Chain Conformation of Aliphatic α,ω -Diamines in Aqueous Solutions

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ABSTRACT: Potentiometric titration of aliphatic α,ω -diamines such as 1,3-, 1,4-, and 1,6-diamines was carried out in aqueous solutions with and without added salt to study the effect of electrostatic interactions on the chain conformations. The ratios of first to second association constants of proton K_1/K_2 were larger than 4 indicating the effects of electrostatic interactions on the second association constant in a similar manner as α,ω -diacids. These data were analyzed by the theories of Bjerrum and Kirkwood–Westheimer, and the resulting charge distances were compared with the end-to-end distances of various chain models.

KEY WORDS: Potentiometric Titration / α,ω -Diamines / Association Constant / Chain Conformation / Charge Distance / Chain Model / Electrostatic Interaction /

In general, conformation of polymer chains in solutions is determined by “long-range” interactions between units far apart along a chain (excluded volume effects) and “short-range” interactions between neighboring units along a chain (chain stiffness).^{1,2} In polyelectrolytes, both are mainly determined by electrostatic interactions between charges, but their contributions to the chain conformation have not been fully understood yet because of long-range nature of electrostatic interactions.³ Bolaform electrolytes, in which the charges are separated from one another by a chain of atoms, are probably the simplest class of molecules suitable for examining the effects of electrostatic interactions on chain conformation. It was reported^{4,5} that the second dissociation constant of bolaform electrolytes such as α,ω -diacids is affected by the charge on the dissociated unit in another end of the molecules. Bjerrum^{4,5} quantitatively studied the ratios of first to second dissociation constants K_1/K_2 or ΔpK ($=pK_2 - pK_1$) for a homologous series of α,ω -diacids, $\text{HOOC}(\text{CH}_2)_n\text{COOH}$, in aqueous solutions without added salt in terms of charge distances by using a simple electrostatic theory, in which the dielectric constant of a medium is assumed to be equal to that of solvent, *e.g.*, water. Later, Kirkwood and Westheimer⁶ improved the theory of Bjerrum by taking account of the dielectric constant of solute molecules, *e.g.*, α,ω -diacids and obtained a better agreement with experimental data. Thus, ΔpK appears to be a useful tool for studying the conformation of bolaform electrolytes. Association constants and conformations of α,ω -bis(ammonium salt)^{7–12} were studied by conductance measurements, and conformation of bolaform electrolytes with fairly long chains was studied experimentally¹³ and theoretically.¹⁴

Physicochemical properties such as counterion activity and conductance,¹⁵ and chain stiffness¹⁶ have been studied for a series of ionenes having repeating units of $[-(\text{CH}_2)_n\text{N}^+(\text{CH}_3)_2-]$ with different n values. Thus, it is useful to study ΔpK of aliphatic α,ω -bis(tertiary amines), $(\text{CH}_3)_2\text{N}(\text{CH}_2)_n\text{N}(\text{CH}_3)_2$ with $n = 3, 4$, and 6

representing the composition units in the corresponding ionenes to clarify the effects of electrostatic interactions on the chain conformation. In this work, we measured potentiometric titration of these amines in aqueous solutions with and without added salt and evaluated their charge distances by the theories of Bjerrum and Kirkwood–Westheimer to compare with the end-to-end distances calculated for free-rotational, interdependent rotational and all-*trans* chains, and evaluated from the distribution function for short polymethylene chain with electrostatic interaction between charges at both ends. Moreover, the probabilities of *trans*-conformation about the C–C bonds adjacent to amino groups were evaluated by NMR to confirm the conformations.

EXPERIMENTAL

Aliphatic α,ω -bis(tertiary amines) used here were *N,N,N',N'*-tetramethyl-1,3-propanediamine, *N,N,N',N'*-tetramethyl-1,4-butanediamine and *N,N,N',N'*-tetramethyl-1,6-hexanediamine, which are hereafter abbreviated as 1,3-diamine, 1,4-diamine and 1,6-diamine, respectively. The samples were of special grade available from Tokyo Kasei Co. and used without further purification. Potentiometric titration of diamines was performed by using 1.0 or 0.8 M HCl solution at $20.0 \pm 0.5^\circ\text{C}$ with a Corning 150 pH/ion meter of Iwaki Glass Co. calibrated by the standard buffer solutions of pH 4.00 and 6.88. The concentrations of diamines were from 0.0144 to 0.0165 M and the concentrations of KCl as added salt, C_s was 0.5 M. ¹H NMR measurements of diamines were performed in D₂O (99.8% atom-D) of Aldrich Chemical Co. with and without added salt with a Varian unity-INOVA operating at 499.9 MHz for proton resonance frequency at $20.0 \pm 1.0^\circ\text{C}$. The total of 16 transients were accumulated for each sample solution. The concentrations of diamines and C_s were *ca.* 0.06–0.07 M and 0.5 M, respectively.

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Figure 1. Plots of pM vs. h for α,ω -diamines in aqueous solutions with and without added salt. The solid lines are fitted to the data at $0 \leq h \leq 1$.

ANALYSIS AND RESULTS

First and second association constants, K_1 and K_2 , of α,ω -diamines, BB are given by

$$K_1 = \frac{[BBH] + [HBB]}{[BB](H)} \quad (1a)$$

$$K_2 = \frac{[HBBH]}{\{[BBH] + [HBB]\}(H)} \quad (1b)$$

where the parenthesis and the bracket denote the activity and the molar concentration, respectively. If diamines are symmetric and independently ionizable, we have $K_1/K_2 = 4$ or $\Delta pK = \log 4 (=0.60)$ from eq 1a and 1b.

When K_1 and K_2 are close to each other, it is useful to define the following function M in order to evaluate these values accurately¹⁷

$$M = \frac{h}{(2-h)(H^+)} = \frac{K_1 + 2K_1K_2(H^+)}{2 + K_1(H^+)} \quad (2)$$

where h ($0 \leq h \leq 2$) is the degree of neutralization determined by

$$h = \frac{[BBH] + [HBB] + 2[HBBH]}{[BB] + [BBH] + [HBB] + [HBBH]} = \frac{K_1(H^+) + 2K_1K_2(H^+)^2}{1 + K_1(H^+) + K_1K_2(H^+)^2} \quad (3a)$$

$$= 2\{V_{HCl} \times c_{HCl} + (10^{-14}/[H^+]) \times (V_{WAT} + V_{HCl}) - [H^+] \times (V_{WAT} + V_{HCl})\} / (V_{fin} \times c_{HCl}) \quad (3b)$$

where V_{HCl} , V_{WAT} , V_{fin} are the added HCl volume, the solvent volume and V_{HCl} at the equivalent point, respectively, and c_{HCl} is the concentration of titrated HCl. Equation 3b was derived from the neutral condition assuming $(H^+) = [H^+]$ and $(OH^-) = [OH^-]$ because $[H^+]$ and $[OH^-]$ are much lower than $[Cl^-]$.

Using eq 3a, we can rewrite eq 2 as a function of h and we have $K_1 = 2M$ ($pK_1 = pM - \log 2$) at the limit of $h \rightarrow 0$ ($(H^+) \rightarrow 0$). Therefore, pK_1 was evaluated from

Figure 2. Plots of $pM - pK_1$ vs. h for α,ω -diamines in aqueous solutions with and without added salt. The solid lines are fitted to all the experimental data.

pM values extrapolated at $h=0$ by fitting eq 2 as a function of h to the data at small h ($0 \leq h \leq 1$) as shown in Figure 1. Dividing eq 2 by K_1 , and using eq 3a, moreover, we can express M/K_1 as a function of h , of which the shape is determined by K_1/K_2 or ΔpK only. Therefore, pK_2 was obtained by fitting $pM - pK_1$ as a function of h to all the experimental data as shown in Figure 2.

Strictly speaking, the association constants should be given in terms of the activities for all the components in eq 1, and the above procedure cannot be generally applied because the activities of ionic components depend on their charges and ionic strength in solution. Since the deviation from ideality is not significant in the present case, however, we employed an approximate method to correct the association constants evaluated by the above procedure as follows. The corrected association constants, pK_1^C , pK_2^C , and their difference, ΔpK^C are related to pK_1 , pK_2 , and ΔpK with the activity coefficients of i -ionic components, f_i as

$$pK_1^C = pK_1 - \log f_{BBH} \quad (4a)$$

$$pK_2^C = pK_2 - \log \frac{f_{HBBH}}{f_{BBH}} \quad (4b)$$

$$\Delta pK^C = \Delta pK + \log \frac{(f_{BBH})^2}{f_{HBBH}} \quad (4c)$$

Here, we assumed that $f_{BBH} = f_{HBB}$ and $f_{BB} = 1$.

According to the Debye-Hückel theory,^{18,19} the activity coefficient of i -ionic component is given by

$$\log f_i = - \frac{0.5056z^2\sqrt{\mu}}{1 + 0.3286a\sqrt{\mu}} \quad (5)$$

where z , a , and μ are the charge, the diameter of ion and the ionic strength, respectively, and we assume $a = 1.0$ nm for all the ionic components since this value does not significantly affect the values of activity coefficient. Since the ionic strengths change as z values change in solutions without added salt, the ranges of correction were

Figure 3. Schematic illustration of rotational isomers about the C-C bond adjacent to an amino group.

Table I. Association constants of protons for α,ω -bis(tertiary amines) in aqueous solutions with and without added salt

Samples	C_s/M	pK_1	pK_2	ΔpK
1,3-Diamine	0	-9.44 ± 0.03	-7.29 ± 0.03	2.15 ± 0.03
	0.5	-10.12	-8.00	2.12
1,4-Diamine	0	-9.87 ± 0.03	-8.38 ± 0.03	1.49 ± 0.03
	0.5	-10.52	-8.87	1.65
1,6-Diamine	0	-10.44 ± 0.03	-9.43 ± 0.03	1.01 ± 0.03
	0.5	-10.69	-9.65	1.04

The pK_1 and pK_2 values are negative as the equilibrium constants are defined for the association reaction of protons.

evaluated by eq 4. In $C_s = 0.5$ M solution, on the other hand, the ionic strengths were practically constant, so that we can evaluate the correct values by eq 4. Since the amounts of correction (± 0.03) are significantly smaller than the total ΔpK values and may be comparable to the errors in the experiments and the fitting procedures, this approximate procedure can be safely assumed to be valid in solutions without added salt too.

Table I lists the corrected values of pK_1 , pK_2 , and ΔpK for 1,3-, 1,4-, and 1,6-diamines. Hereafter, we use pK_1 , pK_2 , and ΔpK for the corrected values. As shown in Table I, ΔpK is larger than $\log 4$ ($=0.60$) and decreases with increasing of charge length implying the effect of electrostatic interactions on the second association constants. Moreover, it should be noted that the absolute values of pK_1 and pK_2 for aqueous solutions with added salt are larger than those without added salt, but both ΔpK values are almost identical.

It is well-known that the vicinal coupling constants obtained by NMR spectra are related to the relative population of rotational isomers about C-C bonds. For a disubstituted ethane, $R-CH_AH_A-CH_XH_X-R'$, the vicinal coupling constants between protons A and X, J_{AX} and between A and X', $J_{AX'}$ are related to the populations of rotational isomers by

$$J_{AX} = J_g P_T + J_t' P_G + J_{g'} P_{G'} \quad (6a)$$

$$J_{AX'} = J_t P_T + J_g P_G + J_{g'} P_{G'} \quad (6b)$$

$$P_T + P_G + P_{G'} = 1 \quad (6c)$$

where P_T , P_G , and $P_{G'}$ are the relative populations of rotational isomers in *trans* (T), *gauche* (G) and another *gauche* (G') forms, respectively, and J_t , J_t' , J_g , $J_{g'}$, and $J_{g''}$ are the vicinal coupling constants for the respective conformations as shown in Figure 3. Assuming that $P_G = P_{G'}$ and rearranging eq 6, we have eq 7 for P_T .

Figure 4. ^1H NMR spectra of a) 1,3- and b) 1,6-diamine in aqueous solutions without added salt, respectively. The stick plots are the theoretical one for AA'XX' spin system calculated with relevant N values.

Table II. Probabilities of *trans*-rotational isomers about the C-C bonds adjacent to amino groups

Samples	C_s/M	
	0	0.5
1,3-Diamine	0.71	0.69
1,6-Diamine	0.74	0.74

$$P_T = \frac{2N - J_t' - J_{g''} - 2J_{g'}}{2J_t + 2J_g - 2J_{g'} - J_t' - J_{g''}} \quad (7)$$

where $N = J_{AX} + J_{AX'}$ is obtained by analyzing the NMR spectra with AA'XX' spin system.²⁰ Here, the analysis was applied to the C-C bonds adjacent to the amino groups for 1,3-, 1,4-, and 1,6-diamines. The comparison between the experimental spectra and theoretical stick plots calculated by relevant N values is shown in Figure 4. Using $J_t = J_t' = 13.0$, $J_g = 5.4$, $J_{g'} = 2.4$, and $J_{g''} = 0.7$ Hz reported for the coupling constants of 1,2-disubstituted ethane²¹ in eq 7, we have P_T values for 1,3- and 1,6-diamines as listed in Table II. For 1,4-diamine, however, we did not evaluate the P_T value since we could not obtain its well-resolved spectrum.

Table III. Charge distances of α,ω -bis(tertiary amines) in aqueous solutions without added salts evaluated by the theories of Bjerrum and Kirkwood–Westheimer, end-to-end distances evaluated for free-rotational, interdependent rotational and all-*trans* chains, and from the distribution function of short real chain with charges at both ends and effective dielectric constants D_E

Samples	r/nm						D_E
	Bjerrum	Kirkwood–Westheimer	Free-rotational	Interdependent	All- <i>trans</i>	Distribution	
1,3-Diamine	0.20 ± 0.01	0.52 ± 0.01	0.44	0.45	0.50	0.46	31
1,4-Diamine	0.35 ± 0.01	0.61 ± 0.01	0.49	0.54	0.63	0.60	46
1,6-Diamine	0.76 ± 0.05	0.78 ± 0.03	0.58	0.71	0.88	0.77	78

DISCUSSION

As mentioned above, the fact that ΔpK is larger than $\log 4$ as shown in Table I implies that there are interactions between the first and second association groups. Bjerrum^{4,5} assumed a simple electrostatic interaction between charges at both ends and gave the relationship between charge distance, r and ΔpK as

$$r = \frac{N_A e^2}{2.303 DRT(\Delta pK - \log 4)} \quad (8)$$

where N_A , e , and D are Avogadro's number, the elementary electric charge and the dielectric constant of solvent, respectively. Later, Kirkwood–Westheimer⁶ modified the theory of Bjerrum by taking into account of effective dielectric constant, D_E influenced by the dielectric constant of solute molecule. According to their theory, the molecule is represented by an ellipsoid of revolution and r is given as a distance between two foci of the ellipsoid of revolution and calculated by the following equations.

$$\lambda_0^3 - \lambda_0 = (6/\pi)(V/r^3) \quad (9)$$

$$\frac{D_E}{(\lambda_0^3 - \lambda_0)^{1/3}} = \frac{e^2}{2.303 kT(\Delta pK - \log 4)} \left(\frac{\pi}{6V} \right)^{1/3} \quad (10)$$

where V is the molecular volume, $\lambda_0 = (r_1 + r_2)/r$ with r_1 and r_2 being the distances of a point on ellipsoid from two foci and D_E is a complicated function of λ_0 and the dielectric constants of solute molecule, D_i and solvent, D . Using the experimental ΔpK values and V estimated by the method of Bondi²² (94.0, 104.3, and 124.7 mL mol⁻¹ for 1,3-, 1,4-, and 1,6-diamine, respectively) assuming an additivity rule of molecular volume of each group, we obtained $D_E/(\lambda_0^3 - \lambda_0)^{1/3}$ from eq 10, and then evaluated r from eq 9 using λ_0 values (1.52, 1.41, and 1.23 for 1,3-, 1,4-, and 1,6-diamine, respectively) obtained from the numerical table between λ_0 and $D_E/(\lambda_0^3 - \lambda_0)^{1/3}$ in their paper,⁶ where D_i was set equal to 2.0, a value in the neighborhood of the dielectric constant of aliphatic hydrocarbons and D was taken as 78 for water at 25°C. The D_E values used to evaluate the r values are listed in the last columns of Table III. Since $D = 80$ at the present experimental temperature, 20°C, the r values expected at 20°C may be slightly smaller (*ca.* 2%) than the r values calculated here, but the differences are within the errors in the experiments and the fitting procedures. Moreover, it should be noted that the molecular volumes evaluated by the method of Bondi are always slightly smaller than those evaluated by the method of Traube²³ since the

former is based on van der Waals radii, while the latter is based on partial molar volume. As mentioned above, we adapted the molecular volumes evaluated by the method of Bondi in the present calculation, because they can be assumed to be closer to real values in terms of dielectric constant than those evaluated by the method of Traube, though both values are not significantly different with each other. The r values or the charge distances, thus evaluated by the theories of Bjerrum and Kirkwood–Westheimer for α,ω -diamines are listed and compared with the end-to-end distances for free-rotational, interdependent rotational and all-*trans* chains, and evaluated from the distribution function for short polymethylene chain with electrostatic interactions between charges at both ends in Table III. The end-to-end distances for the free-rotational, interdependent rotational and all-*trans* chains were evaluated by assuming that the diamines behave as polymethylene chains having the same number of bonds as the diamines. Since the distribution of end-to-end distances of short chains cannot be assumed to be Gaussian even in an unperturbed state, we used the following distribution function of short chains derived by Flory *et al.*²⁴

$$W(r) = (2\langle r^2 \rangle_0 / 3)^{2/3} \pi^{-3/2} \exp(-\rho^2) \times [(1 + 15g_4) - 20g_4\rho^2 + 4g_4\rho^4] \quad (11)$$

where, $\rho = (3r^2/2\langle r^2 \rangle_0)^{1/2}$, $\langle r^2 \rangle_0$ is the mean square of end-to-end distance in an unperturbed state and g_4 is the coefficient of 4th moments in the Fourier transform of the distribution function for chain vector. If charges are introduced at both ends of chain, the distribution function may be written as

$$P(r) \propto W(r) \exp(-F_{el}(r)/kT) \quad (12)$$

Here, $F_{el}(r)$ is the electrostatic potential between charges at both ends, which is given by eq 13 in solutions without added salt.

$$F_{el}(r) = e^2/D_E r \quad (13)$$

Therefore, the mean square of end-to-end distance is given by

$$\langle r^2 \rangle = \frac{\int 4\pi r^4 P(r) dr}{\int 4\pi r^2 P(r) dr} \quad (14)$$

Here, we used the effective dielectric constants obtained in the theory of Kirkwood–Westheimer for D_E .

For comparison, experimental ΔpK data reported for

Table IV. ΔpK , charge distances, end-to-end distances, and D_E for α,ω -bis(primary amines)

Samples	ΔpK	r/nm						D_E
		Bjerrum	Kirkwood–Westheimer	Free-rotational	Interdependent	All- <i>trans</i>	Distribution	
1,3-Propanediamine	1.98 ^a	0.22	0.46	0.44	0.45	0.50	0.49	39
1,4-Butanediamine	1.45 ^a	0.36	0.54	0.49	0.54	0.63	0.60	54
1,5-Pentanediamine	1.31 ^b	0.44	0.58	0.53	0.63	0.75	0.69	60
1,8-Octanediamine	0.90 ^b	1.04	0.87	0.65	0.87	1.13	0.92	96

^a Reference 25. ^b Reference 26.**Table V.** ΔpK , charge distances, end-to-end distances, and D_E for α,ω -diacids

Samples	ΔpK^a	r/nm						D_E
		Bjerrum	Kirkwood–Westheimer	Free-rotational	Interdependent	All- <i>trans</i>	Distribution	
Malonic acid	2.87	0.14	0.41	0.44	0.45	0.50	0.44	27
Succinic acid	1.28	0.46	0.56	0.49	0.54	0.63	0.59	65
Adipic acid	0.99	0.82	0.73	0.58	0.71	0.88	0.76	88

^a Reference 27.

α,ω -bis(primary amines)^{25,26} and α,ω -diacids²⁷ corresponding to the present samples and their calculated r values are listed in Tables IV and V, respectively, where the former data were measured at 20°C and corrected by the Debye–Hückel theory,^{18,19} and the latter data were obtained by extrapolating to infinite dilution at 25°C.²⁷ As shown in Tables I and IV, the ΔpK values of α,ω -bis(primary amines) and α,ω -bis(tertiary amines) with the same numbers of bonds between charged groups are almost identical. As shown in Tables I and V, moreover, the ΔpK values of α,ω -diacids and α,ω -bis(tertiary amines) with the same numbers of bonds between charged groups become closer to each other as the numbers of bonds increase, because the difference of structures between carboxylic acids and tertiary amines at the ends becomes less significant as the numbers of bonds increase. In the calculation of r values in the theory of Kirkwood–Westheimer, we used $V=51.8, 62.0, 72.2, 102.9, 49.3, 59.5$, and 80.0 mL mol^{-1} and $\lambda_0=1.48, 1.40, 1.36, 1.19, 1.58, 1.36$, and 1.23 for 1,3-propanediamine, 1,4-butanediamine, 1,5-pentanediamine, 1,8-octanediamine, malonic acid, succinic acid, and adipic acid, respectively. The D_E values used to evaluate the r values are listed in the last columns of Tables IV and V. Tables III, IV, and V show that the r values evaluated by the theory of Bjerrum are much smaller than those of free-rotational model except for the molecules with long chain lengths such as 1,6-diamine, adipic acid and 1,8-octanediamine. Since the induced effect through the chemical bonds may be disregarded when the groups are separated by more than two carbon atoms,⁵ this result may be understood by considering that the effective dielectric constants are smaller than the dielectric constant of water for the molecules with short chain lengths because more electrostatic interactions go through a solute molecule such as diamine and diacid having lower dielectric constants as the chain length between charged groups decreases. As shown in these tables, actually, the r values evaluated by the theory of Kirkwood–Westheimer taking account of the effective

dielectric constant are larger than those of free-rotational chains even for the molecules with short chain lengths and the r values evaluated by both theories become closer to each other with increasing chain length. Thus, comparing the r values with the end-to-end distances of other models in these tables, we may conclude that the charge distances of these bolaform electrolytes are comparable or slightly larger than the end-to-end distances of the interdependent rotational chains in an unperturbed state and almost agree with those evaluated from the distribution function for short polymethylene chains with charges at both ends. This conclusion is reasonable because the above results are consistent with the fact that the P_T values are higher than that of polymethylene ($P_T=0.60$)²⁸ as shown in Table II.

Finally, we mention the effect of ionic strength on ΔpK . It may be estimated by introducing the Debye–Hückel potential, $e^2 \exp(-\kappa r)/Dr$,¹² in place of the direct Coulomb potential in the theories of Bjerrum and Kirkwood–Westheimer, where κ is the reciprocal of the Debye screening length. As described before, both theories give almost the same result for the charge distances of diamines or diacids having long chain lengths such as 1,6-diamine. For simplicity, therefore, we apply the theory of Bjerrum with the Debye–Hückel potential to 1,6-diamine. Using the experimental $\Delta pK=1.04$, we have $r=0.33 \text{ nm}$ which is smaller than the end-to-end distance of free-rotational chain. Conversely, using the end-to-end distance of interdependent rotational chain in an unperturbed state (0.71 nm) as the r value, we have $\Delta pK=0.68$, which is smaller than the experimental value (1.04). At present, we do not have a clear explanation of this unexpected result, but we speculate that it may be caused by the fact that the charge distance ($\sim 0.71 \text{ nm}$) is smaller than the sum of the Debye screening length of an isolated charge (0.86 nm) in 0.5 M KCl solution. If both charges can be within the same distorted ionic atmosphere, the electrostatic interactions between charges may not be much different in the solutions with and without added salt.

In this work, the charge distances or the chain conformations of α,ω -diamines, which are the simplest class of polyelectrolytes, were studied by analyzing the potentiometric titration data with use of the theories of Bjerrum and Kirkwood–Westheimer. Generally, the potentiometric titration data of polyelectrolytes are related to the local chain conformations, but the analyses are not simple due to strong electrostatic interactions caused by many charges on polyions.³

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