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Effects of Hydrocarbon Chain Length on the Thermodynamics of Formation of Bis(*n*-alkylamino)silver(I) Complex Ions

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Equilibrium constants, enthalpy changes, and entropy changes have been measured for the stepwise formation of bis(*n*-alkylamino)silver(I) complex ions at 25° in dilute aqueous solution. The *n*-alkylamines studied were methylamine, ethylamine, *n*-propylamine, *n*-butylamine, *n*-pentylamine, and *n*-hexylamine. The equilibrium constants were determined from pH measurements and the enthalpy changes were determined from calorimetric measurements. The same general pattern of variations in $\Delta G°$, $\Delta H°$, and $\Delta S°$ with alkyl chain length is found for the formation of the bis(*n*-alkylamino)silver(I) complexes as was previously found for the protonation of *n*-alkylamines.

Introduction

It has previously been noted[1-5] that the length of an alkyl group attached to some ionizing head group affects the thermodynamics of ionization of the head group. Some reactions which have been shown to exhibit this effect are proton ionization from protonated amines, protonated amino acids, aliphatic carboxylic acids, and *n*-alkylarsonic acids. The $\Delta G°$, $\Delta H°$, and $\Delta S°$ values for all of these reactions follow the same general pattern with increasing hydrocarbon chain length; *i.e.*, the $\Delta H°$ and $\Delta S°$ values become more positive for isoelectric reactions (*e.g.*, $HA^+ = A + H^+$) and become more negative for ionogenic reactions (*e.g.*, $HA = A^- + H^+$) while the $\Delta G°$ values remain relatively unaffected for both types of reactions. The explanations that have been advanced for this general pattern of compensating changes in $\Delta H°$ and $\Delta S°$ with changing hydrocarbon chain length are (a) a region of low dielectric constant (*e.g.*, an alkyl group) embedded in a medium of high dielectric constant (*e.g.*, H_2O solvent) would be repelled by a charged group[3] and (b) the charged head group generates a structured solvation shell which restricts the rotational freedom of the alkyl group. Both of these effects would result in a decrease in the rotational enthalpy and entropy of the alkyl group in the charged molecule relative to the neutral molecule.[1]

The purpose of this study was (a) to determine the $\Delta G°$, $\Delta H°$, and $\Delta S°$ values for the formation of the *n*-alkylamino complexes of Ag^+ in aqueous solution and (b) to compare the effect of increasing the hydrocarbon chain length on the $\Delta G°$, $\Delta H°$, and $\Delta S°$ values for formation of the Ag^+ complexes with the effect on the $\Delta G°$, $\Delta H°$, and $\Delta S°$ values for ionization of the protonated *n*-alkylamines.[4] The effect of increasing the chain length on the formation of the Ag^+ complexes might be expected to be different from the effect on the ionization of the proton since the silver ion is larger in size,[6] has a coordination number of 2 instead of 1,[6] and is a type B cation as opposed to the proton which is a type A cation.[7] The reaction of silver ion with amine to give the mono(amino)silver(I) ion is analogous to the reaction for the protonation of amine except for the change of the cation. The addition of the second amino ligand to the mono(amino)silver(I) ion to yield the bis(amino)silver(I) ion was expected to supply some additional information on the underlying causes of the trends observed with changing hydrocarbon chain length.

Experimental Section

Materials.—Methylamine, ethylamine, *n*-propylamine, *n*-butylamine, *n*-pentylamine, and *n*-hexylamine were all Eastman White Label grade and were used without further purification since gas chromatography gave no evidence of impurities other than water in the amines. The silver perchlorate ($AgClO_4 \cdot 4H_2O$) was obtained from Alfa Inorganics and was the best available grade. The pH of the silver perchlorate stock solution (~0.12 *M*) was measured and found to be 5.4, showing that the amount of acid contained in the $AgClO_4 \cdot 4H_2O$ was negligible. The perchloric acid was Baker Analyzed reagent grade 70% solution. All solutions were prepared using freshly boiled, doubly distilled water and were kept under a nitrogen atmosphere. Also, all Ag^+-containing solutions were stored in brown bottles.

Equipment.—A Beckman Research pH meter, Model 1019, was used for the pH measurements. The pH meter was equipped with a Beckman E-3 glass electrode (0–14 pH range) and a Beckman Ag–AgCl reference electrode with a ceramic junction. The buffer solution used for the standardization of the pH meter was a pH 6.862 phosphate buffer prepared according to NBS instructions (supplied with the materials) using KH_2PO_4 (NBS Lot No. 186-I-c) and Na_2HPO_4 (NBS Lot No. 186-II-b).

The reaction vessel, which was immersed in a 25.0 ± 0.1° constant-temperature bath controlled to ±0.01°, was a 200-ml Berzelius beaker with a rubber stopper containing five holes. Two of the holes accommodated the glass and reference electrodes. Another was used for the initial addition of solutions to the reaction vessel and was covered with a cork stopper during the titration. The tip of a 5-ml buret from which the $HClO_4$ titrant was added to the reaction vessel and a capillary tube through which nitrogen could enter the reaction vessel were inserted through the remaining holes.

The calorimetric measurements were made using a Tronac Thermometric titration calorimeter, Model No. 1000A, Serial No. 106, which was modified by changing the temperature sensor from a 5- to a 100-kilohm thermistor and by the changing the complementary resistor in the bridge from 15 to 100 kilohms. The bridge was operated at 12.000 V and the resulting sensitivity was 139.5 mV/deg which was determined to be constant over a 1° range. All experiments were carried out at 25.0 ± 0.1°. A typical run consisted of 30 data points taken in the fore period, 56 data points taken in the main period, and 30 data points taken in the after period at time intervals of 20 sec. (The periods and regions of a thermogram for a typical titration of a Ag^+–amine

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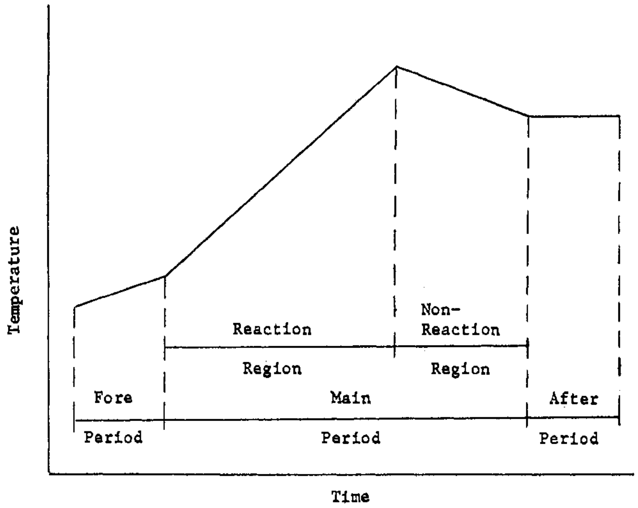

Figure 1.—Periods and regions of a thermogram.

solution with $HClO_4$ solution are shown in Figure 1.) The two different 100-ml reaction vessels which were used had thermal equivalents of 0.7405 ± 0.0014 and 0.7346 ± 0.0017 cal/mV (± values are standard deviations of the mean) when containing 99.91 ml of H_2O. The thermal equivalent was assumed to be the same when a dilute solution of amine or a silver–amine solution was substituted for H_2O.

Standardization of Solutions.—The perchloric acid titrants used in the pK and $\Delta H°$ determinations were standardized against Fisher primary standard grade THAM using a visual indicator (pH 6–7). The silver perchlorate stock solutions were each standardized by both the Volhard and the Mohr methods using $AgNO_3$ and NaCl, respectively, as primary standards. Because of the volatility of the amines, the amine stock solutions could not be standardized; therefore, the amount of amine in each sample was determined from the end point of the pH titration curve or thermogram for the titration of that sample.

pK Determinations.—Solutions of the amines (~100 ml, ~0.03 M) and the silver–amine complexes (~100 ml, ~0.03 M amine, ~0.006 M Ag^+) were titrated with a standard solution of perchloric acid (0.9908 M) in order to determine the equilibrium constants. Although all titrations were run under a nitrogen atmosphere, a continuous flow of nitrogen was not used during the titration because of the volatile nature of the amine.

It was found that the order of addition of reagents used in preparing the silver–amine solutions was very important. The order of addition to the reaction vessel was water, amine solution, and then silver perchlorate solution. If the silver ion solution was added before the amine, upon addition of the amine, a brown precipitate of hydrous silver oxide formed which was very slow to dissolve. In order to minimize any hydrolysis of Ag^+(aq) in the final solution, the ratio of amine concentration to silver ion concentration was approximately 5:1. The amine solution and silver ion solution were always added to the water in the reaction vessel with continuous stirring in order to prevent any precipitation of silver hydroxide due to high local concentrations. In the case of n-hexylamine, it was observed that a white gelatinous precipitate formed if the silver ion solution was added without stirring. This precipitate was probably bis(n-hexylamino)silver(I) perchlorate.

Chloride contamination of the Ag^+-containing solutions by the electrolyte from the Ag–AgCl reference electrode was a possible source of systematic error. The flow rate of saturated KCl solution through the ceramic frit junction of the reference electrode was approximately 0.1 ml/24 hr.[8] The concentration of chloride ion in saturated KCl solution was approximately 4.6 M[9] and the length of a titration was approximately 1 hr. Thus, a maximum of 0.02 mmol of AgCl precipitate could have been formed by the time the titration was terminated. Since a typical titration involved ~0.6 mmol of silver ion, a possible maximum error of 3.4% in the silver ion concentration would result if all of the Cl^- was precipitated. This error in the Ag^+ concentration would cause systematic errors of 0.22 and 0.05 log unit in the pβ_1 and pβ_2 values, respectively. However, the flow rate was diminished by immersing the electrode into the solution and by decreasing the amount of electrolyte in the electrode to within 2 cm of the surface of the solution. Under these conditions, no visible precipitate of AgCl could be observed after allowing the electrode to remain in a solution of Ag^+ (100 ml of 0.006 M) overnight. Therefore, it was assumed that the amount of AgCl precipitate formed was negligible. Further evidence that this assumption was valid was the fact that no significant change in pβ_1 resulted when the total Ag^+ concentration was varied.

ΔH Determinations.—The procedure used in the thermometric titration measurements was to titrate 99.91 ml of the silver–amine solution in the dewar with a 0.5139 M $HClO_4$ solution. In some cases the silver–amine solution added to the dewar already contained a known amount of $HClO_4$.

It was observed, by the appearance of a yellow color, that the silver–amine solutions showed a significant amount of decomposition after about 5 hr. The color was apparently due to a colloidal suspension of silver metal. If the solution was allowed to stand overnight, it became clear and a grayish black precipitate could be seen lying at the bottom of the vessel. Because of this decomposition, any silver–amine solutions which were more than 3 hr old were discarded. That the amount of decomposition during this 3-hr time period was negligible was indicated by the absence of any trend in the experimental data obtained in successive runs.

Calculations

Calculation of Activity Coefficients.—Equation 1[10] was used to calculate the activity coefficients, γ_i, where

$$\log \gamma_i = \frac{-(0.5095)(\mu_i)^{1/2}}{1.0 + (0.3288)(\text{DCA})(\mu_i)^{1/2}} \qquad (1)$$

DCA is the distance of closest approach and μ is the ionic strength. The value for DCA used in this study was 5 Å. It was found that changing DCA to 3 or 7 Å did not appreciably affect the calculated values of the equilibrium constants.

Calculation of Equilibrium Constants.—All equilibrium constants determined in this study were calculated from a least-squares fit of the pH titration data to the appropriate equations.[11]

Table I

pK Values for Protonated n-Alkylamines in Dilute Aqueous Solution at 25°

	pK	
Amine	This study[a]	Lit.[b]
Methylamine	10.666 ± 0.002	10.641
Ethylamine	10.636 ± 0.008	10.63
n-Propylamine	10.564 ± 0.004	10.568
n-Butylamine	10.639 ± 0.003	10.640
n-Pentylamine	10.597 ± 0.007	10.64
n-Hexylamine	10.630 ± 0.001	. . .

[a] Based on molar concentrations. [b] Since these authors selected the "best" literature values available to use in their study, only their selected value is given here: J. J. Christensen, R. M. Izatt, D. P. Wrathall, and L. D. Hansen, *J. Chem. Soc. A*, 1212 (1969).

Calculation of ΔH Values.—The method used to calculate values of the heat changes, Q, from the temperature–time data at each point in the main period of the thermogram (Figure 1) has previously been described.[12] The Q values at each point were first

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TABLE II

$\Delta G°$, $\Delta H°$, AND $T\Delta S°$ VALUES FOR FORMATION OF *n*-ALKYLAMINO COMPLEXES OF Ag^+ IN AQUEOUS SOLUTION AT ZERO IONIC STRENGTH AND 25°[a,b]

$-\Delta G_1°$	$-\Delta G_2°$	$-\Delta G_3°$	$-\Delta H_1°$	$-\Delta H_2°$	$-\Delta H_3°$	$-T\Delta S_1°$	$-T\Delta S_2°$	$-T\Delta S_3°$
			Methylamine					
4.19 ± 0.02	5.21 ± 0.02	9.40 ± 0.01	3	8	11.72 ± 0.05	−1	3	2.32 ± 0.05
4.30[c]		9.11,[c] 9.29,[d] 9.26[e]			11.5[e]			2.23[e]
			Ethylamine					
4.72 ± 0.03	5.32 ± 0.03	10.04 ± 0.03	5	7	12.51 ± 0.03	1	2	2.47 ± 0.03
		9.88,[c] 10.00,[f] 9.99[e]			13.0[e]			3.01[e]
			n-Propylamine					
4.71 ± 0.01	5.44 ± 0.02	10.15 ± 0.02	3	9	12.72 ± 0.01	−1	4	2.57 ± 0.02
		10.48 (16°)[g]						
			n-Butylamine					
4.68 ± 0.03	5.53 ± 0.03	10.20 ± 0.03	4	9	12.57 ± 0.05	−1	3	2.37 ± 0.05
4.68[c]		10.20[c]						
			n-Pentylamine					
4.87 ± 0.02	5.36 ± 0.03	10.23 ± 0.03	5	7	12.34 ± 0.02	1	2	2.11 ± 0.03
			n-Hexylamine					
4.83 ± 0.02	5.49 ± 0.02	10.31 ± 0.02	6	7	12.68 ± 0.10	1	1	2.37 ± 0.10

[a] Subscript 1 refers to reaction 2, subscript 2 to reaction 3, and subscript 3 to reaction 4. [b] All values are in kilocalories per mole. [c] J. Bjerrum, *Chem. Rev.*, 46, 381 (1950). [d] H. von Euler, *Ber.*, **36,** 2878 (1903). [e] W. S. Fyfe, *J. Chem. Soc.*, 1347 (1955). [f] G. Bodländer and W. Eberlein, *Ber.*, **36,** 3945 (1903). [g] A. Tamisier, *Bull. Soc. Chim. Fr.*, **53,** 157 (1933).

corrected for the heat of formation of water, the heat of protonation of the amine, and the heat of dilution of the titrant. Then the ΔH values were calculated from a least-squares fit of the corrected heat change data and the calculated species distribution.[11]

Values of the heats of protonation of the amines were obtained from the literature[4] except for the value for hexylamine which was obtained in this study, 13.93 ± 0.01 kcal/mol (error limit is the standard deviation of the mean). The heat of ionization of water was taken to be 13.40 kcal/mol at all ionic strengths,[13,14] and heat of dilution data for $HClO_4$ were taken from ref 15.

Complete details of all calculations, computer programs (IBM 360-40), and data are given in ref 11.

Results

The pK values determined in this study are given in Table I together with selected pK values from the literature. The values determined in this study are valid at 25°. The ionic strength, which varied from 0.005 to 0.03, had no apparent effect on the pK values. The limits of error given on the pK values are standard deviations of the means between runs. As can be seen in Table I, the agreement between values from this study and literature values is good.

The $\Delta G°$ values determined in this study for the reactions

$$Ag^+(aq) + R(aq) \longrightarrow AgR^+(aq) \qquad \Delta X_1 \qquad (2)$$

$$AgR^+(aq) + R(aq) \longrightarrow AgR_2^+(aq) \qquad \Delta X_2 \qquad (3)$$

$$Ag^+(aq) + 2R(aq) \longrightarrow AgR_2^+(aq) \qquad \Delta X_3 \qquad (4)$$

where R = *n*-alkylamine, together with $\Delta G°$ values from the literature, are given in Table II. The limits of error given for the $\Delta G°$ values are standard deviations of the mean between runs. The values calculated in this study are valid at 25° with μ, the ionic strength, varying from 0.01 to 0.036. The effect of μ on the $\Delta G°$ values for the silver–butylamine complexes was studied by varying the concentrations of silver ion and of amine, and this study indicated that the values were independent of ionic strength. The literature values are in fair agreement with those obtained in this study.

It was found by insertion of the appropriate error into the computer input data that a 1% error in the amine concentration changed $\Delta G_1°$ by 0.02 kcal/mol and $\Delta G_3°$ by 0.20 kcal/mol and a 1% error in the silver ion concentration changed $\Delta G_1°$ by 0.09 kcal/mol and $\Delta G_3°$ by 0.02 kcal/mol. Based on the precision that was obtained in standardizing the silver perchlorate solutions, it is felt that an error of 0.3% in the silver ion concentration is more indicative of the accuracy of the results obtained, *i.e.*, ±0.03 kcal/mol in $\Delta G_1°$ and ±0.007 kcal/mol in $\Delta G_3°$. In order to determine the concentration of amine in each sample the data obtained from the pH titration were treated graphically and an error of 0.2% in the amine concentration is thought to be more realistic, *i.e.*, ±0.004 kcal/mol in $\Delta G_1°$ and 0.04 kcal/mol in $\Delta G_3°$.

The $\Delta H°$ and $T\Delta S°$ values determined in this study for reactions 2–4 are also given in Table II. The standard state is defined to be an ideal 1 *M* solution. The error limits are standard deviations of the mean and represent the precision obtained between runs. The ΔH values were measured in an ionic strength range of 0.006–0.03 and were assumed to be equal to $\Delta H°$ values.

In the calculation of $\Delta H°$ values it was found that a 1% error in the total amine concentration (maximum error expected from the thermogram end point was ~1%[16]) would result in an error of 2.26 kcal/mol in $\Delta H_1°$, a 2.20-kcal/mol error in $\Delta H_2°$, and a 0.05-kcal/mol error in $\Delta H_3°$. Similarly, a 0.3% error in the silver ion concentration would result in an error of 0.29 kcal/mol in $\Delta H_1°$, a 0.28-kcal/mol error in $\Delta H_2°$, and a 0.01-kcal/mol error in $\Delta H_3°$. From the observations of the effects on the $\Delta H_1°$ and $\Delta H_2°$ values of a 1% error in amine concentration, it is apparent that the equations used to calculate $\Delta H_1°$ and $\Delta H_2°$ were ill conditioned. This results from the fact that $K_2 > K_1$, and, therefore, the calculated concentration of the mono(amino)-silver(I) ion present in the solution was very sensitive to the total amine and silver ion concentrations. Because the values of $\Delta H_1°$ and $\Delta H_2°$ given in Table

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II have very large limits of error, they may be taken only to represent the relative magnitudes of the values.

Discussion

The data in Table II show that $\Delta G_1°$, $\Delta G_2°$, and $\Delta G_3°$ are largely unaffected by the chain length except in the case of the mono(methylamino)silver(I) complex. The effect seen in $\Delta G_1°$ for the monomethylamino complex is of course seen again in the overall free energy change ($\Delta G_3°$). The $\Delta H_3°$ values increase negatively as methyl groups are substituted in the hydrocarbon chain and this increase continues through the bis(*n*-propylamino)silver(I) complex. The $\Delta H_3°$ values then decrease slightly for the *n*-butyl- and *n*-pentylamino complexes followed by an increase for the *n*-hexylamino complex. The $T\Delta S_3°$ values follow the same general pattern of variations with chain length as do the $\Delta H_3°$ values. With the exception of the anomalous $\Delta G_1°$ value for the monomethylamino complex and the decrease in $\Delta H_3°$ and $T\Delta S_3°$ for the *n*-butyl- and *n*-pentylamino complexes, the same trends in $\Delta G°$, $\Delta H°$, and $\Delta S°$ values with increasing hydrocarbon chain length have previously been observed for protonation of the *n*-alkylamines.[4]

It is interesting that the difference in the $\Delta H°$ values (between methyl and propyl) for protonation of *n*-alkylamines is $\sim$0.6 kcal/mol[4] while the difference in the $\Delta H_3°$ values (between methyl and propyl) for formation of the bis(*n*-alkylamino)silver(I) complexes is $\sim$1.0 kcal/mol. The protonation reaction involves only one ligand, whereas formation of bis(*n*-alkylamino)silver(I) complexes involves two. Therefore, assuming the difference in $\Delta H°$ for the addition of one amine ligand to be half of the difference observed for the formation of the bis(*n*-alkylamino)silver(I) complexes, it follows that the enthalpic effect on an alkyl group of the silver ion ($\sim$0.5 kcal/mol) is approximately the same as the effect of the proton ($\sim$0.6 kcal/mol).

The difference in the $T\Delta S°$ values (between methyl and propyl) for protonation of the *n*-alkylamines is $\sim$0.7 kcal/mol[4] while the difference in $T\Delta S_3°$ values is $\sim$0.3 kcal/mol. If $T\Delta S°$ for the addition of one amine ligand is again assumed to be half the difference observed for the formation of the bis-amino complexes, the entropic effect of the silver ion on an alkyl chain ($\sim$0.15 kcal/mol) is much smaller than the effect of the proton ($\sim$0.7 kcal/mol), in contrast to what was found in the case of the $\Delta H°$ values. The difference in behavior of the $\Delta H°$ and $T\Delta S°$ values results primarily from the anomalously large negative $T\Delta S_3°$ value (in comparison to $T\Delta S°$ values for protonation) for formation of the bis(methylamino)silver(I) complex ion.

The $\Delta H_3°$ and $T\Delta S_3°$ values in Table II indicate that anomalous effects are operating in the formation of the *n*-butyl- and *n*-pentylamino complexes of Ag^+ in comparison with the protonation reactions. A possible explanation for these anomalies is that there may be some hydrophobic interaction between the two ends of the hydrocarbon chains. In this regard it is disappointing that accurate stepwise $\Delta H°$ and $T\Delta S°$ values could not be obtained, since these data would probably have shown whether or not the above anomalies are the result of having two alkyl groups present in the complex.

In conclusion, the similarities in the trends in $\Delta G°$, $\Delta H°$, and $T\Delta S°$ for formation of bis(*n*-alkylamino)silver(I) complexes and protonation of *n*-alkylamines with hydrocarbon chain length suggest that the major cause of these trends is of a general electrostatic nature and not dependent on the nature of the metal ion involved.

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On the Structure of $Na_2O \cdot 4MgO \cdot 15Al_2O_3$, a Variant of β-Alumina

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A new phase has been found in the ternary system Na_2O–MgO–Al_2O_3, similar in structure to β-alumina. It is hexagonal, with a = 5.62 Å and c = 31.8 Å. Qualitative examination of some single-crystal X-ray intensities and quantitative measurement of powder intensities suggest the following structure. The space group is probably $P6_3/mmc$. The basal mirror planes are 15.9 Å apart, very loosely packed, and contain the sodium ions. Between these planes are spinel-like blocks, consisting of six layers of cubic-close-packed oxygens with Mg and Al in their interstices, in a typical spinel-like M_3O_4 alternation. The spinel blocks are spaced apart by linear Al–O–Al columns. These spacers, together with the loose packing, provide for an extraordinarily high two-dimensional sodium ion mobility. This differs from β-alumina only in that the latter has shorter blocks, containing only four oxygen layers.

Introduction

β-Alumina was originally reported by Rankin and Merwin,[1] who thought they were dealing with a crystallographic modification of pure alumina and thus adopted the designation which has persisted. It was soon recognized, however, a that a small admixture of an alkali oxide was necessary to produce this crystal

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