# Hysteretic Behavior on the Heat of Protonation of Diethylenetriamine in Aqueous Solution

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Hysteretic behavior was found on the heat of protonation of diethylenetriamine (dien) in aqueous solution at 298 K. We propose the presence of two conformers for $Hdien^+$, which have significantly different proton affinities. Mutual transformation between the conformers may be practically forbidden, but is strongly accelerated upon their protonation to form $H_2dien^{2+}$.

Protonation constants of diethylenetriamine (1,4,7-triazaheptane or dien) have been reported in the literature,[1–3] and the corresponding enthalpies as well.[3] No specific aspect is thus expected on the protonation of dien. However, interestingly, an abnormal heat was found upon protonation of dien, and the enthalpic titration curves hardly be reproduced by using protonation constants separately determined by potentiometry. Here, we will propose the presence of two conformers for $Hdien^+$ as the origin of the hysteretic behavior.

Protonation constants were obtained by potentiometry and the corresponding enthalpies by titration calorimetry at 298 K. The procedure of measurements is described in the literature.[4] All solutions prepared contain $0.1\,mol\,dm^{-3}$ NaCl as an ionic medium. **Potentiometric titration**: Acidic solutions containing $2$–$5\,mmol\,dm^{-3}$ dien were titrated with $0.025\,mol\,dm^{-3}$ NaOH solution, and the pHs of solution were obtained by using glass electrode. This procedure was followed by back titration using $0.02\,mol\,dm^{-3}$ HCl as a titrant. The standard electrode potential, $E^\circ$, was determined by the Gran plot in advance of each titration. **Calorimetric titration**: Aliquots of $0.035\,mol\,dm^{-3}$ HCl were added into a basic solution (pH = 10) containing $4$–$10\,mmol\,dm^{-3}$ dien and, in each titration point, a reaction heat was determined within an accuracy of $\pm0.02\,J$. Measured heats were corrected for heats of dilution of the titrant, which had been determined in advance by separate experiment and were found to be very small. Back titration was carried out by titrating an acidic solution of dien with $0.02\,mol\,dm^{-3}$ NaOH solution.

The average number of protons bound per a dien molecule $n_{av}$ is shown in Figure 1, as a function of $-\log([H^+]/mol\,dm^{-3})$ in solution. No significant difference is seen in the $n_{av}$ obtained by normal and back titrations. The stepwise protonation constants $K_n$ ($n = 1$–$3$) were obtained by minimizing the error square sum, $U = \Sigma(E_{obs} - E_{calcd})^2$, where $E_{obs}$ denotes the observed emf and $E_{calcd}$ is given by $E_{calc} = E^\circ + 59.15\log[H^+]_{calcd}$. $[H^+]_{calcd}$ is calculated by knowing the total concentrations of proton and dien at each titration point, $C_H$ and $C_L$, respectively, on the basis of mass balance equations, $C_H = [H^+] + \Sigma n(\Pi K_n)\,[H^+]^n[L] - K_W[H^+]^{-1}$ and $C_L = [L] + \Sigma(\Pi K_n)[H^+]^n[L]$ (L = dien), where $K_W$ denotes the autoprotolysis constant of water.

Calorimetric titration curves obtained by titrating with HCl and NaOH solutions are shown in Figures 2a and 2b, respectively, in which the apparent enthalpy $-q/(\delta v C_{H,tit})$ is plotted against the total concentration ratio $C_H/C_L$ of proton to dien,
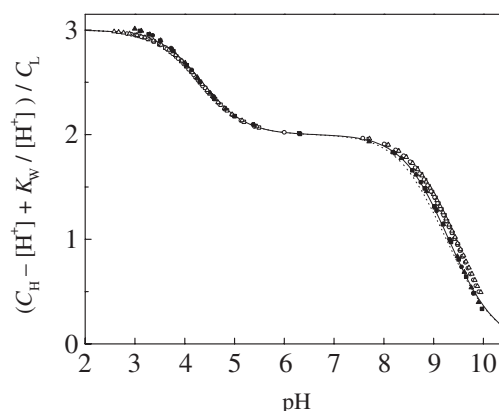


**Figure 1.** The average number of protons bound per a diethylenetriamine (dien) molecule $n_{av}$ obtained by titrating with NaOH (opened symbols) and HCl (filled symbols). The solid and dotted lines show respectively the curves calculated without and with taking into account the presence of $HL^+$ conformers.
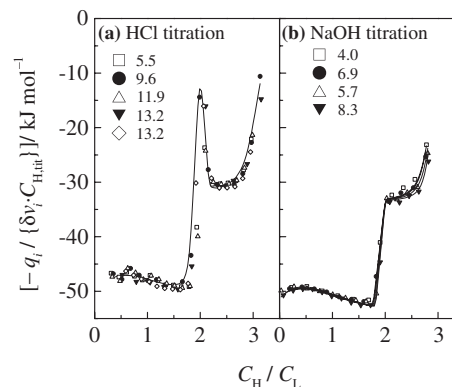


**Figure 2.** Enthalpic titration curves of diethylenetriamine obtained by titrating with HCl (a) and NaOH (b). Initial concentrations of dien, $C_{L,ini}/mmol\,dm^{-3}$, are given. The solid lines show the theoretical curves calculated by using constants in Table 1.

where $q$, $\delta v$ and $C_{H,tit}$ denote the observed heat of reaction, the volume of the added titrant and the concentration of proton, respectively. As seen, the profile in Figure 2a is different from that in Figure 2b, particularly in the range $1.5 < C_H/C_L < 2.5$. By omitting some data over the range $1.5 < C_H/C_L < 2.5$, the enthalpies $\Delta H_n^\circ$ ($n = 1$–$3$) were obtained by minimizing $U = \Sigma(q_{i,obs} - q_{i,calcd})^2$, where $q_{i,obs}$ denotes the observed heat of reaction at the $i$th titration point. The heat $q_{i,calcd}$ is given by $q_{i,calcd} = \Sigma\Delta H_n^\circ(\Pi K_n)(V_i[H_nL]_i - V_{i-1}[H_nL]_{i-1}) - \Delta H_W^\circ K_W(V_i[H^+]_i^{-1} - V_{i-1}[H^+]_{i-1}^{-1})$, in which $V_i$ and $\Delta H_W^\circ$ denote the volume of test solution and the autoprotolysis enthalpy of water, respectively. The obtained thermodynamic parameters for the protonation reaction of dien are listed in Table 1. These values are practically the same as those reported

**Table 1.** Thermodynamic parameters of protonation of diethyl-enetriamine in aqueous solution containing $0.1\,\mathrm{mol\,dm^{-3}}$ NaCl as an ionic medium at 298 K

|  | Case a($\alpha$) | Case a($\beta$) | Case b |
|---|---|---|---|
| $\log K_1$ | 9.67 (5) | 9.85 | 9.85 (2) |
| $\log K_2$ | 8.94 (4) | 7.0 | 9.05 (1) |
| $\log K_3$ | 4.35 (5) | – | 4.32 (1) |
| $N^{\mathrm{a}}$ | 59 |  | 142 |
| $R^{\mathrm{b}}$ | 0.011 |  | 0.006 |
|  | Case a($\alpha$)$^{\mathrm{c}}$ | Case a($\beta$) | Case b |
| $\Delta H_1^{\circ}$ | −45.8 (5) | −46 | −47.1 (5) |
| $\Delta H_2^{\circ}$ | −50.4 (5) | −5 | −52.9 (5) |
| $\Delta H_3^{\circ}$ | −31.2 (6) | – | −33.6 (6) |
| $T\Delta S_1^{\circ}$ | 9.4 (5) | 10 | 9.2 (5) |
| $T\Delta S_2^{\circ}$ | 0.7 (5) | 35 | −1.3 (5) |
| $T\Delta S_3^{\circ}$ | −6.3 (6) | – | −9.0 (6) |
| $N^{\mathrm{a}}$ | 71 |  | 53 |
| $R^{\mathrm{b}}$ | 0.013 |  | 0.034 |

The values in parentheses refer to three standard deviations in the last significant digits. The $\Delta H^{\circ}$ and $T\Delta S^{\circ}$ values are given as $\mathrm{kJ\,mol^{-1}}$. Case a($\alpha$): obtained by HCl titration, Case b: obtained by NaOH titration, Case a($\beta$): assumed values for the folded dien. $^{\mathrm{a}}$The number of data points. $^{\mathrm{b}}$The Hamilton $R$ factor. $^{\mathrm{c}}$Obtained by omitting data over the range $1.5 < C_{\mathrm{H}}/C_{\mathrm{L}} < 2.5$.

in the literature.[1–3] The close $K_1$ and $K_2$ values similar to those of other primary amines (cf. $K_{\mathrm{a}} = 9.97$ for ethylenediamine) indicate that the first and second protonation sites of dien are terminal primary amino groups.

As seen in Figure 2a, an enthalpic spike was found over the range $1.5 < C_{\mathrm{H}}/C_{\mathrm{L}} < 2.5$, which cannot be reproduced simply in terms of successive protonation reactions as described above. Note that the spike is not observed in Figure 2b, and experimental points can be reproduced well by using constants in Table 1. As will be discussed below, such a hysteretic behavior cannot be explained without taking into account the presence of two conformers $HL_{\alpha}^{+}$ and $HL_{\beta}^{+}$ with different proton affinities. The normal profile of titration curves in Figure 2b indicates that a conformer $HL_{\alpha}^{+}$ is formed solely upon deprotonation of $H_2L^{2+}$. This strongly indicates that the conformational change from $HL_{\alpha}^{+}$ to $HL_{\beta}^{+}$ is practically forbidden under the experimental conditions examined. On the other hand, the $HL_{\alpha}^{+}$ and $HL_{\beta}^{+}$ are protonated to yield $H_2L_{\alpha}^{2+}$ and $H_2L_{\beta}^{2+}$, respectively. As the profile of titration curves at $C_{\mathrm{H}}/C_{\mathrm{L}} > 2.5$ is typical for protonation of a single conformer $H_2L_{\alpha}^{2+}$, the conformational change $H_2L_{\beta}^{2+} \rightarrow H_2L_{\alpha}^{2+}$ may occur spontaneously upon protonation of $HL_{\beta}^{+}$. The enthalpic spike is thus ascribed to the conformational change $H_2L_{\beta}^{2+} \rightarrow H_2L_{\alpha}^{2+}$. Here, note that the profile of titration curves is normal over the range $1 < C_{\mathrm{H}}/C_{\mathrm{L}} < 1.5$, indicating that the sole $HL_{\alpha}^{+}$ is protonated in the range to yield $H_2L_{\alpha}^{2+}$ without accompanying conformational change. This means that the $HL_{\alpha}^{+}$ has a larger proton affinity than the $HL_{\beta}^{+}$. After the $HL_{\alpha}^{+}$ is preferentially protonated, the $HL_{\beta}^{+}$ is protonated to form $H_2L_{\beta}^{2+}$, which is spontaneously followed by conformational change to $H_2L_{\alpha}^{2+}$. The solid line in Figure 2a is calculated by assuming $\log K_2 = 7.0$, $\Delta H_2^{\circ} = -5.0\,\mathrm{kJ\,mol^{-1}}$ for $HL_{\beta}^{+}$, and the molar ratio of the conformers $[HL_{\beta}^{+}]/[HL_{\alpha}^{+}]$ to be 0.25. Thermodynamic parameters for oth-

er species are given in Table 1. Although the $\Delta H_2^{\circ}$ value for $HL_{\beta}^{+}$ may involve rather large uncertainty, the enthalpy for the conformational change $H_2L_{\beta}^{2+} \rightarrow H_2L_{\alpha}^{2+}$ is expected to be as large as $45\,\mathrm{kJ\,mol^{-1}}$, which is almost compensated with the corresponding entropy change.
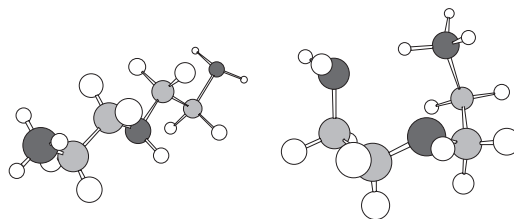


**Scheme 1.** Optimized geometries of expanded (left) and folded (right) form of $Hdien^{+}$.

With regard to the structure of conformers, we propose the expanded and folded forms for $HL_{\alpha}^{+}$ and $HL_{\beta}^{+}$, respectively, in which the atomic distance between terminal amino N atoms is longer in the expanded $HL_{\alpha}^{+}$ than the folded $HL_{\beta}^{+}$. These are protonated at both sites of the amino group to yield $H_2L_{\alpha}^{2+}$ and $H_2L_{\beta}^{2+}$, respectively. Here, as an electrostatic repulsion between terminal $-NH_3^{+}$ groups in the folded $HL_{\beta}^{+}$ is stronger than that in the expanded $H_2L_{\alpha}^{2+}$, the conformational change from the folded to expanded form may easily occur in the present system, i.e., the expanded $H_2L_{\alpha}^{2+}$ is formed as the main species in the solution. Consequently, in the back titration, the expanded $H_2L_{\alpha}^{2+}$ deprotonates to yield the expanded $HL_{\alpha}^{+}$, which stays practically as it is, as the rate of conformational change from $HL_{\alpha}^{+}$ to $HL_{\beta}^{+}$ is slow.

Theoretical *ab initio* MO calculations using Gaussian 03 program suite and 6-311G(d,p) basis set are performed to find two significant conformers of $Hdien^{+}$. With regard to the folded form, a hydrogen bond forms between terminal amino groups with $H\cdots N^{+}$ distance of 1.84 Å and $N–H^{+}\cdots N$ angle of $163.8°$. Similar hydrogen-bonded structure is also reported for 1,5-diaminopentane.[5] The SCF energy for the folded form is lower by $79\,\mathrm{kJ\,mol^{-1}}$ than for the expanded one. An energy barrier as high as $16\,\mathrm{kJ\,mol^{-1}}$ is found during conformational change from $HL_{\alpha}^{+}$ to $HL_{\beta}^{+}$ at the $N–C–C–NH_3^{+}$ dihedral angle of $120°$ (the corresponding dihedral angles are $33°$ and $180°$ for the folded and expanded form, respectively), and it is thus plausible that the conformational change is kinetically hindered. The *ab initio* MO calculation has also been carried out for neutral dien, and it is found that the SCF energy for the expanded form is lower by $13\,\mathrm{kJ\,mol^{-1}}$ than the folded one at their optimized geometries. This implies that an equilibrium between expanded and folded forms are more shifted to the expanded for neutral dien.

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