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Protonation of noncyclic and cyclic diamines in aqueous solution

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Abstract

Potentiometric and calorimetric methods were used to determine the protonation constants and thermodynamic values of the protonation of different noncyclic 1,5-diamines, noncyclic 1,8-diamines and cyclic 1,8-diamines in aqueous solution. The ligands were modified by oxygen and sulfur atoms at the 3- and 6-position. The measured values of the stability constants and reaction enthalpies are compiled with data from the literature. The protonation constants of the alkyl diamines exceed those of the alkyl diamines containing oxygen or sulfur atoms by more than one order of magnitude. The main contribution to the protonation constants of the noncyclic ligands is the reaction enthalpy. The values of the reaction entropies of the noncyclic diamines are nearly constant and close to zero. No intramolecular stabilization of the protonated amines by hetero atoms could be observed in aqueous solution. © 1997 Elsevier Science B.V.

Keywords: Diamines; Protonation; Stability constants; Thermodynamic properties

1. Introduction

The protonation of nitrogen containing macrocyclic and macrobicyclic ligands such as azacrown ethers and cryptands in aqueous solutions has been studied by several authors [1–4]. In contrast, only few investigations have dealt so far with the protonation reaction of the noncyclic diamino analogues. The knowledge of equilibrium constants and the thermodynamic values of the protonation reaction is necessary in order to calculate the stability constants of metal complexes obtained by pH-metric titrations in aqueous solutions.

Protonation reactions have also been measured in the gas phase. From these measurements it is known that an intramolecular stabilization of the protonated amine containing additional donor atoms takes place. This stabilization is possible in case of aliphatic amines with a hetero atom at the 3 or 4 position [5–7]. In aqueous solution the additional donor atoms of the macrocyclic and macrobicyclic diamines (azacrown ethers and cryptands) are involved in the formation of the monoprotonated diamines [8]. Therefore, it is interesting to find out if such an intramolecular stabilization of a noncyclic protonated diamine also occurs in aqueous solution. This is studied by measuring the thermodynamic values of the protonation of several noncyclic diamines in aqueous solution. The influence of the inductive effect by the methylene groups is also taken into account. Finally the influence of oxygen and sulfur atoms in the chain of the noncyclic ligands and the influence of the macrocyclic and macrobicyclic ring structure for

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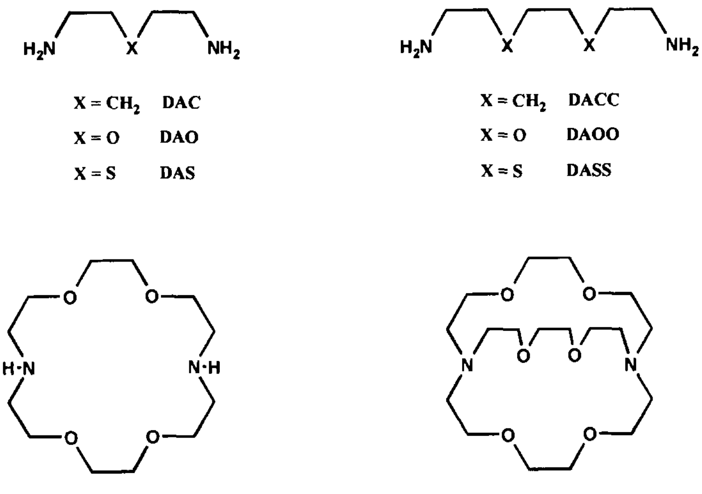
the protonation reaction are discussed. All available data from the literature are enclosed in this interpretation.

2. Experimental

The following commercially available ligands were used: methylamine, ethylamine, propylamine butylamine, pentylamine (all from Fluka, New Ulm, Germany), 1,5-diaminopentane (DAC, Fluka, New Ulm, Germany), 1,5-diamino-3-oxa-pentanehydrochlorid (DAO, Fluka, New Ulm, Germany), 1,5-diamino-3-thia-pentane (DAS, K and K), 1,8-diaminooctane (DACC, Fluka, New Ulm, Germany), 1,8-diamino-3,6-dioxaoctane (DAOO, Merck, Darmstadt, Germany), 1,10-diaza-4,7,13,16-tetraoxa-cyclooctadecane (Kryptofix 22, Merck, Darmstadt, Germany) and 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo [8.8.8] hexacosan (Kryptofix 222, Merck, Darmstadt, Germany). 1,8-diamino-3,6-dithiaoctane (DASS) was synthesized as described in the literature [9,10]. The chemical structures of the ligands are given in Fig. 1. All solutions were prepared with double distilled water.

The protonation constants of the diamines were determined by potentiometric titrations [8,11]. A solution of tetramethylammonium hydroxide (0.06 mol l^{-1}) was titrated into 20 ml aqueous solution containing the ligand (0.01 mol l^{-1}), to which hydrochloric acid (0.1 mol l^{-1}) was added to achieve a low pH-value. The ionic strength was kept constant during the measurement by a supporting electrolyte (tetraethylammonium perchlorate) at 0.05 mol l^{-1}. The titration was automatically performed using a Metrohm Dosimat 665 and a pH-electrode (Metrohm 6.0203.100).

The reaction enthalpies were determined using a Tronac Model 450 calorimeter. During the calorimetric titration a solution of hydrochloric acid (0.02–0.05 mol l^{-1}) was titrated continuously into 40 ml solution of ligand (0.02-0.05 mol l^{-1}) for one minute. In this case the actual proton concentration in the reaction vessel is much lower than the ligand concentration. Under these experimental conditions only monoprotonation takes place. The measured heat after correction for all non-chemical effects depends on the number of moles and the reaction enthalpy of the monoprotonated ligand formed during the titration. To determine the reaction enthalpy of the second protonation step it is necessary to titrate a solution of ligand (0.02–0.05 mol l^{-1}) into 40 ml hydrochloric acid (0.02–0.05 mol l^{-1}). Thus, the proton concentration is much higher than the ligand concentration, so both nitrogen atoms are protonated. According to the prior measured value of the reaction enthalpy for the



Ligand (22) Ligand (222)

Fig. 1. The chemical structures of the ligands.

monoprotonation, the reaction enthalpy for the second protonation step can be calculated [12–14]. In the case of the bis-(2-aminoethyl)ether hydrochloride the deprotonation of the amines is measured using tetramethylammonium hydroxide as titrant. Then the thermodynamic data can be calculated based on the known enthalpy of -55.84 kJ mol^{-1} [15] for the formation of water by neutralisation. Due to the fact that the calorimetric titrations were performed in non-buffered solutions, the formation of water has to be taken into account. Based on the stability constant for the protonation reactions the concentration of hydroxyl ions was calculated for each calorimetric titration. The experimentally obtained values for both protonation reactions were corrected with respect to the water formation.

3. Results and discussion

The protonation reaction of amines in solution is influenced by the inductive effect of the methylene groups in the alkyl chain and a possible intramolecular stabilization with hetero atoms. The heats of protonation of some primary alkylamines are given in Table 1 together with data from the literature. The value of the reaction enthalpy increases with the number of methylene groups in the alkyl chain, caused by the inductive effect of the substitute. As shown in Fig. 2 the enthalpy of the protonation reaction reaches a maximum depending on the increasing number of methylene groups. Due to the problems with solubility of alkylamines in aqueous solution it is not possible to measure the heat of protonation with alkylamines containing six or more carbon atoms.

Table 1
Reaction enthalpies ΔH for amine protonation in aqueous solution at 25°C

Amine	$-\Delta H$/(kJ mol^{-1})				
Ammonia	52.3[a]	52.0[b]	52.3[c]	52.4[d]	
Methylamine	54.9	55.6[d]	55.5[e]	54.8[f]	
Ethylamine	56.9	57.4[d]	56.9[g]		
Propylamine	57.4	57.9[d]	58.0[g]	57.6[h]	
Butylamine	58.7	58.5[d]	58.9[g]	58.5[h]	58.2[i]
Pentylamine	59.5	58.5[d]			

[a] [18], [b] [19], [c] [20], [d] [17], [e] [21], [f] [22], [g] [23], [h] [24], [i] [25].

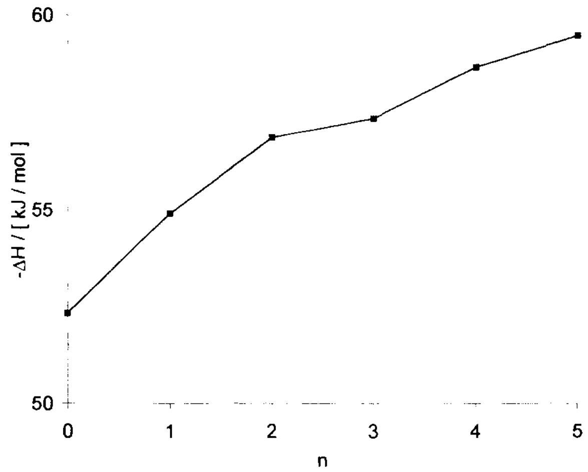


Fig. 2. Plot of the protonation reaction enthalpy of primary alkylamines versus the number of methylene groups n in the alkyl chain

In Table 2 the equilibrium constants and thermodynamic values of the protonation reaction are compiled and compared with published results, which are generally in accordance with the measured data. The values of the protonation constant and the reaction enthalpy of the alkylamines without hetero atoms are higher than those with hetero atoms. The inductive effect of the methylene groups between the two amino groups is responsible for this effect. The value of the protonation enthalpy of the alkylmonoamines with three or four methylene groups is 57.4 or 58.7 kJ mol^{-1}, which corresponds to the reaction enthalpy of the first protonation (ΔH_1) of DAC (60.5 kJ mol^{-1}) and DACC (60.3 kJ mol^{-1}). This result clearly demonstrates that in the case of the alkyl diamines the proton only interacts with one nitrogen atom. In contrast to observations in the gas phase [5–7] no intramolecular cyclization of the alkyl diammonium ion is found in the solution.

The first protonation constants of the alkyldiamines containing oxygen or sulfur atoms are nearly two orders of magnitude lower than those for the alkyl diamines, a fact which can be explained as a prevention of the inductive effect by the hetero atoms. The calculated reaction enthalpy of the first protonation step of DAO, DAOO, DAS and DASS should nearly be the same as for the methylamine, which is confirmed by measurements. The values of the

Table 2
Stability constants log K, [K in l/mol] and thermodynamic values ΔH, $T\Delta S$ for the protonation reaction of noncyclic and cyclic diamines in aqueous solutions at 25°C

Compound	log K_1	$-\Delta H_1$/[kJ mol^{-1}]	$T\Delta S_1$/[kJ mo l^{-1}]	log K_2	$-\Delta H_2$/[kJ m ol^{-1}]	$T\Delta S_2$/[kJ mol^{-1}]
DAC	11.57	60.5	5.5	9.55	53.1	1.4
	10.92[c]	58.1[c]	4.2[c]	10.15[c]	56.9[c]	1.0[c]
	10.78[a]			9.85[a]		
	10.96[b]			10.02[b]		
	11.39[d]			10.59[d]		
DAO	9.76	53.4	2.3	8.70	54.2	−4.6
	9.88[e]	49.0[e]	6.1[e]	8.94[e]	55.3[e]	−4.9[e]
	9.75[o]	50.7[o]	4.9[o]	8.90[o]	54.3[o]	−3.5[o]
DAS	9.68	52.6	2.6	8.39	43.2	4.7
	9.68[r]	54.1[r]	1.1[r]	8.82[r]	53.3[r]	−3.0[r]
	9.58[f]			8.82[f]		
DACC	11.40	60.3	4.7	10.08	54.7	2.8
DAOO	9.79	53.6	2.3	8.83	47.1	3.3
	9.88[e]	47.7[e]	7.4[e]	8.87[e]	46.1[e]	3.7[e]
	9.71[g]	49.8[g]	6.7[g]	8.91[g]	50.7[g]	−0.8[g]
DASS	9.51	50.7	3.6	8.91	48.5	2.3
	9.46[r]	51.1[q]	3.9[o]	8.56[o]	51.1[q]	−2.3[q]
	9.64[s]	54.5[s]	0.5[s]	8.97[s]	53.9[s]	−2.7[s]
	9.61[f]			9.00[f]		
22	8.95	36.8	14.3	7.94	40.5	4.8
	8.92[h]	38.4[h]	12.5[h]	7.56[h]	53.8[h]	−10.8[h]
	9.08[g]	36.0[g]	15.8[g]	7.94[g]	39.8[g]	5.5[g]
	9.20[i]			8.02[i]		
	9.25[l]			8.23[l]		
222	10.21[h]	51.9[h]	6.4[h]	7.55[h]	29.9[h]	13.0[h]
	9.71[g]	45.2[g]	10.2[g]	7.31[c]	18.8[g]	22.8[g]
	10.00[i]			7.53[i]		
	9.60[m]			7.28[m]		
	10.66[n]			9.86[n]		
	9.95[k]			7.59[k]		

[a] [33], [b] [34], [c] [35], [d] [36], [e] [26] at 20°C, [f] [27] at 30°C, [g] [28], [h] [8], [i] [29], [k] [30], [l] [31], [m] [11], [n] [32], [o] [37], [p] [38], [q] [39], [r] [40].

protonation constants are nearly identical for the diamines containing one or two hetero atoms. No effect can be observed from the exchange of sulfur and oxygen in the alkyl chain. The values of the reaction enthalpy for the second protonation step are nearly the same for DAOO, DAS and DASS. For the unusual behavior of DAO no reason can be given yet.

In the case of the noncyclic diamines the values of the reaction entropy are low and close to zero so that the stability constant log K is mainly influenced by the reaction enthalpy. Therefore the quotient of the reaction enthalpy over the stability constant log K should give a nearly constant value. This is shown in Table 3.

For the noncyclic diamines the quotient of the reaction enthalpy over the logarithm of the stability constant is nearly constant at 5.38±0.15 kJ mol^{-1}.

The macrocyclic and macrobicyclic diamines are not directly comparable with the alkyl diamines. The basicity of the nitrogen atoms decreases from primary to secondary and tertiary amines. The first protonation reaction enthalpy of (222) ($\Delta H_1 = -51.9$ kJ mol^{-1}) has to be compared with the protonation reaction of trimethylamine ($\Delta H = -36.9$ kJ mol^{-1}) and the first reaction enthalpy of (22) ($\Delta H_1 = -36.8$ kJ mol^{-1}) with dimethylamine ($\Delta H = -50.3$ kJ mol^{-1}) [16]. The observed differences are caused by additional interactions between the proton and hetero atoms of

Table 3
Values of the reaction enthalpy in [kJ mol^{-1}] divided by the protonation constant

	$-\Delta H/\log K_1$	$-\Delta H/\log K_2$
DAC	5.23	5.56
DAO	5.31	6.23
DAS	5.43	5.40
DACC	5.29	5.43
DAOO	5.47	5.33
DASS	5.33	5.44
22	4.11	5.10
222	5.08	3.96

the ligands [8]. The second proton is located outside the cavity due to the repulsion between two positive charges inside the cavity. Thus the behavior of macrocyclic and macrobicyclic diamines is quite different compared with the alkyl diamines, where no additional interactions between the proton and the other donor atoms are observed.

In conclusion it can be stated that according to the measured data the protonation of amines is influenced by the inductive effect and the molecular structure. Oxygen or sulfur atoms are involved in the inductive effect of the methylene groups. This applies to the noncyclic ligands, but not to the cyclic analogues. In the case of the macrobicyclic cryptand (222) the second nitrogen atom is close enough to the protonated nitrogen to allow a further stabilization of the positive charge. The observed intramolecular stabilization of the protonated amine by hetero atoms in the gas phase could not be measured for the flexible ligands in aqueous solution.

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