Thermochimica Acta, 68 (1983) 83–89
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CALORIMETRIC STUDY OF THE INTERACTION OF TRI- AND TETRAMETAPHOSPHATE WITH SOME TRIVALENT CATIONS

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(Received 5 April 1983)

ABSTRACT

Tri- and tetrametaphosphate were used in calorimetric titrations of Al^{3+}, Y^{3+}, La^{3+} and $[Co(NH_3)_6]^{3+}$ in aqueous solutions. The enthalpies of reaction and equilibrium constants were determined for the complexation reactions. In every case, the ion pair of metal to cyclic phosphate in a 1 : 1 proportion is the complex species. The thermodynamic data as calculated by the least-squares method range between 2.28 and 37.8 kJ mole^{-1} for the enthalpies, and 56 and 190 J K^{-1} mole^{-1} for the entropies. These thermodynamic data indicate that the stability of these complexes is mainly due to the gain in entropy.

INTRODUCTION

The cyclic phosphates, when compared with the corresponding linear polyphosphates, are considered as relatively weak complexing agents. This fact has contributed to the lesser attention given to tri- and tetrametaphosphate.

The formation of ion pairs between M^{n+} cations and $P_3O_9^{3-}$ and $P_4O_{12}^{4-}$ anions, has been studied mainly for bivalent ions by conductometry and by potentiometry [1,2]. Trivalent cations also react with tri- and tetrametaphosphate with formation of an apparently stronger ion pair [3,4].

Although the stability constants have been determined in some of the systems studied, no determination of the heats of the reactions have been performed. These parameters are important in order to investigate the nature of ion association in solution.

In this work, we present results concerning the interaction of tri- and tetrametaphosphate with Al^{3+}, Y^{3+}, La^{3+} and $[Co(NH_3)_6]^{3+}$ in aqueous solution as investigated by titration calorimetry.

EXPERIMENTAL

$Na_3P_3O_9 \cdot 6\ H_2O$ and $Na_4P_4O_{12} \cdot 4\ H_2O$ were prepared and purified according to procedures described elsewhere [3,4].

0040-6031/83/$03.00

Preparation of the solutions

The solution of Al^{3+} was prepared by dissolving $AlCl_3 \cdot 6\ H_2O$ in bidistilled water and the H_3O^+ concentration maintained at 0.1 M, since in this condition, the hydrolysis of Al^{3+} is negligible [5]. The concentration of the Al^{3+} solution utilized in every titration was 0.04653 M.

The solutions of YCl_3 and $LaCl_3$ were prepared by dissolution of the corresponding oxide of 99.99% purity, previously calcined at 900°C, with hydrochloric acid. The concentrations utilized were 0.00990 M for Y^{3+} and 0.00981 M for La^{3+}. In both solutions, the H_3O^+ concentrations were maintained at 0.1 M in order to avoid hydrolysis of the ions [6].

The solution of $[Co(NH_3)_6]^{3+}$ was prepared by dissolution of the chloride in bidistilled water. The solution utilized was 0.00400 M and in this case the solution was not acidified.

Solutions of tri- and tetrametaphosphates were always prepared immediately before use. Standardizations were made by passing the solution of the salt through a strong cationic resin and titrating the liberated acid. The concentrations utilized were 0.1860 M for both salts for titration of Al^{3+}, Y^{3+} and La^{3+} and 0.0800 M for both salts for titration of $[Co(NH_3)_6]^{3+}$.

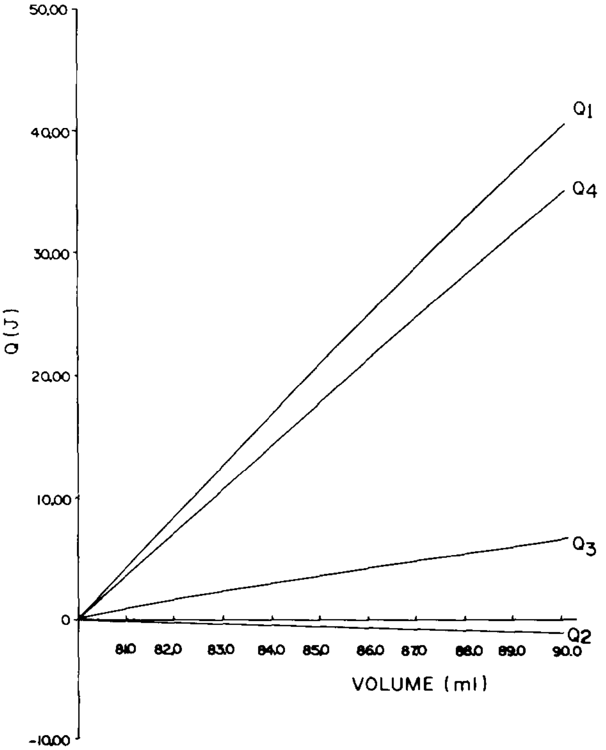

Fig. 1. Calorimetric titration of Al^{3+} with $P_3O_9^{3-}$.

Measurements

The measurements were made in a precision calorimeter LKB8700-2 and the temperature of the system was maintained at 25.00 ± 0.05°C. The equipment was calibrated as described in our previous work [7]. The incremental titrations were made in three steps: (i) 80.00 ml of the MCl_3 solution was placed in the calorimetric vessel and titrated with the cyclic phosphate solution through an automatic buret; (ii) 80.00 ml of MCl_3 was titrated with pure water in order to determine the heat of dilution of the metal; (iii) 80.00 ml of pure water was titrated with cyclic phosphate in order to determine the heat of dilution of the anion.

A typical result is shown in Fig. 1 for the titration of Al^{3+} with $P_3O_9^{3-}$ where Q_1 is due to the reaction $Al^{3+}_{(aq)} + P_3O^{3-}_{9(aq)} = AlP_3O_{9(aq)}$, the heat of dilution of the metal is Q_2 and the heat of the dilution of the $P_3O_9^{3-}$ is Q_3. The net heat of the reaction is $Q_4 = Q_1 + Q_2 + Q_3$.

IR measurements

Infrared spectra of aqueous solutions of tri- and tetrametaphosphate alone and containing Al^{3+} were obtained. A liquid cell equipped with Irtran II windows and a path length of 0.015 mm was utilized to record the spectra. The equipment used was the Perkin-Elmer model 180.

CALCULATIONS

The calculations were carried out considering the equilibrium

$$M^{3+}_{(aq)} + \text{Phosphate}^{n-}_{(aq)} = \text{MPhosphate}^{3-n}_{(aq)}$$

K is defined by

$$K = \frac{[\text{MPhosphate}^{3-n}]}{[M^{3+}][\text{Phosphate}^{n-}]}$$

The values of K and ΔH of the reaction were calculated by the method of least squares and the best values for K and ΔH were those which minimized the function

$$U(K_i, \Delta H_i) = \sum_{i=1}^{n} [Q_i(\text{obsd.}) - Q_i(\text{calcd.})]^2$$

where Q_i(obsd.) and Q_i(calcd.) are the observed and calculated heats of reaction, respectively [8,9].

RESULTS AND DISCUSSION

Table 1 shows the results of the calorimetric titration of Al^{3+} with $P_3O_9^{3-}$. The fit between the calculated curve and the experimental one, considering only the species AlP_3O_9 is reasonably good. The formation of the 1 : 1 ion pair as the main species is also observed for all titrations. Table 2 presents the calculated thermodynamic data corresponding to each system, giving the best fit [minimum $U(K_i, \Delta H_i)$].

It is observed that in every case the change in enthalpy as well as entropy is positive. For the systems studied here in which the interactions are essentially of an ionic type, the formation of the complex should be assigned to a high gain in entropy since a positive change in the enthalpy counteracts the formation of the chemical bond. The origin of these entropy gains observed here, may arise from the liberation of water molecules from the hydration shells of the cation and anion in the formation of the complexes [10]. The trivalent cations show a high overall hydration number, especially Al^{3+}, Y^{3+} and La^{3+} [11,12], while for $[Co(NH_3)_6]^{3+}$, which has only a secondary hydration shell, this number should be lower [13]. This should explain why $[Co(NH_3)_6]^{3+}$ reacts with $P_3O_9^{3-}$ and $P_4O_{12}^{4-}$ with less positive entropy.

The value of ΔS is related to the electrostatic interaction [10,14], i.e. it increases as the ionic charge increases. With respect to this, we studied the vibrational spectra in solution in order to obtain qualitative information about what happens to the ligand IR bands when the anion is in the presence of highly charged cations. Reliable measurements were made only

TABLE 1

Distribution of the species and the calculated heats of reaction

$[P_3O_9^{3-}]\times 10^3$ (mole l^{-1})	$[Al^{3+}]\times 10$ (mole l^{-1})	$[AlP_3O_9]\times 10$ (mole l^{-1})	Q(calcd.) (J)	δ [a] (J)
	0.46530			
0.04557	0.43705	0.02251	3.582	−0.185
0.09596	0.40954	0.04441	7.154	−0.132
0.15192	0.38277	0.06571	10.715	0.042
0.21442	0.35671	0.08643	14.263	−0.016
0.28461	0.33136	0.10657	17.796	0.195
0.36394	0.30670	0.12613	21.311	−0.035
0.45420	0.28274	0.14512	24.804	0.035
0.55768	0.25948	0.16352	27.270	0.072
0.67728	0.23692	0.18132	31.704	0.069
0.81671	0.21509	0.19851	35.099	−0.045

[a] $\delta = [Q_i(\text{obsd.}) - Q_i(\text{calcd.})]$

TABLE 2

Thermodynamic data [a] for MP_3O_9 and $MP_4O_{12}^-$

	$P_3O_9^{3-}$				$P_4O_{12}^{4-}$			
	Al^{3+}	Y^{3+}	La^{3+}	$[Co(NH_3)_6]^{3+}$	Al^{3+}	Y^{3+}	La^{3+}	$[Co(NH_3)_6]^{3+}$
log K	3.05 ± 0.03	3.19 ± 0.03	3.24 ± 0.05	3.11 ± 0.03	3.29 ± 0.04	3.44 ± 0.04	2.65 ± 0.04	2.28 ± 0.04
ΔH	19.6 ± 2.0	32.0 ± 3.0	18.9 ± 1.9	2.28 ± 0.2	37.8 ± 3.8	17.8 ± 1.8	10.8 ± 1.1	3.79 ± 3.8
ΔG	−17.4 ± 1.7	−18.2 ± 1.8	−18.5 ± 1.9	−17.7 ± 1.7	−18.8 ± 1.9	−19.6 ± 1.9	−15.1 ± 1.5	−13.0 ± 1.3
ΔS	124 ± 12	168 ± 17	126 ± 13	67 ± 7	190 ± 19	125 ± 12	87 ± 9	56 ± 6

[a] Units: K, l mole^{-1}; ΔH and ΔG, kJ mole^{-1}; ΔS, J K^{-1} mole^{-1}.

TABLE 3

Vibrational frequencies[a] (cm^{-1}) of the tri- and tetrametaphosphate in aqueous solution

$P_3O_9^{3-}$			$P_4O_{12}^{4-}$		
Raman, sodium[b] salt	Infrared		Raman, sodium[b] salt	Infrared	
	Sodium[c] salt	$\frac{[P_3O_9^{3-}]}{[Al^{3+}]} = 0.6$		Sodium[c] salt	$\frac{[P_4O_{12}^{4-}]}{[Al^{3+}]} = 0.6$
		1280s			1290s
	1266s	1265sh		1271s	1270w
1155s,p		1175m	1155s,p		1163m
		1107w		1102m	1108m
	1088s	1088m			
	1005	1005		1005	1010

[a] Abbreviations used: s = strong, w = weak, m = medium, sh = shoulder, p = polarized.

[b] Saturated solution.

[c] $[P_3O_9^{3-}] = 0.09$ M and $[P_4O_{12}^{4-}] = 0.08$ M.

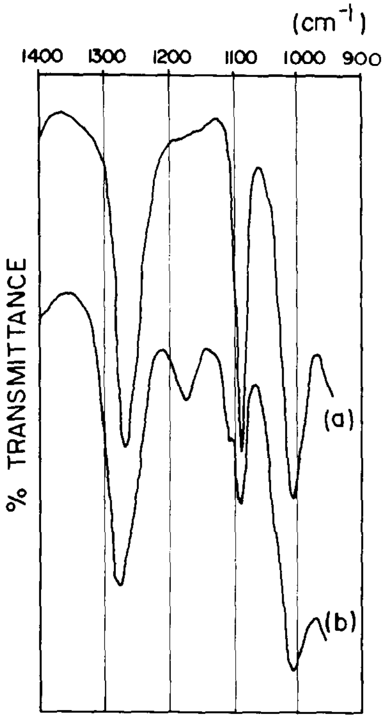

Fig. 2. Infrared spectra of aqueous solutions of (a) $Na_3P_3O_9$, 0.09 M and (b) $|P_3O_9^{3-}|/|Al^{3+}| = 0.6$.

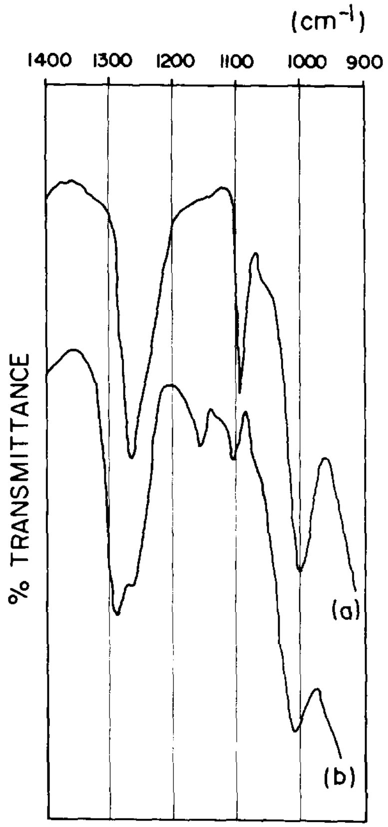

Fig. 3. Infrared spectra of aqueous solutions of (a) $Na_4P_4O_{12}$, 0.08 M and (b) $|P_4O_{12}^{4-}|/|Al^{3+}| = 0.6$.

with the ion pairs AlP_3O_9 and $AlP_4O_{12}^-$ since good spectra could not be obtained for the other metals due to precipitation of the compounds.

Results in Table 3 show that both $Na_3P_3O_9$ and $Na_4P_4O_{12}$ show one polarized band in the Raman spectra at 1155 cm^{-1}. This band corresponds to the symmetric stretching vibration $\nu_s PO_2^-$. The infrared spectra show the $\nu_{as}PO_2^-$ band at 1266 cm^{-1} for $P_3O_9^{3-}$, and 1271 cm^{-1} for $P_4O_{12}^{4-}$. In the presence of Al^{3+}, these infrared bands (Figs. 2 and 3) are split with the appearance of new bands at 1280, 1175 and 1107 cm^{-1} for the AlP_3O_9 ion pair and 1290 and 1163 cm^{-1} for the $AlP_4O_{12}^-$ ion pair. This is possible because $P_3O_9^{3-}$ and $P_4O_{12}^{4-}$ have a flexible ring and several conformations are possible for the free anion [4]. Therefore, the coulombic interaction of Al^{3+} with the anions is probably sufficiently strong to distort and change the symmetry of the $P_3O_9^{3-}$ and $P_4O_{12}^{4-}$ ions. The degree of intimate contact between the ions in each case is difficult to assess by vibrational spectroscopy, because symmetry changes of the ligand may occur within a solvent-separated ion pair [15].

ACKNOWLEDGEMENT

One of us (R.G.) is indebted to Conselho Nacional de Pesquisa for the award of a fellowship.

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