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A potentiometric study on the complexation of Ag(I) with various N-methyl and C-methyl substituted ethylenediamines in 1 M NO_3^-

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Abstract

The complexation of Ag(I) with five different N-methyl substituted, two C-methyl substituted ethylenediamines and ethylenediamine itself is studied using potentiometric pH and pAg measurements in 1 M KNO_3 at 25.0 °C. Mononuclear complexes, polynuclear complexes and their protonated forms are detected and the respective stability constants are tabulated. The stability constant of a given species generally decreases as the methylation increases on the terminal amino groups probably due to an increased steric hindrance. The number of species also decreases as the methylation increases. The stability constants of the ethylenediamines are also compared with previously determined stability constants of Ag(I)–propylenediamine complexes and some relationships are identified.

Keywords: Potentiometric titration; Stability constants; Silver complexes; Diamine complexes

1. Introduction

The characteristic coordination number of Ag(I) with an amino group is 2, resulting in a linear complex [1]. However, the situation is more intricate for the complexation of the aliphatic diamines with this metal ion. Ethylenediamine (EN) [2–5] and 1,3-propylenediamine (TN) [5–7], for example, are known to form polynuclear and protonated species; the cyclic dimeric species Ag_2L_2 probably being the most stable complex. According to Bjerrum and Bang [8] polynuclear species might be formed through dimerization of AgL. If the metal concentration is high enough, polymerization could even pass the dimeric stage. Because X-ray examination of the solid $AgENClO_4$ shows that the complex forms infinite chains with a bridging ethylenediamine between the silver atoms [9], some authors [10] doubt the existence of the cyclic structure Ag_2L_2 and think that only linear complexes are formed in solution. Paoletti [11] surveyed the thermodynamic data available in the literature up to 1982 on the complexation of several metal ions with ethylenediamine and showed that in the case of Ag(I) there is a general acceptance of the species AgLH, AgL_2 and Ag_2L_2. He could not, however, draw any definitive conclusions on the species AgL, AgL_2H_2 and Ag_2L.

To our knowledge there are only a few formation constants available in the literature on the complexation of Ag(I) with the N-methylethylene derivatives [12] in aqueous solution. With respect to the C-methylethylene derivatives, Ohtaki and Ito [13] published some indicative values for the formation constants of Ag(I) with 1,2-propylenediamine in 3 M $LiClO_4$.

In this work, the complexation of the following ethylenediamine derivatives with Ag(I) are investigated in 1 M KNO_3: ethylenediamine (EN), *N*-methylethylenediamine (MEN), *N,N'*-dimethylethylenediamine (SDIMEN), *N,N*-dimethylethylenediamine (ADIMEN), *N,N,N'*-trimethylethylenediamine (TRIMEN), *N,N,N',N'*-tetramethylethylenediamine (TETMEN), 1,2-diaminopropane (PN) and 1,2-diamino-2-methylpropane (MPN). The shorthand notation of the name of the ligand is given between brackets. The abbreviations used for the propylenediamines (= trimethylenediamines) are explained in a previous paper,

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see Ref. [22], and are analogous with the ethylenediamines.

The complexation of the N-methyl derivatives with Ag(I) are studied using two different potentiometric approaches: 'dilution technique' [14–16] and the standard 'ratio technique'.

2. Experimental

2.1. Reagents

$AgNO_3$ (Merck p.a.), KNO_3 (Merck 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 an N_2 atmosphere with freshly boiled doubly distilled, deionized water and were kept under a CO_2 free atmosphere in a polyethylene bottle and used within two weeks of preparation. The ionic strength of all solutions was kept constant with KNO_3 at 1 M NO_3^-.

The following diamines were purchased in the amine form: ethylenediamine (Aldrich Chem. 99%), *N*-methylethylenediamine (Aldrich Chem. 99%), *N,N'*-dimethylethylenediamine (Aldrich Chem. 99%), *N,N*-dimethylethylenediamine (Janssens Chem. 99%), *N,N,N'*-trimethylethylenediamine (Aldrich Chem. 97%), *N,N,N',N'*-tetramethylethylenediamine (Janssens Chem. 99%). 1,2-Diaminopropane (Janssens Chem. 99%) and 1,2-diamino-2-methylpropane (Janssens Chem. 99%) were neutralized with 2 equiv. HNO_3. The corresponding dinitrate salts were purified by repeated crystallization in EtOH and dry diethyl ether and dried on P_4O_{10} in a vacuum desiccator until colorless white crystals were obtained.

2.2. Measurements

Because a large diversity of complexes is expected, it is desirable that the free ligand concentration be calculable without making any assumptions about the stoichiometric composition of the complexes formed. The dilution technique uses pH and pM measurements to calculate the free ligand concentration and the complexity sum. This technique was developed earlier [14–16] and has recently been fully automated [17]. The titration curves are recorded for the C_{Ag}/C_L ratio = 1/2 as this seems to be the most promising ratio. An idea of the composition of the complexes in solution can be obtained by calculating the average stoichiometric coefficients: $\bar{p}$ (average bound metal ions per complex), $\bar{q}$ (average bound ligands per complex) and $\bar{r}$ (average bound protons per complex) using the proper equations mentioned in Ref. [14]. Values of the formation constants can then be calculated using the linear regression program STACAL3. STACAL3 calculates the stability constants of all possible combinations of species for a given set of species. No initial values are needed to calculate the formation constants. Work is still being done on the automated set-up to minimize the occurrence of systematic errors during complexation and calculation. Therefore the values obtained from this technique remain at the moment estimates. The possibility of an unbiased starting model makes the technique even at this moment worthwhile. Nevertheless, for the system Ag(I)–MEN [17], very good results were obtained with the most updated set-up.

In a second series of experiments the standard ratio technique is used measuring pH and pAg data for each titration point investigating the C_{Ag}/C_L ratios from 2/1 to 1/8. Higher C_{Ag}/C_L were not possible due to the occurrence of Ag_2O very early during titration. The models obtained from the dilution technique with its estimates of formation constants were used as a starting model. The model was then further refined using the non-linear least-squares program SUPERQUAD [18–21].

Experimental details of the ratio technique [22], the dilution technique [17], the experimental set-ups used and calibration of the glass electrode, the Ag/Ag_2S electrode and the automated burettes are described in more detail in previous papers [23,24]. The acidity constants of the diamines under investigation have been determined previously [25]. The models are tested using the weighted option in SUPERQUAD ($\sigma_{E\ \mathrm{glass}} = 0.2$ mV, $\sigma_{E\ \mathrm{Ag/Ag_2S}} = 0.1$ mV and $\sigma_V = 0.002$ ml). As possible complex species the following are considered: AgL, AgLH, AgL_2, AgL_2H, AgL_2H_2, Ag_2L, Ag_2L_2, Ag_2L_2H, Ag_2L_3, AgLOH and AgL_2OH.

The model-selection-criteria are discussed in a previous article [22]. The acidity constants, the pK_w, the mass balances and the electrode parameters are not included in the list of refineable parameters. All calculations were performed in double precision. The drawings were made using the Disspla® drawing package.

3. Results

The formation reaction between a metal ion M, a proton H and a ligand L is given by Eq. (1)

$$pM + qL + rH \rightleftharpoons M_pL_qH_r \qquad \beta_{pqr} = \frac{[M_pL_qH_r]}{[M]^p[L]^q[H]^r} \qquad (1)$$

β_{pqr} being the formation constant of the complex $M_pL_qH_r$. For $r < 0$ hydroxo complexes and $r > o$ protonated complexes are formed. β_{011} and β_{012} refer to the equilibrium of the ligand with its two dissociable protons and $\beta_{00\text{-}1}$ is the autodissociation constant of water with 1 M KNO_3 (= 13.775 ± 0.005) [25].

A compilation of the formation constants obtained from the dilution method is shown in Table 1, together

Table 1

A list of the best models of the N-methyl substituted ethylenediamines with Ag(I) obtained from the dilution technique calculated with STACAL3 using unit weights. The formation constants (in log units), the standard deviations (between brackets) and maximum % species presence over the total complexation area of the individual species are shown

Species	En	%	MEN	%	ADIMEN	%	SDIMEN	%	TRIMEN	%	TETMEN	%
AgL					3.1(3)	11	3.4(1)	21	3.24(2)	34	2.75(7)	20
AgL_2	8.15(5)	27	7.30(3)	27	7.21(4)	53	6.80(3)	27	6.39(3)	29	6.03(4)	35
AgLH	12.8(1)	22	12.68(7)	25								
AgL_2H_2	25.83(7)	18	25.48(7)	16	24.46(4)	18	25.24(5)	15	23.7(2)	4	23.0(2)	7
AgL_2H	18.18(3)	27	16.83(8)	8	16.38(1)	28	16.67(4)	19	15.0(3)	6	14.7(1)	11
Ag_2L_2	13.69(6)	78	12.05(1)	79	10.15(2)	18	10.62(1)	46				
Ag_2L_2H												
Ag_2L_3					13.2(1)	16						
χ^2_{red}	2.22×10^{-8}		6.79×10^{-9}		6.30×10^{-9}		4.21×10^{-9}		3.08×10^{-9}		5.40×10^{-9}	
R_{mul}	0.983		0.991		0.992		0.993		0.992		0.992	
R_{fac}	0.120		0.0856		0.085		0.073		0.088		0.110	

with three indicators for the goodness-of-fit: the reduced chi-squared χ^2_{red}, the multiple correlation coefficient R_{mul} and the crystallographic R factor as discussed previously [17]. For these cases, the model and the values are used as estimates for further modeling with the ratio technique. A typical data set obtained from the dilution technique (e.g. ADIMEN with Ag(I)) is shown in Fig. 1(a) (pH values) and Fig. 1(b) (η values $= \log (C_{Ag}/[Ag^+])$). A plot of the average stoichiometric coefficients $\bar{p}$, $\bar{q}$ and $\bar{r}$ of Ag(I) of this ligand in a 1/2 ratio with Ag(I) versus pH is shown for the total concentrations of silver $C_{Ag}=0.001825$ M and of ligand $C_L=0.003634$ M (Fig. 2(a)). From these curves one can see that there is evidence for the formation of AgL_2, AgL_2H and AgL_2H_2. Similar curves can be derived for the other N-methyl substituted diamines but the pH area where accurate values can be calculated is strongly dependent on the amount of complexated Ag(I). It was shown in a previous article [17] that the relative complexation function η should be at least 0.2 before accurate values for the free ligand concentration and the complexity sum can be obtained. Experimentally, it soon became clear that as the methylation increased, the amount of complexated Ag(I) decreased so that accurate values of the average stoichiometric coefficients of, for example, TETMEN (Fig. 2(b)) are only available in a relatively small pH domain.

A list of the formation constants of the best models obtained from the ratio method and S values (goodness-of-fit values from SUPERQUAD [18–20]) are shown in Tables 2 and 5. As an example, half of the experimental points obtained from the titrations of ADIMEN with Ag(I) in the various ratios is fitted with the obtained constants from Table 2 and is shown in Fig. 3(a) (pH measurements) and (b) (η values).

4. Discussion

We define the following equilibria and their constants to make the further discussion more clear [15,16].

$$AgL + L \rightleftharpoons AgL_2 \qquad K_2 = \beta_{120}/\beta_{110} \tag{2}$$

$$Ag + LH \rightleftharpoons AgLH \qquad K_{111} = \beta_{111}/\beta_{011} \tag{3}$$

$$AgLH + LH \rightleftharpoons AgL_2H_2 \qquad K_{122} = \beta_{122}/(\beta_{111}.\beta_{011}) \tag{4}$$

$$Ag + 2LH \rightleftharpoons AgL_2H_2 \qquad K'_{122} = \beta_{122}/\beta^2_{011} \tag{5}$$

$$2AgL \rightleftharpoons Ag_2L_2 \qquad K_D = \beta_{220}/\beta^2_{110} \tag{6}$$

The charges are omitted for clarity. The stability constants corresponding to the reactions are presented in Table 3 and are in log units.

4.1. *The N-methyl substituted ethylenediamines*

4.1.1. *General*

Generally speaking, more species seem to occur with the ethylenediamines than with the propylenediamines [22].

The constants β_{120}, β_{220}, β_{110}, K_{111} and K_{122} referring to the species AgL_2, Ag_2L_2, AgL, AgLH, AgL_2H_2 all show the same decreasing tendency as the number of methyl groups increases on the terminal amino functions, completely analogous to the propylenediamines [22]. The magnitude of the formation constants or individual constants of the N-methyl substituted ethylenediamines are generally smaller than the propylene analogues. For instance, K_{111} and K_{122} are systematically between 0.4 and 0.6 log units smaller.

4.1.2. *The mononuclear protonated complexes: AgLH and $Ag(LH)_2$*

As with the propylenediamines, these species can be considered as aliphatic monoamine complexes of the type AgL′ and AgL_2' where LH^+ reacts as a mono-

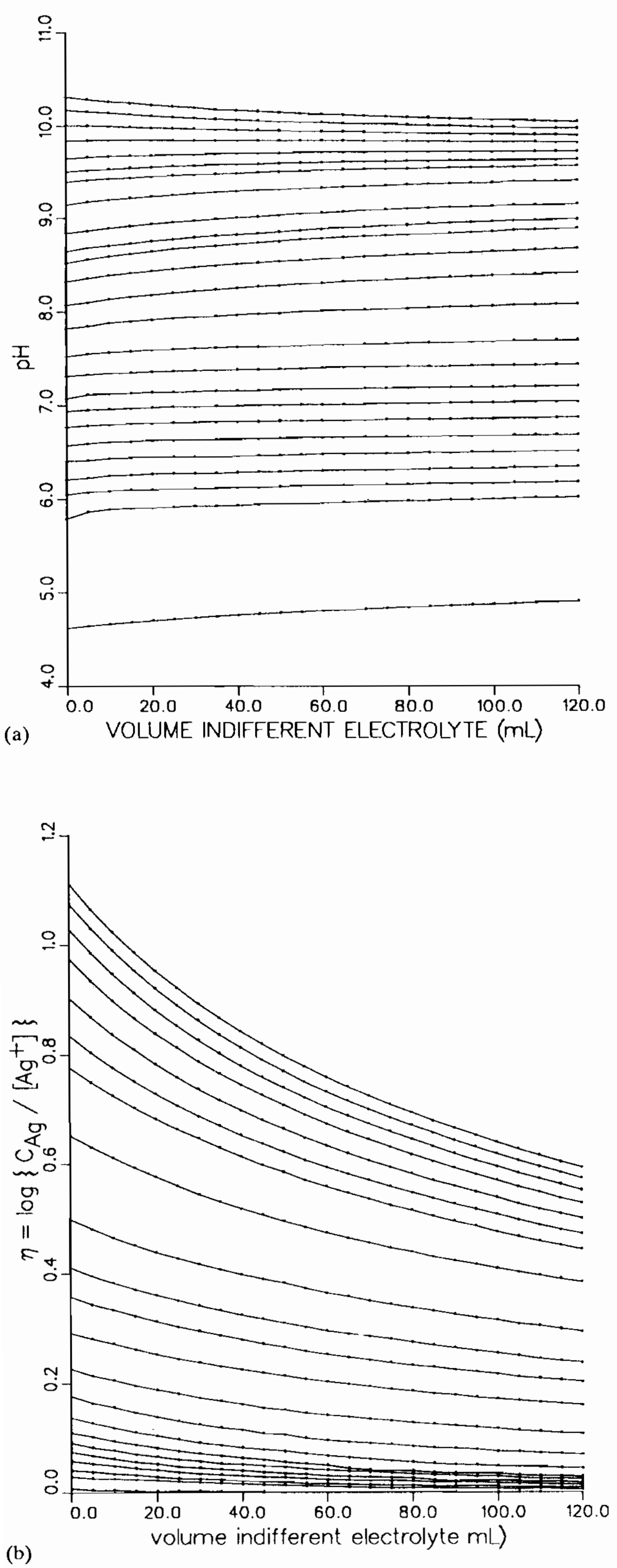

Fig. 1. (a) pH data of ADIMEN with Ag(I) from the dilution method vs. volume of added indifferent electrolyte. $C_{Ag}=0.1004$ mmol, $C_L=0.1999$ mmol, C_H varies from 0.41976 to 0.000 mmol. (b) η data of ADIMEN with Ag(I) from the dilution method (mass balances same as mentioned in (a).

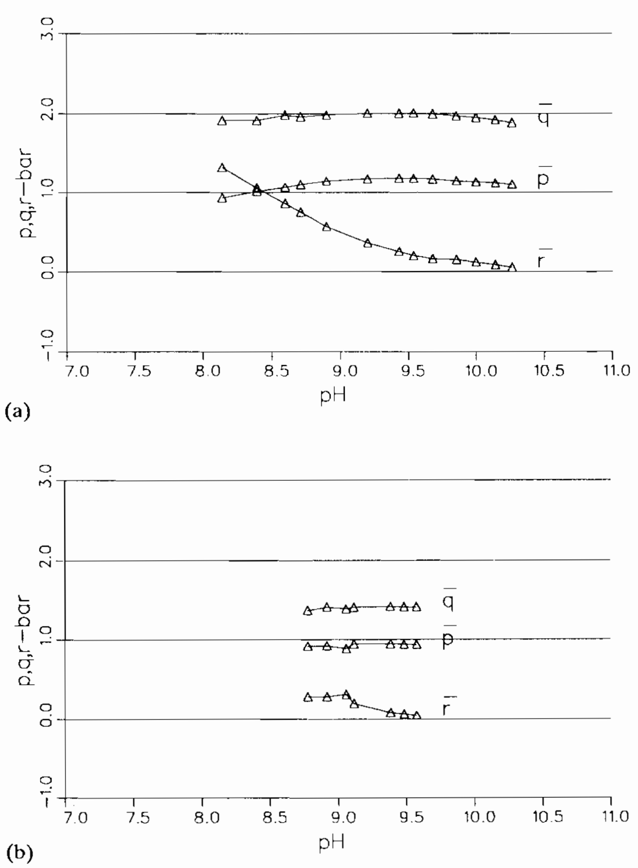

Fig. 2. (a) Average stoichiometric coefficients $\bar{p}$, $\bar{q}$ and $\bar{r}$ of ADIMEN vs. pH. (△) $C_{Ag}=0.001825$ M, $C_L=0.003634$ M. (b) Average stoichiometric coefficients $\bar{p}$, $\bar{q}$ and $\bar{r}$ of TETMEN vs. pH. (△) $C_{Ag}=0.001820$ M, $C_L=0.003638$ M.

dendate ligand L′. Because all N-methyl substituted ethylenediamines form the AgLH complex, its stability constant gives us a comparative picture of the average availability of a first N atom towards complexation with Ag(I). It is more appropriate to compare the association constant of Eq. (3), K_{111}, instead of β_{111}, as the influence of the first dissociable proton has been subtracted from the stability constant of β_{111}. In Fig. 4, the association constants of Eq. (3) have been plotted versus the number of substituted methyl groups. Due to an expected extra tautomeric reaction of the asymmetric diamines, we divided the data into two groups: values for the symmetrical and values for the asymmetrical ligands. The distinction was maintained for the propylenediamines as well as for the ethylenediamines. From the symmetrical values it is quite clear that values for primary bonded complexes (EN) are larger than secondary (SDIMEN) and both are larger than tertiary complexes. Furthermore the curve drawn for the asymmetric values crosses the symmetric curve between 2 and 3 methyl groups. This can be explained by the replacement of a primary function by a secondary function in the asymmetric ligands, yielding a sharp decrease in the stability of the formed complexes.

Table 2
The formation constants (in log units), the standard deviations (between brackets) and maximum % species presence of N-methyl substituted ethylenediamines with Ag(I) using the weighted option in SUPERQUAD

Species	EN	%	MEN	%	ADIMEN	%	SDIMEN	%	TRIMEN	%	TETMEN	%
AgL					3.74(2)	20	3.49(3)	27	3.22(*)	40	2.97(*)	46
AgL_2	7.67(*)	45	7.26(*)	71	7.15(*)	89	6.53(*)	59	6.14(*)	66	5.48(*)	46
AgLH	12.63(*)	24	12.60(*)	28	11.78(*)	20	12.09(*)	17	11.07(*)	5	10.25(1)	3
AgL_2H_2	25.93(*)	16	25.28(*)	21	23.57(2)	7						
AgL_2H	16.59(5)	4	16.74(*)	20	15.92(1)	25	15.69(7)	7				
Ag_2L_2	13.41(*)	93	11.99(*)	84	9.74(3)	17	10.52(1)	56	8.29(5)	5		
Ag_2L_2H	20.20(2)	4	19.42(2)	5								
Ag_2L_3					13.09(3)	12						
S statistic	2.88		3.15		3.05		2.50		3.46		2.82	
No. titration points	663		731		722		757		778		730	
No. data points	1326		1462		1444		1514		1556		1460	

Asterisk indicates less than 0.01.

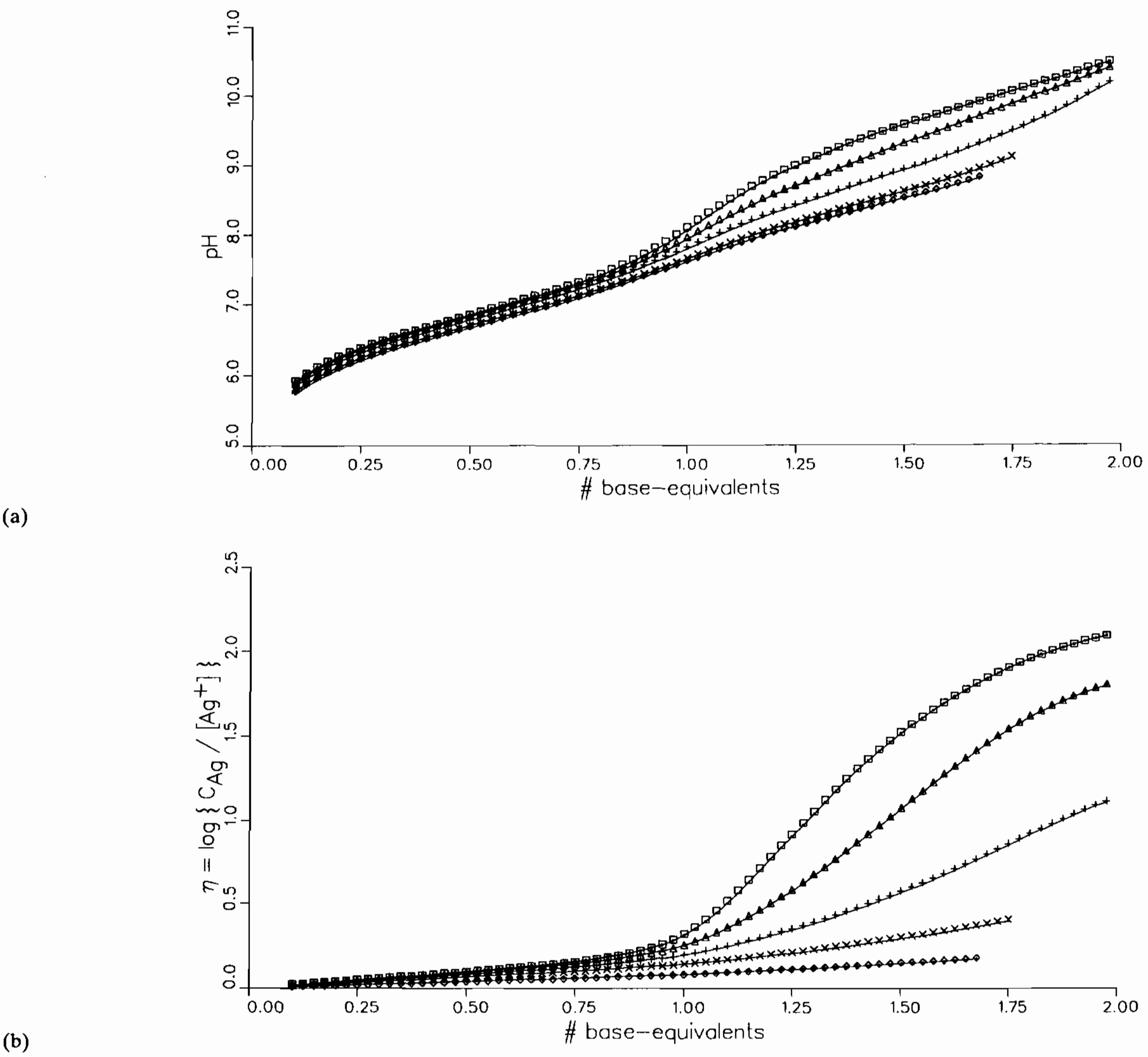

Fig. 3. (a) pH data from the complexation of ADIMEN with Ag(I) vs. the number of base equivalents using ratios 1/8 (□), 1/4 (△), 1/2 (+), 1/1 (×), 2/1 (◇). (b) Relative complexation function η from the complexation of ADIMEN with Ag(I) vs. the number of base equivalents using ratios as given in (a). The full line is the fitted curve using the formation constants from Table 2.

Table 3
Stability constants corresponding to the reactions (2)–(6)

	EN	MEN	ADIMEN	SDIMEN	TRIMEN	TETMEN	PN	MPN
K_2			3.68	3.04	2.92	2.51		
K_{111}	2.46	2.30	1.93	1.78	1.15	0.81	2.47	2.27
K_{122}	2.59	2.38	1.94				2.47	2.25
K'_{122}	5.05	4.68	3.87				4.94	4.52
K_D			2.80	3.54	1.85			

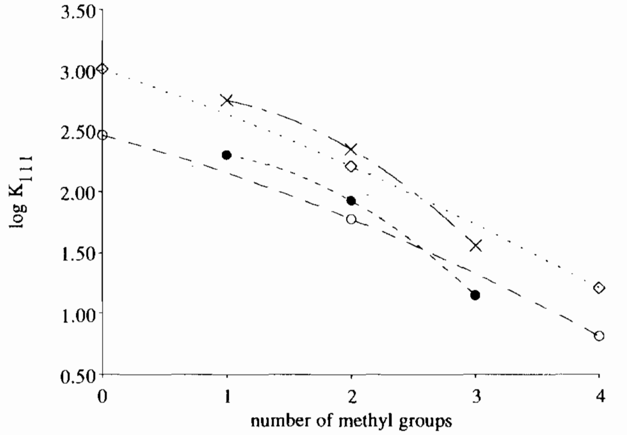

Fig. 4. Log K_{111} vs. the number of methyl substituted groups on the terminal amino groups on the ethylene and propylene backbone. –○– symmetric ethylenediamines, --●-- asymmetric ethylenediamines, ···◇··· symmetric propylenediamines, –×– asymmetric propylenediamines.

The lower values for K_{111} and K_{122} for the ethylenediamines in comparison with the propylenediamines can be understood by the increased destabilization of the species through the $Ag^+ \leftrightarrow LH^+$ repulsion due to the shorter length of the ethylene backbone in comparison with a propylene backbone.

4.1.3. The non-protonated mononuclear and polynuclear complexes AgL, AgL$_2$ and Ag$_2$L$_2$

A similar systematic decrease of the stability constants with increasing methyl substitution as mentioned in the discussion of the AgLH complexes is also visible for the formation constants of the species AgL, AgL_2 and Ag_2L_2.

The AgL complex was not detected with EN, MEN, PN and MPN. It is remarkable that this complex becomes well defined as soon as the Ag_2L_2 species loses its predominance, indicated by a lower maximum % presence (Table 2). The large formation constant of this dimeric species might be the reason for the undetectability of the AgL complex. The dimerization constant K_D could provide some interesting information about the simultaneous existence of these species. The problem with this constant K_D is the fact that β_{110} is needed, to calculate it. However, when log β_{120} values are plotted versus log β_{110} values a roughly linear relationship (Fig. 5) between the constants seems to exist given by Eq. (7) making an estimation of K_D possible.

$$\log \beta_{110} = 0.4\ \beta_{120} + 0.8 \qquad (R = 0.95) \qquad (7)$$

From Table 4, it is clear that the estimated values for K_D are rather large. This means the equilibria of reaction (6) are shifted towards the formation of the dimeric Ag_2L_2. It confirms the statement that it is almost impossible to determine the AgL complex in the presence of Ag_2L_2. Furthermore the magnitude of the estimated formation constant of AgL for EN and MEN indicate that it is more likely a linear species than a chelate.

When the formation constants of Ag_2L_2 are plotted versus the number of substituted N-methyl groups one can again observe that the formation constants of Ag_2L_2

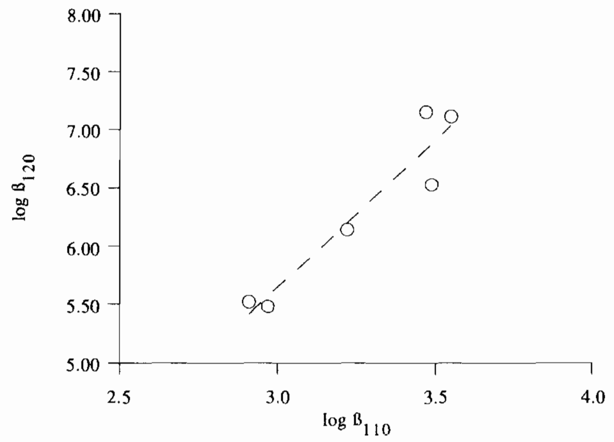

Fig. 5. Log β_{120} vs. log β_{110}.

Table 4
Values for the dimerization constant K_D and β_{110}. The estimated values based on extrapolation of Eq. (7) for β_{110} and K_D are given between square brackets

	Log β_{110}	Log K_D		Log β_{110}	Log K_D
EN	[3.8]	[5.7]	TN	[3.9]	[7.0]
MEN	[3.6]	[4.7]	MTN	[3.7]	[6.1]
ADIMEN	3.47	2.80	ADIMTN	3.55	3.92
SDIMEN	3.49	3.54	SDIMTN	[3.1]	[5.8]
TRIMEN	2.97	1.85	TRIMTN	2.91	3.79

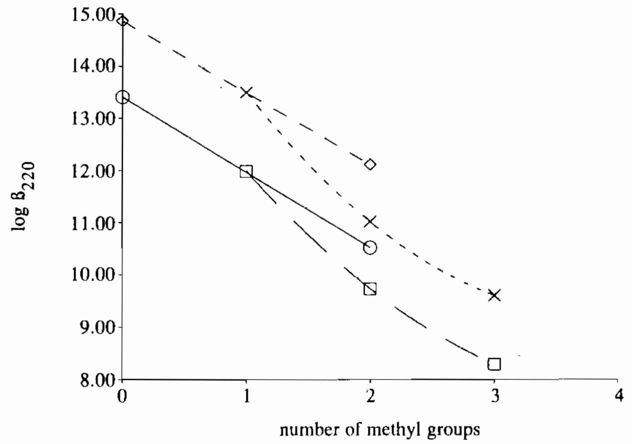

Fig. 6. Log β_{220} vs. the number of methyl substituted groups on the terminal amino groups on the ethylene and propylene backbone. –○– symmetric ethylenediamines, –□– asymmetric ethylenediamines, –◇– symmetric propylenediamines, –×– asymmetric propylenediamines.

of the propylenediamines are larger than the ethylenediamines (Fig. 6). The parallel tendencies of the curves fitted through the values of Ag_2L_2 from the asymmetric ethylene- and propylenediamines and of the symmetric ethylene- and propylenediamines are quite conspicuous. A closer inspection reveals that the results can be divided into two groups: a first series containing no tertiary amino function which practically forms a linear relationship with the number of methyl groups and a second series of ligands which do contain a tertiary amino function.

If one assumes that Ag_2L_2 of TN and EN have a cyclic structure, then according to Cassol and Di Bernardo [6,7] TN would be more stable than EN because a twelve-membered ring resembles more closely the linear N–Ag–N configuration than a ten-membered ring with EN. Another explanation might be that the $Ag^+ \leftrightarrow Ag^+$ repulsion is less in a twelve-membered ring than in a ten-membered ring through the slightly larger distance between the two metal ions. This idea would also explain the higher stability of the propylenediamines in comparison with the ethylenediamines in linear polynuclear structures.

The division into two groups of the stability constants of Ag_2L_2 can perhaps be correlated with the fact that no measurable formation of Ag_2L_2 seems to take place with TETMEN and TETMTN. It is evidently impossible to form the species when two tertiary functions are simultaneously present on the ligand. Even the presence of one tertiary function on the ligand makes complex formation difficult as indicated by the fact that the stability constants of ADIMEN are less than SDIMEN and ADIMTN are less than SDIMTN.

4.1.4. The protonated species AgL_2H and Ag_2L_2H

The species AgL_2H and Ag_2L_2H occur more often in comparison with the propylenediamines but never become a predominant species. It is suggested that these species be considered as intermediates between AgLH and AgL_2 and between AgL_2H_2 and Ag_2L_2.

Table 5
A survey of the formation constants (in log units), the standard deviations (between brackets) and maximum % species presence of C-methyl substituted ethylenediamines with Ag(I) using the weighted option in SUPERQUAD

Species	PN	%	MPN	%
AgL_2	7.92(*)	75	8.04(*)	89
AgLH	12.55(*)	29	12.30(*)	27
AgL_2H_2	25.10(*)	21	24.58(1)	15
AgL_2H	16.87(2)	13	16.96(*)	27
Ag_2L_2	13.29(*)	94	12.70(*)	88
Ag_2L_2H	20.07(2)	6	19.67(1)	7
Ag_2L_3			15.20(2)	12
S statistic	3.61		3.09	
No. titration points	763		764	
No. data points	1526		1528	

Asterisk indicates less than 0.01.

4.2. The C-methyl substituted ethylenediamines

Methylation on the ethylene backbone does not have the same effect towards complexation of Ag(I) as methylation on the terminal amino groups as could be expected. This can be seen by the increasing stability of AgL_2 as the methylation increases (Table 5). In fact, the magnitude of the other formation constants suggest that PN and MPN react like ethylenediamine. The methyl groups on the ethylene backbone might be able to decrease the N↔N repulsion on the ethylene backbone through a space-filling effect [26,27]. This would explain the higher stability of AgL_2. The slightly lower values for the other species of MPN in comparison with PN and EN could be explained as a combination of this effect with an increase in steric hindrance.

The species Ag_2L_3 was found only with ADIMEN and MPN.

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