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A THERMODYNAMIC STUDY OF THE PROTONATION OF SOME SULPHUR-CONTAINING α,ω-DIAMINES IN AQUEOUS SOLUTION

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ABSTRACT

The protonation equilibria in aqueous solution of α,ω-thiadiamines of general formula $(R)(R')N(CH_2)_nS(CH_2)_mNH_2$ (R,R′ = CH_3 or H) have been investigated potentiometrically and calorimetrically at 25°C in 0.5 mole dm^{-3} KNO_3 solution. The enthalpy and entropy changes are discussed in terms of intrinsic proton affinities and solvation effects.

INTRODUCTION

In some previous papers [1–3] we reported the thermodynamic properties of the protonation of some sulphur-containing primary amines and diamines and the protonation constants of some secondary and tertiary diamines. These investigations on ligands of the type $(R)(R')N(CH_2)_nS(CH_2)_mNH_2$ are now extended to some new compounds (n,m = 2,4; 3,4; 4,4) or completed (for the compounds with R and/or R′ = CH_3) with a calorimetric study. The thermodynamic parameters were determined at 25°C in 0.5 mole dm^{-3} KNO_3 solution. The aim of this study was to gain a better insight into the influence of increasing chain length or increasing *N*-methyl substitution and the corresponding change in solvation on the thermodynamics of protonation.

EXPERIMENTAL

Abbreviations

For naming the ligands a symbolism is used which mentions first the numbers of carbon atoms between the donor groups and then the donor

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atoms themselves in the aliphatic chain. Methyl substituents on the nitrogen donor are abbreviated as (Me), e.g. 2,4-(Me)NSN for 2,10-diaza-5-thiadecane.

Reagents

The preparation of the sulphur-containing secondary and tertiary diamines has already been described [3]. 1,10-Diaza-5-thiadecane (3,4-NSN) was prepared by adding dropwise a solution of 0.5 mole of 4-bromo-*n*-butylphthalimide in 0.250 dm^{-3} ethanol to an ethanolic solution (0.5 dm^3) of 0.5 mole NaSH. Subsequently, 0.5 mole Na was added and also an alcoholic solution (0.5 dm^3) of 0.5 mole of 3-bromo-*n*-propylphthalimide. After filtration of the precipitated NaBr, the reaction product was hydrolized [4] (3,4-NSN: b.p. = 111°C; 0.5 mm Hg).

1,11-Diaza-6-thiaundecane (4,4-NSN) (b.p. = 130°C; 1 mm Hg) and 1.9-diaza-4-thianonane (2,4-NSN) b.p. = 100°C; 0.5 mm Hg) were prepared in the same manner.

Solutions of the amines were made and standardized as usual [5].

Potentiometric and calorimetric titrations

Experimental details regarding the measurement of pH data were reported in an earlier paper [2]. All measurements were carried out at 25.00°C ± 0.05°C using a total nitrate concentration of 0.5 mole dm^{-3}. Experimental data for the titrations of the protonated amines with KOH are given in Table 1.

The calorimetric titrations were performed with an LKB-8700/2 titration calorimeter, thermostatted at 25 ± 0.001°C. The titrant (a standardized HNO_3 solution) was added stepwise with an automatic piston burette to a

TABLE 1

Experimental details for the potentiometric titrations

Amine	Amine (mmoles)	HNO_3 (mmoles)	Titre KOH	V_0 [a] (cm^3)
2,4-NSN	3.840	8.526	1.001	60.0
	1.955	6.030	1.001	60.0
3,4-NSN	2.519	7.517	1.003	65.0
	1.511	4.989	1.003	40.0
4,4-NSN	2.429	7.546	1.002	65.0
	1.944	7.546	1.002	55.0

[a] Initial volume in the titration vessel.

TABLE 2

Experimental details for the calorimetric titrations

Amine	Amine (mmoles)	Titre titrant HNO_3	V_0 [a] (cm^3)
2,4-NSN	2.420	0.5	70.0
3,4-NSN	3.260	0.5	70.0
4,4-NSN	3.048	0.5	70.0
2,2-(Me)NSN	3.132	0.5	70.0
2,3-(Me)NSN	1.466	0.5	70.0
2,4-(Me)NSN	2.751	0.5	70.0
2,2-(Me_2)NSN	2.987	0.5	70.0
2,3-(Me_2)NSN	3.399	0.5	65.0
2,3-NSN(Me_2)	3.474	0.5	65.0
3,3-(Me_2)NSN	3.051	0.5	80.0

[a] Initial volume in the titration vessel.

solution of the amine. The solutions were kept at constant ionic strength, $I = 0.5$, by the addition of KNO_3. The heat, Q, generated at each titration step was determined according to the method described by Wadsö [6]. Experimental data are listed in Table 2.

Calculations

The protonation constants were calculated with a FORTRAN IV program based on the minimisation procedure of Davidon [7]. The heats of protonation (ΔH) were calculated from the experimental Q-values, which were corrected for dilution of the titrant, with an appropriate FORTRAN IV program. Details concerning this calculation procedure have been reported elsewhere [1]. The entropy changes ΔS were then derived from the obtained ΔH values and the protonation constants

$$RT \ln K = -\Delta G = -\Delta H + T\Delta S$$

RESULTS AND DISCUSSION

The equilibrium constants and the corresponding thermodynamic functions for the succcessive and overall protonation of the amines are listed in Tables 3 and 4. The results for the previously investigated amines (2,2-NSN, 2,3-NSN, 3,3-NSN) are given for comparison. The heats of protonation of 2,4-NSN were found to deviate slightly from the formerly determined value [2].

The symbols used are consistent with the following individual and overall

TABLE 3

Protonation constants and corresponding thermodynamic functions [a,b]

Amine	log K_1	log K_2	$-\Delta G_1$ (kJ mole^{-1})	$-\Delta G_2$ (kJ mole^{-1})	$-\Delta H_1$ (kJ mole^{-1})	$-\Delta H_2$ (kJ mole^{-1})	$T\Delta S_1$ (kJ mole^{-1})	$T\Delta S_2$ (kJ mole^{-1})
2,2-NSN [c]	9.682(2)	8.821(2)	55.25(2)	50.34(2)	54.1(3)	53.3(6)	1.1(3)	−2.9(6)
2,3-NSN [c]	10.139(2)	9.161(2)	57.89(1)	52.30(3)	56.0(2)	54.8(5)	1.9(2)	−2.5(5)
2,4-NSN	10.441(2)	9.249(3)	59.59(2)	52.78(2)	56.9(3)	55.1(6)	2.7(3)	−2.3(6)
3,3-NSN [c]	10.365(2)	9.628(2)	59.16(1)	54.95(2)	56.5(2)	55.9(4)	2.7(2)	−1.0(4)
3,4-NSN	10.509(5)	9.809(4)	59.97(3)	55.98(3)	57.3(2)	56.3(5)	2.7(2)	−0.4(5)
4,4-NSN	10.730(5)	10.047(4)	61.24(3)	57.34(2)	57.6(3)	56.9(6)	3.6(3)	0.5(6)
2,2-(Me)NSN	9.855(5)	8.892(4)	56.24(3)	50.75(2)	49.2(3)	51.9(5)	7.0(3)	−1.2(5)
2,3-(Me)NSN	10.255(5)	9.437(5)	58.53(3)	53.86(3)	54.3(4)	50.9(7)	4.2(4)	3.0(7)
2,4-(Me)NSN	10.510(6)	9.551(5)	59.98(3)	54.51(3)	55.6(3)	50.7(5)	4.4(3)	3.8(5)
2,2-(Me_2)NSN	9.430(9)	8.384(9)	53.82(5)	47.85(5)	48.0(3)	40.5(6)	5.8(4)	7.4(7)
2,3-(Me_2)NSN	10.052(6)	8.721(5)	57.37(3)	49.77(3)	52.3(3)	38.4(5)	5.1(3)	11.4(5)
2,3-NSN(Me_2)	9.753(5)	9.005(5)	55.66(3)	51.39(3)	44.9(3)	47.1(5)	10.8(3)	4.3(2)
3,3-(Me_2)NSN	10.16(2)	9.32(1)	58.0(1)	53.19(6)	52.6(4)	43.0(6)	5.4(5)	10.2(2)

[a] 25°C; 0.5 mole dm^{-3} KNO_3.

[b] Number in parentheses is the standard deviation on the last significant figure.

[c] Results obtained in a previous investigation: see ref. 2.

TABLE 4

"Overall" protonation constants and thermodynamic functions [a,b]

Amine	log K_β	$-\Delta G_\beta$ (kJ mole^{-1})	$-\Delta H_\beta$ (kJ mole^{-1})	$T\Delta S_\beta$ (kJ mole^{-1})
2,2-NSN [c]	18.503(4)	105.59(4)	107.4(3)	−1.8(3)
2,3-NSN [c]	19.300(4)	110.19(4)	110.8(3)	−0.6(3)
2,4-NSN	19.689(5)	112.37(4)	112.0(3)	0.4(3)
3,3-NSN [c]	19.993(4)	114.11(3)	112.4(2)	1.7(2)
3,4-NSN	20.318(9)	115.95(6)	113.6(3)	2.3(3)
4,4-NSN	20.777(9)	118.58(5)	114.5(3)	4.1(3)
2,2-(Me)NSN	18.747(9)	106.99(5)	101.1(2)	5.9(2)
2,3-(Me)NSN	19.69(1)	112.39(6)	105.2(3)	7.2(3)
2,4-(Me)NSN	20.06(1)	114.49(6)	106.3(2)	8.2(2)
2,2-(Me_2)NSN	17.81(2)	101.7(1)	88.5(3)	13.2(3)
2,3-(Me_2)NSN	18.77(1)	107.14(6)	90.7(2)	16.4(2)
2,3-NSN(Me_2)	18.76(1)	107.05(6)	92.0(2)	15.1(2)
3,3-(Me_2)NSN	19.48(3)	111.19(7)	95.6(2)	15.6(2)

[a] 25°C; 0.5 mole dm^{-3} KNO_3.

[b] Number in parentheses is the standard deviation on the last significant figure.

[c] Data from ref. 2, given for comparison.

protonation reactions

$L + H^+ \rightleftharpoons LH^+ \qquad K_1, \Delta G_1, \Delta H_1, \Delta S_1$

$LH^+ + H^+ \rightleftharpoons LH^{2+} \qquad K_2, \Delta G_2, \Delta H_2, \Delta S_2$

$L + 2H^+ \rightleftharpoons LH^{2+} \qquad \beta, \Delta G_\beta, \Delta H_\beta, \Delta S_\beta$

The thermodynamic functions for the "overall" protonation

For asymmetric diamines such as $(R)(R')N(CH_2)_nS(CH_2)_mNH_2$, the protonation in the first step may occur at either of the two nitrogen atoms, so that the LH^+ ion may exist in two tautomeric forms

$$^+H(R)(R')N(CH_2)_nS(CH_2)_mNH_2 \rightleftharpoons (R)(R')N(CH_2)_nS(CH_2)_mNH_3^+$$

(I) (II)

Hence, the initial discussion concerns the thermodynamic functions for the overall protonation reaction. From Table 4 it follows that within a series of diamines with equal n and m values the effect of increasing N-methyl substitution compares well with that within the series CH_3NH_2, $(CH_3)_2NH$ and $(CH_3)_3N$ [8].

$-\Delta G_\beta$ values follow the orders

$(Me_2)NH$	$> (Me)NH_2$	$> (Me_3)N$
2,2-(Me)NSN	> 2,2-NSN	> 2,2-(Me_2)NSN
2,3-(Me)NSN	> 2,3-NSN	> 2,3-(Me_2)NSN
	2,3-NSN	> 2,3-NSN(Me_2)
	3,3-NSN	> 3,3-(Me_2)NSN
2,4-(Me)NSN	> 2,4-NSN	

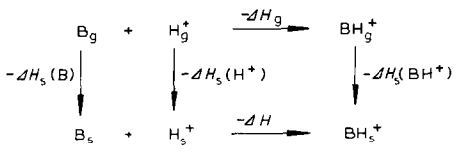
$-\Delta H_\beta$ values follow the orders

$(Me)NH_2$	$> (Me_2)NH$	$\gg (Me_3)N$
2,2-NSN	> 2,2-(Me)NSN	$\gg$ 2,2-(Me_2)NSN
2,3-NSN	> 2,3-(Me)NSN	$\gg$ 2,3-(Me_2)NSN
2,3-NSN		$\gg$ 2,3-NSN(Me_2)
3,3-NSN		$\gg$ 3,3-(Me_2)NSN
2,4-NSN	> 2,4(Me)NSN	

$T\Delta S_\beta$ values follow the orders

$(Me)NH_2$	$< (Me_2)NH$	$< (Me_3)N$
2,2-NSN	< 2,2(Me)NSN	< 2,2-(Me_2)NSN
2,3-NSN	< 2,3(Me)NSN	< 2,3-(Me_2)NSN
2,3-NSN		< 2,3-NSN(Me_2)
3,3-NSN		< 3,3-(Me_2)NSN
2,4-NSN	< 2,4-(Me)NSN	

As may be seen from these sequences, the irregular order for $-\Delta G_\beta$ (*sec.* > *prim.* > *tert.*) is obviously the result of more regular enthalpy and entropy terms, which compensate each other. This similar behaviour with increasing *N*-methyl substitution can be explained on the basis of an electrostatic model for protonation [8].



Scheme 1. Thermodynamic cycle of protonation.

From the thermodynamic cycle of protonation in Scheme 1 it can be deduced that the proton affinity in solution ($-\Delta H$) is the result of the proton affinity in the gas phase ($-\Delta H_g$) and terms arising from the

solvation of the amine $[-\Delta H_s(B)]$ and the ammonium ion $[-\Delta H_s(BH^+)]$.

$$[-\Delta H] = [-\Delta H_g] + [-\Delta H_s(BH^+)] - [-\Delta H_s(B)] - [-\Delta H_s(H^+)] \quad (1)$$

According to Aue et al. [8] the solvation of alkylammonium ions may be thought of as involving two steps. (i) The introduction of a neutral molecule with the same size as the ion into the solvent. A reference for the enthalpy associated with this step is the enthalpy of hydration of the amine, $[\Delta H_s(B)]$. (ii) The interaction of the ionic charge with the solvent. This step may be defined as electrostatic since it reflects those solvation effects that result from addition of a positively charged proton to the neutral amine, $[\Delta H_s(BH^+)^{el}]$.

An approximation may then be used

$$\Delta H_s(BH^+) \simeq \Delta H_s(B) + \Delta H_s(BH^+)^{el} \quad (2)$$

The difference in proton affinity between a more (B) and a less (A) *N*-methyl-substituted amine, or the enthalpy for the reaction

$$AH^+ + B \rightleftharpoons A + BH^+ \quad (3)$$

may then be expressed as

$$\delta[-\Delta H] \simeq \delta[-\Delta H_g] + \delta[-\Delta H_s(BH^+)^{el}] \quad (4)$$

Increasing the substitution on nitrogen will cause (i) an increase of the proton affinity $(-\Delta H_g)$, due to a greater positive inductive effect and (ii) a decrease of the charge density on the ion and, as a consequence, a decrease of the electrostatic interaction with the solvent or a decrease of the solvation of the ion $[-\Delta H_s(BH^+)^{el}]$. Moreover, it must be noted that increasing the substitution on nitrogen reduces the ability to form hydrogen bonds to the solvent, yielding a further decrease of the solvation of the ion.

Hence, the observed decrease in proton affinity for the overall protonation $\delta(-\Delta H_\beta)$ with increasing substitution is obviously due to a positive $\delta(-\Delta H_g)$ term that is overruled by a greater negative solvation term due to a decreased solvation around the ammonium ion.

As was the case for the enthalpy, the entropy of protonation in solution (ΔS) may be divided into an intrinsic term (ΔS_g) and terms arising from the solvation [cf. eqn. (1)]. Increasing *N*-methyl substitution will cause a slight increase of the intrinsic entropy term [9]. Moreover, the lower degree of solvation with increasing substitution (see earlier) is attented by a great loss of solvent molecules leading to a strong increase of the translational entropy. As a consequence, increasing substitution on nitrogen causes a remarkable increase of the entropy of protonation in solution.

Finally, it can be said that with increasing substitution the changes in both the enthalpy and the entropy of protonation in solution are dominated by terms arising from changes in the solvation of the ions. So, it is not surprising that, with increasing substitution, plots of the enthalpy of proto-

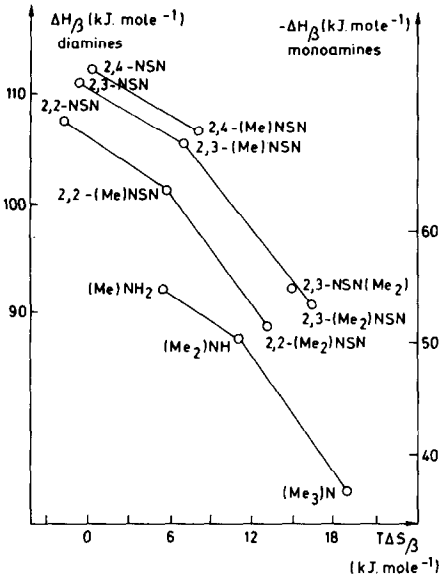


Fig. 1. $-\Delta H_\beta$ vs. $T\Delta S_\beta$ for monoamines and diamines.

nation vs. the entropy yield straight lines that are quite parallel for different series of amines (see Fig. 1).

Within a series of equally substituted diamines with varying n, m values, the sequences for both $-\Delta H_\beta$ and $T\Delta S_\beta$ are

2,2-NSN	< 2,3-NSN	< 2,4-NSN
2,2-NSN	< 3,3-NSN	< 4,4-NSN
2,3-NSN	< 3,3-NSN	< 4,3-NSN
2,4-NSN	< 3,4-NSN	< 4,4-NSN
2,2-(Me)NSN	< 2,3-(Me)NSN	< 2,4-(Me)NSN
2,2-(Me_2)NSN	< 2,3-(Me_2)NSN	
	2,3-NSN(Me_2)	< 3,3-(Me_2)NSN

The electrostatic protonation model may also be applied here. Increasing n/m values reduce the electron-withdrawing effect of the central S group, which causes the intrinsic proton affinity $[-\Delta H_g]$ to increase. But increasing chain length will also lower the charge density on the ammonium group, leading to a lower degree of solvation. But, insertion of a methylene group between sulphur and nitrogen is less effective in reducing charge density than direct substitution on nitrogen [8]. Moreover, within such a series there is no change in the ability to form hydrogen bonds to the solvent. Therefore, the increase in the intrinsic proton affinity $(-\Delta H_g)$ seems to be more important than the decrease in solvation of the ion and hence the proton affinity in solution $(-\Delta H)$ will increase with increasing chain length. The slightly decreasing solvation around the ammonium group and the concom-

itant positive translational entropy contribution is reflected in the $T\Delta S_\beta$ sequences. The differences, however, are much smaller than in the case of increasing *N*-methyl substitution.

Thermodynamic functions for the individual protonation steps

Because of the existence of two tautomeric forms, the protonation constants for the individual protonation steps of these asymmetric diamines are mixed constants. The percentage of the two tautomeric forms will be determined by the difference in the individual or micro-basicity ($-\Delta G$) of each amino group.

Hence, it can be expected that, within a series of asymmetric primary diamines with constant *n* value, the percentage of the tautomeric form II (with the proton on the nitrogen that is the farthest remove from sulphur) will increase with increasing *m* values. And indeed, taking the basicities ($-\Delta G_1$ and $-\Delta G_2$) of the symmetrical 2,2-NSN as a reference, it is seen from Table 3 that the increase in $-\Delta G_1$ for 2,3-NSN (2.64 kJ) is more important than the increase in $-\Delta G_2$ (1.96 kJ). For 2,4-NSN, the increase in $-\Delta G_1$ (4.34 kJ) is relatively still more important than that in $-\Delta G_2$ (2.44 kJ).

On the contrary and for the same reason, taking the basicities of the symmetrical 4,4-NSN as a reference, it is seen from Table 3 that the decrease in $-\Delta G_1$ for both 3,4-NSN (1.27 kJ) and 2,4-NSN (1.65 kJ) is less important than the decrease in $-\Delta G_2$ (1.36 kJ and 4.56 kJ, respectively). Here too, the relative difference in change of $-\Delta G_1$ vs. $-\Delta G_2$ is more pronounced in the case of 2,4-NSN. The same conclusions can be drawn from the enthalpy and entropy changes.

The *N*-methyl-substituted diamines may be asymmetrical for two different reasons: (i) unequal *n* and *m* values and (ii) non-equivalent nitrogen atoms, i.e. primary versus secondary or tertiary amine groups.

So, within the series of 2,*m*-(Me)NSN, the percentage of each tautomeric form will depend on both effects. As the individual basicity ($-\Delta G$) of a secondary amine is stronger than that of a primary one, the percentage of tautomeric form I (with the proton on the secondary nitrogen) should, at least for 2,2-(Me)NSN, be greater than for the tautomeric form II. As the corresponding proton affinity ($-\Delta H$) of a secondary amine is smaller than that for a primary one, it is seen from Table 3 that for 2,2-(Me)NSN, $-\Delta H_1 < -\Delta H_2$. However, on increasing *m* or *n* and thereby increasing the distance of the electron withdrawing thioether group from the primary nitrogen, the percentage of tautomeric form II (in which the primary nitrogen is protonated) should also increase and, as a consequence, for 2,3-(Me)NSN and 2,4(Me)NSN a reversed sequence is found: $-\Delta H_1 > -\Delta H_2$ (see Table 3).

Within the series of amines of the type *n*,*m*-(Me_2)NSN and by analogy

with the greater basicity of primary amines versus tertiary amines, the percentage of tautomeric form II (with the proton on the primary nitrogen) will be the greatest. Increasing m values, or decreasing n values should increase this percentage. As a consequence, it is seen from Table 3 that the proton affinity in the first step $(-\Delta H_1)$ is greater than in the second step $(-\Delta H_2)$ and that their mutual difference is greater for 2,3-(Me_2)NSN (13.9 kJ) than for 2,2-(Me_2)NSN (7.5 kJ) and 3,3-(Me_2)NSN (9.6 kJ).

Finally, for 2,3-NSN(Me_2) the primary nitrogen should be the easier to protonate but its shorter distance to electron withdrawing thioether group may alter this ability. The lower value of the proton affinity in the first step $(-\Delta H_1 < -\Delta H_2)$ proves that the second effect is the more important.

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