-]) = \beta^*_{10-1}[OH^-] + \beta^*_{10-2}[OH^-]^2$$

The first Leden function F_1 can be calculated from these values:

$$F_1([OH^-]) = \frac{F_0([OH^-])}{[OH^-]} = \frac{(C_{Ag} - [Ag^+])}{([Ag^+]\,[OH^-])} = \beta^*_{10-1} + \beta^*_{10-2}[OH^-]$$

Theoretically, if $F_1([OH^-])$ is plotted *vs* $[OH^-]$ a straight line with slope β_{10-2} and intercept β_{10-1} should be obtained. It can be demonstrated that very small errors in $[OH^-]$ and/or $[Ag^+]$ can result in large errors in $F_1([OH^-])$. In Figure 1b, using the experimental data, no linear function is found. Very small errors (0.2%; *i.e.*, of the same magnitude as the inevitable potentiometric experimental errors) in either the $[OH^-]$ data or $[Ag^+]$ make the curls disappear.

An alternative method is to calculate the derivative of $[OH^-]$ from the F_0 function:

$$\frac{\partial F_0([OH^-])}{\partial([OH^-])} = F_0'([OH^-]) = \beta^*_{10-1} + 2\,\beta^*_{10-1}\,[OH^-]$$

By plotting F_0' *vs* $[OH^-]$ a better straight line is obtained (Figure 1c). This is probably due to cancelling out of the errors in $[OH^-]$ and subsequently in $F_0'([OH^-])$:

$$F_0' \cong \frac{F_{0,1} + \Delta F_{0,1} - F_{0,2} - \Delta F_{0,2}}{[OH^-]_1 + \Delta[OH^-]_1 - [OH^-]_2 - \Delta[OH^-]_2}$$

$F_{0,1}$ and $F_{0,2}$ are the Leden F_0 values of two successive points with their respective errors $\Delta F_{0,1}$ and $\Delta F_{0,2}$ and the hydroxyl concentrations of the two points $[OH^-]_1$ and $[OH^-]_2$ have respective errors $\Delta[OH^-]_1$ and $\Delta[OH^-]_2$.

The constants obtained from this graphical analysis, reported in Table 1, are used as initial values for further refinement using the weighted option in Superquad[24-26] with σ_v = 0.002 mL, $\sigma_{E\text{-glass}}$ = 0.2 mV and $\sigma_{E\text{-Ag/Ag}_2S}$ = 0.1 mV. Superquad

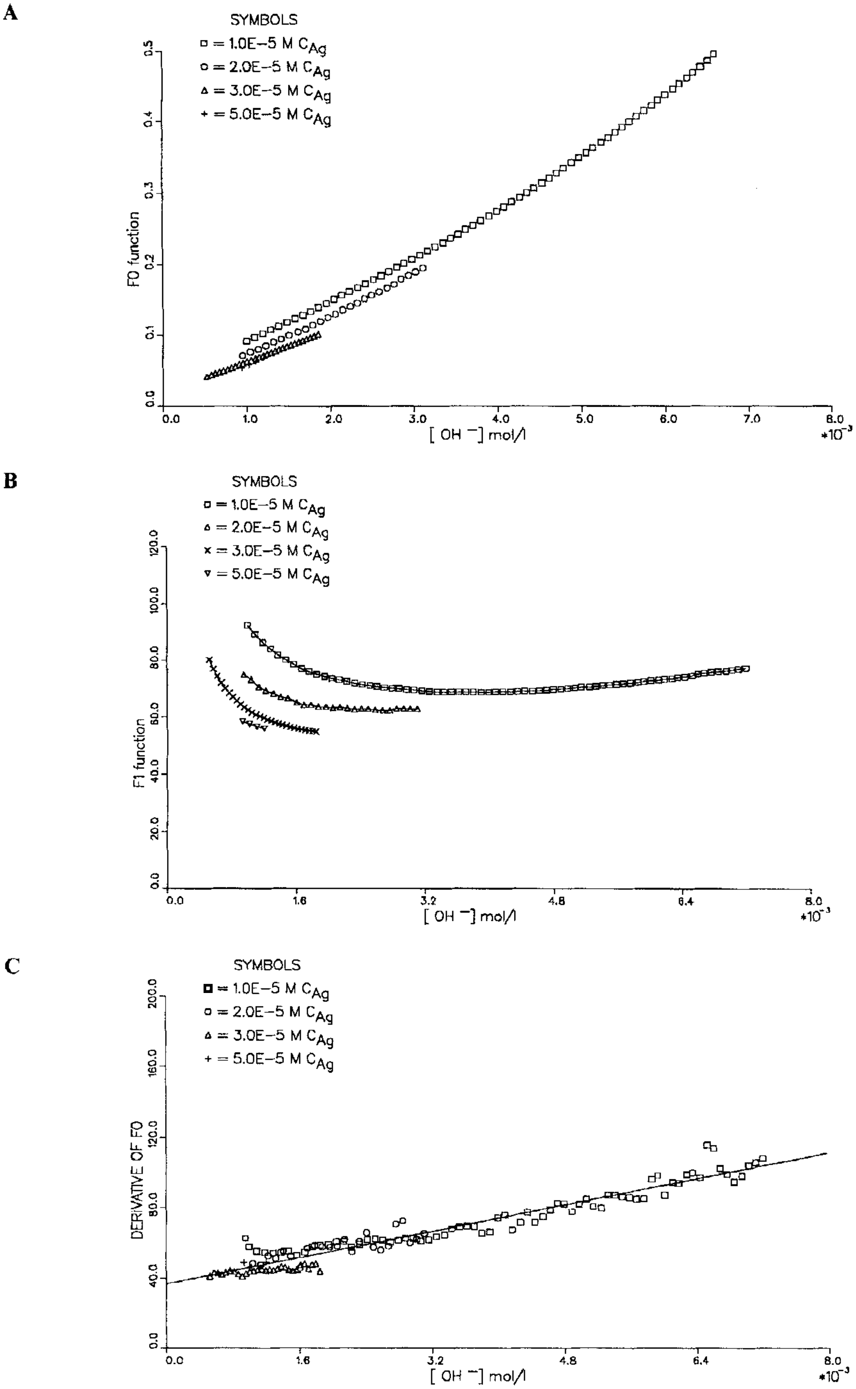

Figure 1 Different graphical functions used for the calculation of the silver hydrolysis constants; a: F_0 function *vs* $[OH^-]$ b: F_1 function *vs* $[OH^-]$ c: F'_0 function *vs* $[OH^-]$.

Table 1 A comparison of results of graphical analysis with those obtained using Superquad for the successful models.

Technique	model 1: [AgOH]	model 2: [AgOH],$[Ag(OH)_2^-]$
Graphical analysis	($F_O$function)	(F'_Ofunction)
	$\log \beta^*_{10\text{-}1}$ = 1.874 ± 0.003	$\log \beta^*_{10\text{-}1}$ = 1.561 ± 0.007
		$\log \beta^*_{10\text{-}2}$ = 3.673 ± 0.009
	R = 0.998	R = 0.965
Superquad	$\log \beta_{10\text{-}1}$ = -11.933 ± 0.002	$\log \beta_{10\text{-}1}$ = -12.005 ± 0.006
		$\log \beta_{10\text{-}2}$ = -24.17 ± 0.03
	S = 3.39	S = 2.78
	$\log \beta^*_{10\text{-}1}$ = 1.842 ± 0.002	$\log \beta^*_{10\text{-}1}$ = 1.770 ± 0.006
		$\log \beta^*_{10\text{-}2}$ = 3.38 ± 0.03

The results from Superquad for model 2 agree well with literature values for dilute solutions: $\log \beta_{10\text{-}1} = -12.0$ and $\log \beta_{10\text{-}2} = -24.0$[21-23]. The difference in values between the two different calculation techniques of model 2 may be attributed to the high correlation of the constants (0.97) and to the difference in weighting used in both techniques. The constants obtained for model 2 by Superquad were used to correct for background silver hydrolysis when calculating the silver-amine stability constants.

minimizes the error square sum $U = \Sigma w_i(E_i^{exp} - E_i^{calc})^2$ with weight $w_i = 1/\left(\sigma_E^2 + \left(\frac{\partial E}{\partial V}\right)^2 \sigma_V^2\right)$. The goodness-of-fit is judged by the overal fit statistic $S = \left[\frac{\varepsilon^T w \varepsilon}{m - n}\right]^{1/2}$ where ε is a vector of residuals in the potential, ε^T its transpose, w is the weight matrix, m is the number of data points and n is the number of parameters to be refined. Ideally this S value should be 1. An S value between 1 and 3 is generally accepted for a good fit.[25-26] Several models were tested in Superquad but only the models successfully refined are reported in Table 1.

Silver-amine complexes

The mass balances for Ag(I)-amine systems with N = 2, if silver hydrolysis is expected and any possible mixed hydroxo ligand complexes are temporary ignored, are:

$$\begin{aligned} C_{Ag} &= [Ag^+] + \beta_{110}[Ag^+][L] + \beta_{120}[Ag^+][L]^2 + \beta^*_{10-2}[Ag^+][OH^-] + \\ &\quad \beta^*_{10-2}[Ag^+][OH^-]^2 \\ C_L &= [L] + \beta_{011}[L][H^+] + \beta_{110}[Ag^+][L] + 2\,\beta_{120}[Ag^+][L]^2 \\ C_H &= [H^+] - [OH^-] + \beta_{011}[L][H^+] - \beta^*_{10-1}[Ag^+][OH^-] - \\ &\quad 2\,\beta^*_{10-2}[Ag^+][OH^-]^2 \end{aligned}$$

Corrected for silver hydrolysis these become:

$$\begin{aligned} C'_{Ag} &= C_{Ag} - \beta^*_{10-1}[Ag^+][OH^-] - \beta^*_{10-2}[Ag^+][OH^-]^2 \\ &= [Ag^+] + \beta_{110}[Ag^+][L] + \beta_{120}[Ag^+][L]^2 \\ C'_L &= C_L \\ C'_H &= C_H + \beta^*_{10-1}[Ag^+][OH^-] + 2\,\beta^*_{10-2}[Ag^+][OH^-]^2 \\ &= [H^+ - [OH^-] + \beta_{011}[L][H^+] \end{aligned}$$

Quite a number of graphical methods for the determination of mononuclear formation constants with $N = 2$ have been proposed in the literature.[27–29] One of the most convenient equations was developed by Irving and Rossotti.[30] A least-squares fit for the function $\bar{n}/((1 - \bar{n})[L])$ plotted against $(2 - \bar{n})[L]/(1 - \bar{n})$ yields β_{110} as the intercept and β_{120} as the slope. Generally, only values of $\bar{n}$ between 0.2 and 0.8 and between 1.2 and 1.8 are used for the calculations. The main advantage of this technique is that besides the mass balances only $[H^+]$ needs to be known to calculate this function. If however pH and pM measurements are performed, the first Leden function $((C'_{Ag}/[Ag^+]) - 1)/[L]$ can be plotted *vs* [L] and a straight line with slope β_{120} and intercept β_{110} is obtained. [L] can be calculated from the corrected proton mass balance C'_H if the model supposed is correct.

The alternative technique using the derivative function described above in the Ag-hydrolysis section can also be used here, but does not seem necessary because no erratic values for the Leden function turned up at the beginning of each titration. This is probably due to the fact that the errors in [L] are smaller than in the respective $[OH^-]$.

However, curls are found in the formation curves and in the Leden function despite the fact that C'_{Ag} and C'_H are corrected for metal hydrolysis. These phenomena suggest that other complexes are formed, most likely mixed hydroxo ligand species[31] (Figure 2a and 2b). The data points, where these curls originate, are excluded from the calculation of the formation constants using the Leden function, but were included when calculating different models using Superquad. The results from the graphical technique are presented in Table 2 and do not give good results for the tertiary amines due to very low C_{Ag}/C_L ratios.

No special weighting procedure is used to calculate the Leden function. The correlation coefficient is given as a measure of the goodness-of-fit.

The obtained constants are used as initial values for further refinement using the weighted option in Superquad. The values of pK_W, pK_A, silver hydrolysis constants and mass balances are kept constant during optimisation. Three models, two of them including mixed hydroxo ligand complexes, were tested. The results are

Table 2 Stability constants determined using the Leden Function.

primary monoamines	log (β_{110}) log (β_{120})	secondary monaomines	log (β_{110}) log (β_{120})
NH_3	3.35 ± 0.01 7.275 ± 0.003 R = 0.9984	$(CH_3)_2NH$	2.465 ± 0.006 5.269 ± 0.005 R = 0.9976
CH_3NH_2	3.085 ± 0.007 6.843 ± 0.002 R = 0.9993	$CH_3CH_2NHCH_3$	2.737 ± 0.008 5.913 ± 0.004 R = 0.9947
$CH_3CH_2NH_2$	3.519 ± 0.004 7.513 ± 0.001 R = 0.9990	$(CH_3CH_2)_2NH$	3.164 ± 0.006 6.476 ± 0.006 R = 0.9937
$CH_3CH_2CH_2NH_2$	3.39 ± 0.01 7.491 ± 0.002 R = 0.9969		
$CH_3CH_2CH_2CH_2NH_2$	3.41 ± 0.01 7.608 ± 0.002 R = 0.9981		

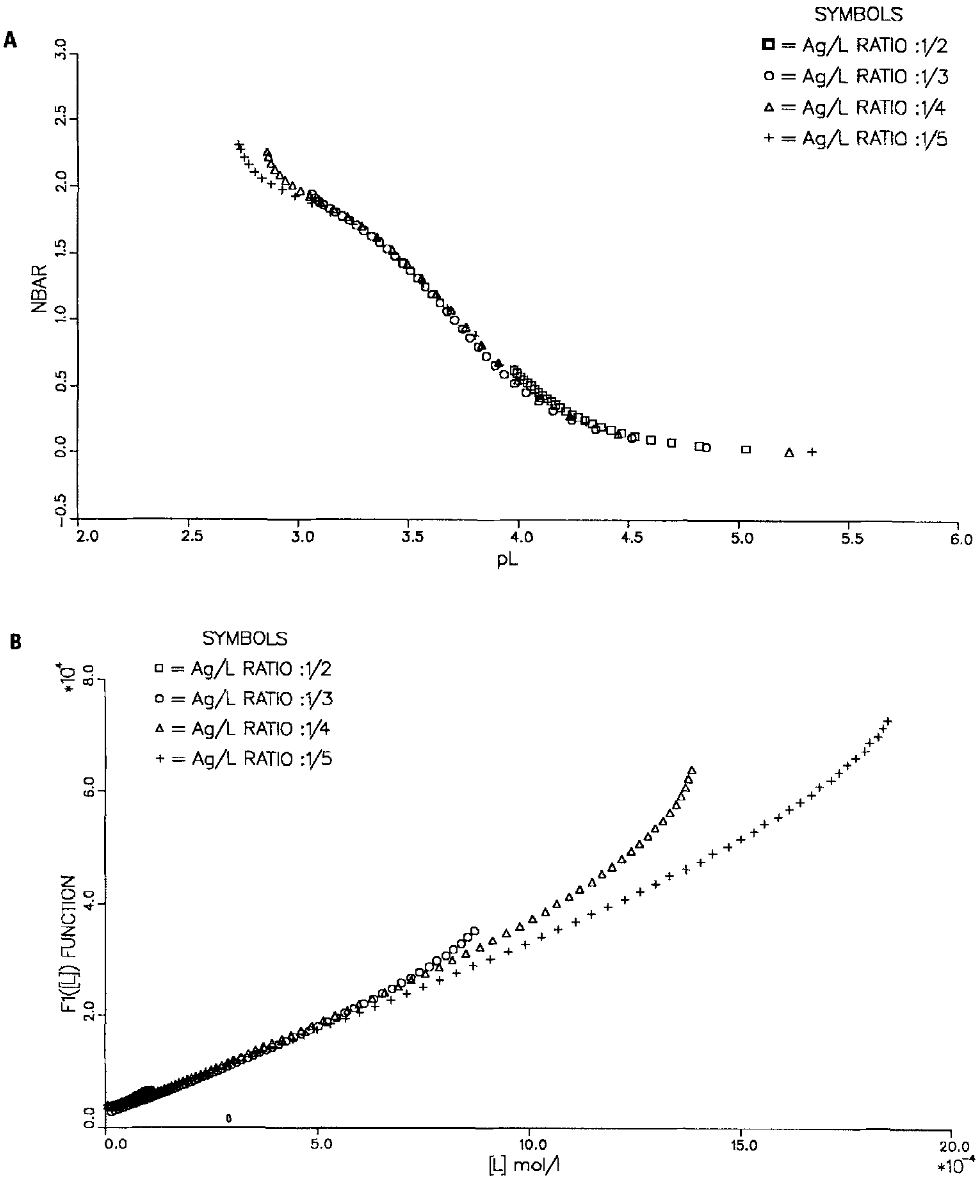

Figure 2 a: Formation curve for propylamine with silver *versus* pL; b: F_1 function *versus* [L].

presented in Table 3, together with the overall fit statistic S and the standard deviations in the constants. When the added mixed hydroxo ligand complex, compared with model 1, is rejected during optimisation, the model is noted as "rejected". If another species is rejected, the relevant species is noted as "not accepted" (n.a).

Table 3 A survey of the models refined using Superquad. The formation constants are in log units.

A. Primary monoamines	Model 1: AgL, AgL_2	Model 2: AgL, AgL_2, AgL_2H_{-1}	Model 3: AgL, AgL_2, $AgLH_{-1}$
NH_3	3.356 ± 0.002	3.367 ± 0.005	3.360 ± 0.005
	7.259 ± 0.005	7.251 ± 0.002	7.254 ± 0.002
		-4.08 ± 0.08	-7.2 ± 0.2
	S = 2.95	S = 2.73	S = 2.89
CH_3NH_2	3.086 ± 0.005	3.106 ± 0.004	
	6.820 ± 0.002	6.806 ± 0.002	rejected
		-5.30 ± 0.05	
	S = 2.5	S = 2.18	
$CH_3CH_2NH_2$	3.442 ± 0.006	3.492 ± 0.003	rejected
	7.485 ± 0.004	7.493 ± 0.002	
		-3.60 ± 0.01	
	S = 7.8	S = 3.7	
$CH_3CH_2CH_2NH_2$	3.440 ± 0.003	3.463 ± 0.003	rejected
	7.440 ± 0.003	7.435 ± 0.001	
		-4.30 ± 0.03	
	S = 4.5	S = 3.5	
$CH_3CH_2CH_2CH_2NH_2$	3.399 ± 0.006	3.453 ± 0.004	rejected
	7.573 ± 0.003	7.571 ± 0.002	
		-3.66 ± 0.02	
	S = 6.8	S = 4.5	
B. Secondary monoamines			
$(CH_3)_2NH$	2.484 ± 0.007	rejected	rejected
	5.263 ± 0.007		
	S = 2.48		
$CH_3CH_2NHCH_3$	2.789 ± 0.004	rejected	rejected
	5.828 ± 0.002		
	S = 3.16		
$(CH_3CH_2)_2NH$	3.11 ± 0.02	rejected	rejected
	6.43 ± 0.02		
	S = 7.95		
C. Tertiary monoamines			
$(CH_3)_3N$	1.701 ± 0.003	rejected	rejected
	n.a.		
	S = 2.9		
$(CH_3)_2NCH_2CH_3$	1.979 ± 0.006		
	3.49 ± 0.07	rejected	rejected
	S = 2.07		
$(CH_3CH_2)_2NCH_3$	2.175 ± 0.002		
	3.86 ± 0.06	rejected	rejected
	S = 3.49		
$(CH_3CH_2)_3N$	2.326 ± 0.004	2.356 ± 0.002	2.341 ± 0.003
	4.29 ± 0.03	n.a.	n.a.
		-6.79 ± 0.02	-9.37 ± 0.02
	S = 2.32	S = 2.12	S = 2.17

DISCUSSION

Several interesting features can be noted for the models mentioned above. With the primary monoamines the model containing the species $[AgL_2OH]$ systematically seems to have the best fit. The addition of this species alters the other stability constants only by between 0.01 and 0.05 log units. At first glance, no trends in the formation constants of the mixed hydroxo ligand complexes could be observed. The association constant for the equilibrium:

$$AgL_2 + OH^- \rightleftharpoons AgL_2OH$$

can be calculated from these values. The constants are, passing from ammonia to butylamine, respectively, 2.44 ± 0.08, 1.67 ± 0.05, 2.68 ± 0.01, 2.04 ± 0.03, and 2.54 ± 0.02. Hydrolysis of the AgL_2 complex for most primary monoamines is greater than the hydrolysis of the silver ion itself. A parallel might be drawn with mononuclear complex formation where $K_1 < K_2$, *i.e.*, a monocoordinated complex seems more 'reactive' than a hydrated Ag(I) ion. One might wonder why the $[AgL_2OH]$ species is preferred above [AgLOH], the latter having the usual coordination number 2. The only mixed hydroxo ligand complex Yperman *et al.*[10–11] and Ohtaki *et al.*[12–13] found for their aliphatic polyamines was [AgLOH]. This should not be seen as a contradiction because L in those cases is a bidentate. The hydrolysis of the predominant basic species could explain why $[AgL_2OH]$ is formed with the monoamines. For the polyamines[10–13] the predominant species is $[Ag_2L_2]$ instead of $[AgL_2]$ so that the hydrolysis would result in two [AgLOH] species.

The inclusion of mixed hydroxo ligand species with the secondary and tertiary monoamines do not improve the fit significantly and is more often rejected than accepted as a model. It is not yet clear why these mixed hydroxo ligand complexes are mainly found with the primary monoamines. A contributing factor will certainly be the C_{Ag}/C_L ratio. High C_{Ag}/C_L ratios cannot be obtained with the secondary and tertiary monoamines due to Ag_2O precipitation. As can be seen from Figures 2a and 2b, the lower the C_{Ag}/C_L ratio the less the F_1 Leden function is curled. This might

Table 4 Comparison of the stability constants obtained in this work (1 N KNO_3) with literature values.

AMINE	$\log(K_1)$	$\log(K_2)$	$\log(K_1/K_2)$	Literature $\log(K_1)$; $\log(K_2)$
NH_3	3.37	3.88	−0.52	3.19; 3.98(1 N KNO_3)[33] 3.27; 3.97(1 N $NaNO_3$)[33] 3.31; 3.90 (1 N KNO_3)[6] 3.37; 3.78 (1 N NH_4NO_3)[6]
CH_3NH_2	3.11	3.70	−0.59	3.15; 3.53(0.5 m $LHNO_3$)[5] 3.06; 3.72(0.1 M $LHNO_3$)[32] 3.07; 3.82(I −>0)[34]
$CH_3CH_2NH_2$	3.49	4.00	−0.51	3.37; 3.93(0.5m KNO_3)[37] 3.44; 3.90 (0.1 M $LHNO_3$)[32] 3.46; 3.90(I −>0)[34]
$CH_3CH_2CH_2NH_2$	3.46	3.97	−0.51	3.45; 3.99(I −>0)[34]
$CH_3CH_2CH_2CH_2NH_2$	3.45	4.12	−0.66	3.74; 4.36(0.5 m $LHNO_3$)[5] 3.43; 4.05 (I −>0)[34]
$(CH_3)_2NH$	2.48	2.78	−0.29	
$CH_3CH_2NHCH_3$	2.79	3.04	−0.25	
$(CH_3CH_2)_2NH$	3.11	3.32	−0.21	4.93; 2.15(2N NH_4NO_3)[35] 3.43; 4.05 (I −>0)[36]
$(CH_3)_3N$	1.70			
$(CH_3)_2NCH_2CH_3$	1.98	1.51	0.47	
$(CH_3Ch_2)_2NCH_3$	2.17	1.69	0.49	
$(CH_3CH_2)_3N$	2.33	1.96	0.36	2.6; 2.1(0.4m $LHNO_3$)[5]

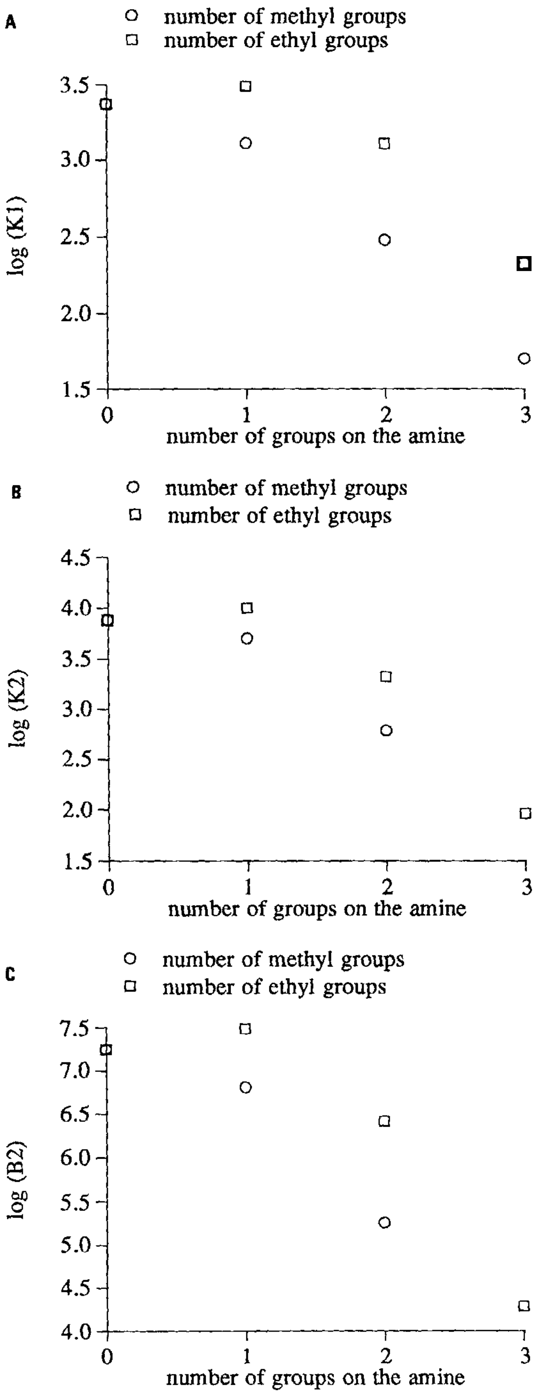

Figure 3 a-c: Individual and global formation constants *versus* number of substituents.

explain why the mixed hydroxo ligand complexes were not detected earlier using the self-medium technique with a low C_{Ag}/C_L ratio.

It is interesting to note that $[AgL_2]$ is rejected as a species with trimethylamine. $[AgL_2]$ presumably comes into competition with the more stable species [AgOH] due to the high $[OH^-]$ concentration. For triethylamine, model 1 is preferred above the other models, because these reject $[AgL_2]$.

Individual stepwise constants are reported in Table 4, together with the ratio log (K_1/K_2). Comparative references are mentioned only if log (K_1) and log (K_2) have been measured at 25°C in aqueous solution.

As already mentioned, the inversion of log (K_1/K_2) is clear upon going from secondary to the tertiary amines. Every replacement of a methyl group by an ethyl group increases the global, as well as the individual, formation constants (Figures 3a, 3b and 3c). This suggests that the extra inductive effect of an ethyl group is more important for complexation than increase in steric bulk.

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