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Thermodynamic Parameters for the Formation of Pyrophosphate-protonated Polyamine Complexes†

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This work reports thermodynamic parameters for the complex formation of pyrophosphate-protonated amines (ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine and pentaethylenehexamine): as already found for log *K*, the $T\Delta S^\circ$ parameter also shows a linear dependence on the charges involved in the formation reaction.

Previous work[1] included stability data concerning the formation of pyrophosphate-protonated polyamine complexes. The results of this work showed that the stability of these complexes is high enough to justify the hypothesis that in some biochemical reactions catalysed by a metal ion the protonated amine might replace these metal ions. We also found that the stability of the pyrophosphate with variously protonated amines is directly proportional to the charges involved in the formation reaction: this makes it possible, through the study of a relatively small number of systems, to identify the characteristics of virtually any amine-pyrophosphate system. Little work[2,3] is to be found in the literature regarding the determination of the enthalpy of formation ΔH° for anion coordination species, and in most cases only cyclic polyamines have been considered. Labadi *et al.* have made calorimetric studies of spermidine– and spermine–pyrophosphate systems.[4]

This work describes calorimetric studies of H^+-pyrophosphate–ethylenediamine, –diethylenetriamine, –triethylenetetramine, –tetraethylenepentamine, and –pentaethylenehexamine systems in the hope both of providing a more complete picture of the thermodynamics of these systems and of making it possible to convert stability data at 25 °C into data at other temperatures (in particular to 37 °C, body temperature).

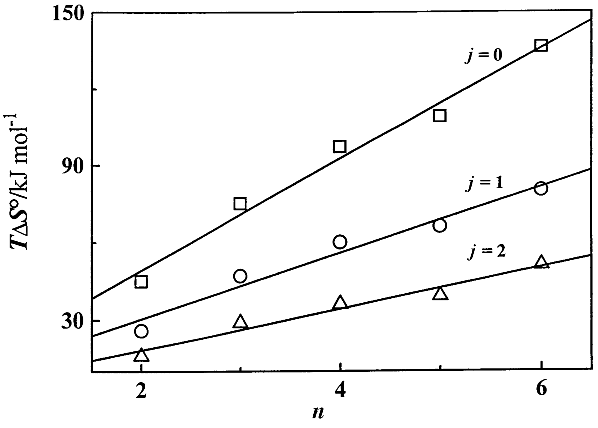

Fig. 1 $T\Delta S^\circ$ values *versus n* (maximum degree of amine protonation) for reaction (1)

Formation constants of $P_2O_7^{4-}$-protonated complexes have been already reported,[1] and ΔG° values, for all the species formed in the various systems, are given in Table 1. For the complexes of methylamine and polyamines having the general formula $C_{(2n-2)}N_nH_{(5n-2)}$, by considering the reaction

$$H_iA^{i+} + H_jP_2O_7^{(j-4)+} = A(P_2O_7)H_{i+j}^{(i+j-4)+} \qquad (1)$$

we have the simple relationship (ΔG°/kJ mol^{-1}):

$$-\Delta G^\circ_{ij} = 4.1(\pm 0.2)\zeta \qquad (2)$$

where $\zeta = |z_{\text{anion}} \times z_{\text{cation}}| = i(j-4)$. By assuming that the number of possible salt bridges is roughly given[5] by $n = \zeta/2$, we have

$$-\Delta G^\circ = 8.2(\pm 0.4)\ \text{kJ mol}^{-1}\ n^{-1} \qquad (3)$$

Table 1 ΔG° Values for $P_2O_7^{4-}$-protonated amine[a] complexes, at $T = 25$ °C and $I = 0$ mol dm^{-3}; reaction (1)

i	*j*	$-\Delta G^\circ$/kJ mol^{-1}	*i*	*j*	$-\Delta G^\circ$/kJ mol^{-1}	*i*	*j*	ΔG°/kJ mol^{-1}
		meta[b]			en[b]			dien
1	0	17.2 ± 1.0	1	0	17.5 ± 0.7	1	0	18.25 ± 1.8
1	1	11.6 ± 0.4	1	1	19.1 ± 0.1	2	0	31.1 ± 0.1
1	2	7.3 ± 0.3	2	1	22.5 ± 0.2	2	1	23.7 ± 0.2
			2	2	13.9 ± 0.4	2	2	21.6 ± 0.2
			2	3	7.0 ± 1.2	3	2	25.3 ± 0.3
						3	3	18.5 ± 0.5
		trien			tetren			penten
1	0	16.1 ± 1.8	1	0	15.2 ± 1.8	1	0	20.7 ± 0.7
2	0	31.5 ± 0.2	2	0	26.6 ± 0.3	2	0	28.5 ± 0.5
2	1	29.9 ± 0.3	2	1	29.1 ± 0.2	2	1	30.3 ± 0.2
3	1	37.3 ± 0.4	3	1	31.0 ± 0.2	3	1	36.4 ± 0.3
3	2	30.5 ± 0.2	3	2	29.0 ± 0.3	4	1	45.9 ± 0.6
4	2	35.7 ± 0.7	4	2	31.7 ± 0.4	4	2	40.3 ± 0.9
4	3	23.7 ± 1.2	5	2	33.9 ± 0.6	5	2	43.6 ± 1.2
						6	2	44.1 ± 1.8

[a] meta = methylamine, en = ethylenediamine, dien = diethylenetriamine, trien = triethylenetetramine, tetren = tetraethylenepentamine and penten = pentaethylenehexamine. [b] meta also forms $A_2LH_2^{2-}$, $A_2LH_3^-$ and $A_4LH_4^0$ species, en also forms $A_2LH_4^0$ and $A_2LH_5^+$ species (see ref. 1).

This value is in reasonable accordance with the ones ($-\Delta G^\circ_{ij} = 7.5$ and 6.2 kJ mol^{-1} n^{-1} obtained for several inorganic anion–polyammonium complexes[5] and ATP–polyammonium complexes,[6] respectively) already reported.

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Table 2 Thermodynamic parameters (kJ mol^{-1}) for the formation of H^+–amine–$P_2O_7^{4-}$ complexes at $T = 25$ °C and $I = 0$ mol dm^{-3} [reaction (1), $i = n$]

		$j = 0$			$j = 1$			$j = 2$		
	n	$-\Delta G^\circ$	ΔH°[a]	$T\Delta S^\circ$	$-\Delta G^\circ$	ΔH°[b]	$T\Delta S^\circ$	$-\Delta G^\circ$	ΔH°[c]	$T\Delta S^\circ$
en	2	34.7	10.0	45	22.5	4.0	26	13.9	2.1	16
dien	3	57.6	17.2	75	39.0	7.7	47	25.3	4.0	29
trien	4	78.5	18.9	97	55.3	5.1	60	35.7	0.4	36
tetren	5	89.2	19.5	109	59.3	6.4	66	33.9	5.3	39
penten	6	106.7	28.9	136	72.8	6.8	80	44.1	7.0	51

[a]±1.5. [b]±1.5. [c]±2.

If we consider reaction (1) with $i = n$ (maximum degree of protonation of amine)[7] we have a fairly good linear fit[8] of ΔG°_{nj} *versus* n. A more accurate equation with respect eqn. (2) is given by

$$-\Delta G^\circ_{nj} = 2.90\zeta + 0.40\zeta^2/n \qquad (4)$$

ΔH° values, associated with the reaction (1) for $i = n$, are reported in Table 2. All the values are positive, indicating that mainly electrostatic interactions are involved in the formation of these complexes. The $T\Delta S^\circ$ values in Table 2 follow a regular trend, as shown in Fig. 1, and can be expressed by the equation ($T\Delta S^\circ$/kJ mol^{-1})

$$T\Delta S^\circ_{nj} = 5.2(\pm 0.3)\zeta \qquad (5)$$

and

$$T\Delta S^\circ = 10.4(\pm 0.6)\ \mathrm{kJ\ mol^{-1}}\ n^{-1} \qquad (6)$$

A more accurate equation is given by

$$T\Delta S^\circ_{nj} = 5.8\zeta - 0.15\zeta^2/n \qquad (7)$$

By using eqns. (2), (5) and (4), (6) we have (ΔH°/kJ mol^{-1})

$$\Delta H^\circ_{nj} = 1.1\zeta \qquad (8)$$

[from experimental data, $\Delta H^\circ_{nj} = 0.8(\pm 0.3)\zeta$], and

$$\Delta H^\circ = 2.2(\pm 0.7)\ \mathrm{kJ\ mol^{-1}} n^{-1} \qquad (9)$$

Labadi *et al.* reported[4] ΔH°_n values for pyrophosphate–spermidine and –spermine complexes (19.7 and 26.5 kJ mol^{-1}, respectively) which are in fairly good agreement with our findings for diethylenetriamine and triethylenetetramine. Temperature corrections (quite small) for log K_{ij} are obtained using eqn. (8) (by considering, as a first approximation, ΔH° to be independent of temperature):

$$\delta(\log\ K_{ij}) = 6 \times 10^{-4}(T/^\circ\mathrm{C} - 25)\zeta \qquad (10)$$

The main conclusions are that this work, together with previous results,[1] gives a full description of the thermodynamic parameters for the formation of protonated amine–pyrophosphate complexes, and the electrostatic nature of the interactions is confirmed by considering both the positive values of ΔH° and the linear dependence of ΔG°, ΔH° and $T\Delta S^\circ$ on charges [Fig. 1; eqns. (2)–(9)]. Approximate temperature corrections (which can be used, presumably, also for other similar systems) are given by eqn. (10).

Experimental

Amines (ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine and pentaethylenehexamine, Fluka products) were purified by transformation into the corresponding hydrochlorides, and were used in this form. Tetrasodium diphosphate [$Na_4P_2O_7$, Fluka, puriss.] was used without further purification. The $Na_3HP_2O_7$ solution was prepared by adding standard HCl to an $Na_4P_2O_7$ solution. The purity of these reagents was tested by potentiometric titrations. The HCl solution was prepared by diluting concentrated ampoules (Fluka) and standardised by sodium carbonate. All the solutions were prepared using doubly distilled water and grade A glassware. Calorimetric measurements were performed at 25.000 ± 0.001 °C with a Tronac isoperibol titration calorimeter mod. 450 coupled with a Keithley 196 system Dmm digital multimeter. A computer program was used for the acquisition of the calorimetric data. Some 25 cm^3 of the amine solution 0.01 mol dm^{-3} was titrated with $Na_3HP_2O_7$ or $Na_2H_2P_2O_7$ 0.15 mol dm^{-3}. By following this procedure the formation of $A(P_2O_7)H_r^{(r-4)+}$ complexes with $n \le r \le (n + 2)$ (n = maximum protonation degree of amine) was considered. Separate titrations were performed to calculate dilution heats. Calorimetric titration data were analysed by the computer program ES5CM.[9] The dependence on ionic strength of formation enthalpies was taken into account as already proposed in the literature.[10] The ΔH° values for the protonation of pyrophosphate and amines have been reported previously.[11,12] Throughout, errors are given as ≥95% confidence interval.

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7 Note that the equilibrium constants (and the ΔG° values reported in Table 1) for reaction (1) refer to the most probable reaction, as a function of protonation constant values of pyrophosphate and amines, whilst the formation parameters (Table 2) for $i = n$ (maximum degree of amine protonation) often refer to a hypothetical reaction. Nevertheless, these last parameters are useful in recognising patterns and empirical relationships.

8 Correlation coefficients are: ΔG°, $r = 0.9953$, 0.9905 and 0.9274, and for $T\Delta S^\circ$, $r = 0.9914$, 0.9819 and 0.9797, for $j = 0$, 1 and 2, respectively. On the basis of a student's t test these values are always highly significant.

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