Thermochimica Acta, 157 (1990) 335–345
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

A THERMOMETRIC TITRATION STUDY OF THE INTERACTION OF Al^{3+}, Cd^{2+}, Pb^{2+} AND Zn^{2+} WITH ETHYLENEDIAMINETETRAACETIC ACID

R. BIN OTHMAN

Department of Chemistry, University Kebangsaan Malaysia, Kota Kinabalu,
Sabah 88996 (Malaysia)

N.G. BUCKMAN

Materials Chemistry Section, Herman Research Laboratory, State Electricity Commission,
Richmond, Victoria 3121 (Australia)

J.O. HILL and R.J. MAGEE

Department of Chemistry, La Trobe University, Bundoora, Victoria 3083 (Australia)

(Received 12 June 1989)

ABSTRACT

The molar reaction enthalpies for the interaction of Al^{3+}, Cd^{2+}, Pb^{2+} and Zn^{2+} with ethylenediaminetetraacetic acid (EDTA) in aqueous solution, at pH 8.7, have been determined by thermometric titrimetry as: 48.96 ± 2.56; -40.90 ± 1.52; -45.59 ± 0.43; and -14.98 ± 0.20 kJ mol^{-1} respectively. A concentration range for the analytical determination of each of these metal ions is established and some rationalisation of the reactions involved is attempted.

An interference study involving mixed metal–EDTA systems is interpreted in terms of the relative magnitudes of the corresponding complex stability constants involved, and supports the analytical significance of the overall enthalpy data for these systems.

INTRODUCTION

Complexometric titrations have progressively been developed over the last four decades for the analytical determination of a wide variety of metal ions in aqueous solution. This is essentially due to the parallel development of a variety of selective chelating agents which react with metal ions to give very stable 1 : 1 complexes. These reagents are generally water soluble macro-organic molecules containing 4–6 strategically located donor atoms which, when coordinated to a metal, form multiple chelate ring systems. A major family of these chelating agents consists of structures based on the ethylene-

0040-6031/90/$03.50

diamine skeleton, which upon complexation with metals form, primarily, five-membered ring systems. The best known are the polyaminepolycarboxylic acids, such as ethylenediaminetetraacetic acid (EDTA), 1,2-diaminocyclohexane-*N,N,N′,N′*-tetraacetate (DCTA), nitrilotriacetic acid (NTA), ethylenediaminediacetate (EDDA) and a variety of other aminocarboxylates [1–8]. Of these, EDTA is the most important, and has been used to determine a wide variety of metals by conventional volumetric procedures [9] based on the general reaction

$$M^{n+}(aq) + Y^{4-}(aq) \rightleftharpoons [MY]^{n-4}(aq) + H_2O$$

There has been much controversial debate on the structures of metal–EDTA complexes. In the solid state, Hoard and co-workers [10–12] have determined the structures of numerous metal–EDTA complexes by X-ray crystallography. Invariably, the ligand is bound to the metal via six donor atoms, and no evidence has been found for the presence of an uncomplexed acetate residue. Additional water molecules are bound in the manganous and ferric complexes, which are associated with seven-coordinated structures. X-ray studies of the crystalline protonated complexes $Co(OH_2)YH_2$ and $Ni(OH_2)YH_2$ (H_4Y = EDTA) reveal the presence of one unchelated acetate residue with the EDTA ligand bound in a quinquedentate mode. In solution, the structures of EDTA complexes are less certain, and have been deduced primarily from free energy, kinetic and spectroscopic data [5]. The similarity of acid dissociation constants [13] of the protonated complexes, $M(OH_2)YH^-$, of a large number of metal ions led Higginson [14] to conclude that this corresponded to the protonation of a free acetate arm, and to propose quinquedentate coordination in $M(OH_2)Y^{2-}$ complexes except, perhaps, for manganese(II). Conversely, marked changes in the visible spectrum of the Cu^{2-} and CoY^{2-} species during protonation indicated that these complexes contain at least a proportion of six-coordinated species [15].

EDTA has found extensive application in the determination of metals by thermometric titrimetry. In this context, the thermochemistry of metal–EDTA complexes has been concisely reviewed by Grime [16] and the principal thermodynamic data for these systems have been systematically summarised by Christensen et al. [17]. Significant early thermometric titrimetry studies of metal–EDTA complexes are those of Priestley et al. [18,19], Jordan and co-workers [20–22], Carini and Martell [23–25] and Charles [2], and these studies collectively have been assessed and reviewed by Tyrrell and Beezer [26]. More recent studies of these systems by thermometric titrimetry are those of Doi [27,28]. It is relevant here to review the thermodynamic data, as derived by thermometric titrimetry, for the environmentally significant Al^{3+}, Cd^{2+}, Pb^{2+} and Zn^{2+} $EDTA^{4-}$ systems.

For the $Al^{3+}/EDTA^{4-}$ system, Moeller and Chu [29] give $\Delta H_m^{\ominus}$ (298 K) = 0.4 kJ mol^{-1} and Yatsimirskii and Karacheva [30] quote 8.8 kJ mol^{-1}, both of these values refer to an aqueous medium of $\mu > 0$. Jordan and Alleman [22] give $\Delta H_m^\ominus$ (298 K) = 52.6 kJ mol^{-1}.

For the $Cd^{2+}/EDTA^{4-}$ system, Jordan and Alleman [22] give $\Delta H_m^\ominus$ (298 K) = −38.5 kJ mol^{-1}, Charles [2] gives −38.1 kJ mol^{-1} and Wright et al. [31] quote −42.3 kJ mol^{-1}, all for an aqueous medium of $\mu \geqslant 0$.

For the $Pb^{2+}/EDTA^{4-}$ system Jordan and Alleman [22] give $\Delta H_m^\ominus$ (298 K) = −53.6 kJ mol^{-1} and Wright et al. [31] quote −54.8 kJ mol^{-1}, both for an aqueous medium of $\mu \geqslant 0$.

For the $Zn^{2+}/EDTA^{4-}$ system, Jordan and Alleman [22] give $\Delta H_m^\ominus$ (298 K) = −19.3 kJ mol^{-1}, Charles [2] gives −18.8 kJ mol^{-1} and Wright et al. [31] quote −23.4 kJ mol^{-1}, all for an aqueous medium of $\mu \geqslant 0$.

It is apparent from these thermodynamic data for four metal–EDTA systems that considerable discrepancy exists between $\Delta H_m^\ominus$ values for each of these systems, and it is difficult to assess the accuracy of these data collectively as, in most cases, the reaction conditions are not precisely given.

Despite the extensive range of thermodynamic data available for M^{2+}–EDTA systems, the application of thermometric titrimetry to the direct determination of metals in environmental and biological samples, using EDTA as the selective complexing agent, has received little attention. In view of the recognised need for sensitive and rapid analytical methods for the determination of environmental pollutants such as aluminium, cadmium, lead and zinc in natural waters, the metal–EDTA system was reinvestigated by thermometric titrimetry with the aim of assessing this technique for the direct determination of specified metals in water. The molar enthalpies of the Al^{3+}, Cd^{2+}, Pb^{2+} and Zn^{2+}–EDTA reactions are determined and the interference effect on the reaction heat resulting from the presence of a variety of cations is established.

EXPERIMENTAL

Calorimeter and accessories

The thermometric titrimetry system employed and the associated calibration and data analysis procedures have been described in detail previously [32,33]. All derived thermodynamic data refer to 298 K, and the uncertainty associated with such data is quoted as the standard deviation from the mean.

Analytical procedures

Reaction heat Q_R, and molar reaction enthalpy, ΔH_R (kJ mol^{-1}), are calculated on the basis of the determined temperature variation, ΔT (mV), for the relevant quantitative calorimetric reaction and the associated average heat capacity, $\overline{C}_p$ (kJ mV^{-1}). $\overline{C}_p$ is the mean of the determined heat capacities before (C_{p_B}) and after (C_{p_A}) the thermometric titration.

$$Q_R = -\overline{C}_p \Delta T = n_p \Delta H_R$$

where n_p = number of moles of product formed. ΔH_R is determined on the assumption of a 1 : 1 titrant : titrate reaction. Titrant dilution heats, as determined by titration of EDTA (0.1 M) into titrate solutions minus metal, were found to be less than the overall experimental error of $\pm 5 \times 10^{-5}$ mV in ΔT determination.

Interference studies were conducted on the basis of a 1 : 1 cation : interferent mole ratio. The interference effect is expressed as the ratio Q'_R/Q_R, where Q'_R is the metal–EDTA reaction heat in the presence of an interfering ion. The extent of interference of a particular ion is interpreted in terms of the corresponding deviation of Q'_R/Q_R from unity.

Titrants and titrates

The titrant in all cases was 0.1 M EDTA prepared from AR grade EDTA tetrasodium salt (BDH). A stock solution was prepared using degassed, deionised water and stored under nitrogen. The burette delivery rate was 1.0355 ± 0.0001 cm^3 min^{-1}.

The titrate in all cases was an aqueous solution of the cation of interest $AlCl_3 \cdot 6H_2O$ (M&B); $CdSO_4 \cdot 8H_2O$, $Pb(NO_3)_2$ and $Zn(NO_3)_2 \cdot 4H_2O$ (BDH); 0.1 M stock solutions were prepared using deionised, degassed water and were diluted to the required concentration prior to use. For the interference studies, the titrate was spiked with a predetermined quantity of the interfering ion of interest using a 'Finpipette' (5–50 or 200–1000 μl). Adjustment of the titrate to the required pH was effected by incremental addition of H^+ to an ammonia–ammonium nitrate buffer (pH 9.5) and the pH was subsequently determined using a Labmos pH Electrometer, standardised using pH 4 and 7 (Radiometer) buffer solutions. The titrate volume throughout was 90.00 cm^3.

RESULTS AND DISCUSSION

A preliminary study of the effect of pH on the reaction heat for selected metal–EDTA reactions was undertaken, and the overall results are given in Table 1. As a general trend, as pH increases, the overall reaction becomes progressively more exothermic, as a result of the secondary formation of the metal hydroxide according to the reaction

$$MY^{(n-4)-} + nOH^- \rightleftharpoons M(OH)_n + Y^{4-}$$

TABLE 1

pH effect on M^{n+}–$EDTA^{4-}$ thermometric titrations

M^{n+} [a]	pH	$\Delta T \times 10^{-2}$ (mV)	C_{p_B}	C_{p_A}	$\bar{C}_p$	$Q_R \times 10^{-3}$ (kJ)
Al^{3+}	4.0	−0.32632	0.21233	0.21806	0.21520	0.70224
	8.7	−0.18426	0.20772	0.21323	0.21048	0.38781
	10.5	0.49474	0.21483	0.21778	0.21631	−1.07015
Cd^{2+}	4.0	−0.01053	0.21023	0.21521	0.21272	0.02239
	8.7	0.12983	0.21438	0.21696	0.21567	−0.27999
	10.5	0.37895	0.21219	0.21700	0.21460	−0.81319
Pb^{2+}	4.0	−0.05965	0.21391	0.21812	0.21602	0.12885
	8.7	0.21053	0.21200	0.21722	0.21461	−0.45181
	10.5	0.58597	0.20670	0.21108	0.20890	−1.22403
Zn^{2+}	4.0	−0.18233	0.20976	0.21480	0.21228	0.38704
	8.7	0.20211	0.21764	0.21813	0.21789	−0.44036
	10.5	0.50175	0.21622	0.21733	0.21677	−1.08766

[a] $[M^{n+}] = 10^{-4}$ mol dm^{-3}, except $[Zn^{2+}] = 3 \times 10^{-4}$ mol dm^{-3}.

Based on these data, pH = 8.7 was chosen for the systematic studies of these systems and to avoid metal hydroxide precipitation throughout.

Thermochemical data relating to the interaction of Al^{3+}, Cd^{2+}, Pb^{2+} and Zn^{2+} with $EDTA^{4-}$ (0.1 M) at pH 8.7 are given in Tables 2–5 respectively. For each of these metal ions, Q_R linearly correlates with $[M^{n+}]$ over the concentration ranges 1.80×10^{-5} to 2.25×10^{-4} (Al^{3+}); 1.13×10^{-5} to 2.71×10^{-4} (Cd^{2+}); 1.93×10^{-5} to 9.65×10^{-5} (Pb^{2+}); and 1.87×10^{-5} to 5.63×10^{-4} (Zn^{2+}) mol dm^{-3}. A least squares analysis of these data indicates that, over the concentration ranges given, the following relationships apply: $\Delta T = a[M^{n+}] + b$; Al^{3+}, $a = 20.4448$, $b = -0.00015$; Cd^{2+},

TABLE 2

Thermometric titration of Al^{3+} with $EDTA^{4-}$ (0.1 M)

$[Al^{3+}] \times 10^{-5}$ (mol dm^{-3})	$-\Delta T$ (mV)	Heat capacity (kJ mV^{-1})			$Q_R \times 10^{-4}$ (kJ)
		C_{p_B}	C_{p_A}	$\bar{C}_p$	
1.80000	0.00039	0.21361	0.21670	0.21515	0.83912
2.70000	0.00035	0.21230	0.22862	0.22046	0.77163
4.50000	0.00072	0.21482	0.21565	0.21523	1.54971
6.30000	0.00105	0.21691	0.22221	0.21956	2.30544
8.10000	0.00133	0.21320	0.21429	0.21394	2.84282
9.90000	0.00182	0.20784	0.21335	0.21060	3.83297
13.50000	0.00281	0.21008	0.21458	0.21233	5.96661
18.00000	0.00365	0.21860	0.22017	0.21938	8.00769
22.50000	0.00435	0.21356	0.21717	0.21537	9.39013

TABLE 3

Thermometric titration of Cd^{2+} with $EDTA^{4-}$ (0.1 M)

$[Cd^{2+}] \times 10^{-4}$ ($mol\ dm^{-3}$)	ΔT (mV)	Heat capacity ($kJ\ mV^{-1}$)			$-Q_R \times 10^{-4}$ (kJ)
		C_{p_B}	C_{p_A}	$\bar{C}_p$	
0.11292	0.0002	0.20913	0.21442	0.21178	0.44474
0.22584	0.0003	0.21093	0.21489	0.21291	0.83036
0.45168	0.0006	0.21509	0.21652	0.21581	1.44593
0.67752	0.0010	0.21176	0.21351	0.21263	2.12630
1.01628	0.0014	0.21450	0.21579	0.21515	3.01211
1.35504	0.0020	0.21473	0.21515	0.21513	4.45319
1.69380	0.0031	0.21036	0.21285	0.21160	6.68675
2.03256	0.0036	0.20952	0.21417	0.21185	7.62660
2.37132	0.0040	0.21020	0.21334	0.21177	8.61932
2.71008	0.0044	0.21436	0.21579	0.21508	9.50654

TABLE 4

Thermometric titration of Pb^{2+} with $EDTA^{4-}$ (0.1 M)

$[Pb^{2+}] \times 10^{-5}$ ($mol\ dm^{-3}$)	ΔT (mV)	Heat capacity ($kJ\ mV^{-1}$)			$-Q_R \times 10^{-4}$ (kJ)
		C_{p_B}	C_{p_A}	$\bar{C}_p$	
1.93060	0.00049	0.21046	0.21331	0.21189	1.03828
2.89590	0.00070	0.20949	0.21967	0.21458	1.50209
3.86210	0.00084	0.21391	0.21641	0.21516	1.80739
4.82650	0.00109	0.20888	0.21254	0.21071	2.29677
5.79180	0.00123	0.21154	0.21802	0.21478	2.64182
6.75710	0.00144	0.21103	0.21778	0.21440	3.08746
7.72240	0.00160	0.20992	0.21752	0.21372	3.41958
8.68770	0.00179	0.21213	0.21735	0.21474	3.84386
9.65300	0.00197	0.21352	0.21517	0.21434	4.22268

TABLE 5

Thermometric titration of Zn^{2+} with $EDTA^{4-}$ (0.1 M)

$[Zn^{2+}] \times 10^{-4}$ ($mol\ dm^{-3}$)	ΔT (mV)	Heat capacity ($kJ\ mV^{-1}$)			$-Q_R \times 10^{-4}$ (kJ)
		C_{p_B}	C_{p_A}	$\bar{C}_p$	
0.18733	0.00018	0.21408	0.21422	0.21415	0.38547
0.37547	0.00035	0.20909	0.22174	0.21042	0.73647
0.75094	0.00060	0.21304	0.21460	0.21382	1.28295
1.12638	0.00070	0.21504	0.21582	0.21543	1.50804
1.50185	0.00109	0.21405	0.21581	0.21493	2.34281
2.25279	0.00151	0.21508	0.21671	0.21589	3.26006
3.00373	0.00196	0.21777	0.21801	0.21787	4.27078
3.75467	0.00239	0.21936	0.22114	0.22025	5.26405
4.50561	0.00284	0.21669	0.21852	0.21760	6.18010
5.63199	0.00365	0.21325	0.21461	0.21393	7.80866

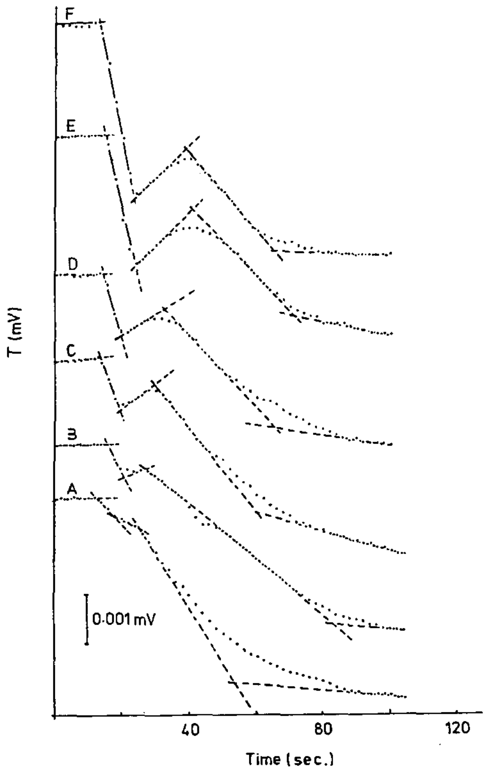

Fig. 1. Enthalpograms of Al^{3+}–$EDTA^{4-}$ titrations at pH = 8.7. [EDTA] = 0.1 mol dm^{-3}, $[Al^{3+}](\times 10^{-5}$ mol dm^{3-}): A = 1.8, B = 4.5, C = 6.3, D = 8.1, E = 13.5, F = 18.0.

$a = 17.2724$, $b = 0.00009$; Pb^{2+}, $a = 19.1368$, $b = 0.00014$; Zn^{2+}, $a = 6.2250$, $b = 0.00009$. It is noted that the overall reaction of Al^{3+} with $EDTA^{4-}$ is endothermic, whereas those of Cd^{2+}, Pb^{2+} and Zn^{2+} are exothermic. A typical family of thermograms, as related to Al^{3+}–$EDTA^{4-}$ titrations at pH 8.7, is shown in Fig. 1. The first break in these curves corresponds to the commencement of titrant addition to the calorimeter. In all cases, for each of the metal ions investigated, linear primary reaction periods are obtained and sharp extrapolated end-points are identified, thereby verifying that quantitative M^{n+}–EDTA reactions are proceeding in the calorimeter at the specified pH. The calculated molar reaction enthalpies are $\Delta H_R = 48.96 \pm 2.56$, -40.90 ± 1.52, -45.59 ± 0.43 and -14.98 ± 0.20 kJ mol^{-1} for Al^{3+}, Cd^{2+}, Pb^{2+} and Zn^{2+}–$EDTA^{4-}$ interactions respectively.

It is difficult to compare these ΔH_R data with corresponding $\Delta H_m^{\ominus}$ data owing to the complexity of each system involved. Such complexity is revealed by the Q_R data given in Table 1. For all four systems investigated, the sign of the overall reaction heat depends on the pH of the medium involved.

Further, for the Al^{3+}–$EDTA^{4-}$ system, it is apparent from the family of thermograms shown in Fig. 1 that the overall reaction is composed of at least three sequential reactions, with the extent of each of these being dependent on pH and ionic strength. According to Brunetti et al. [5], the following equilibria are of importance in metal–EDTA systems

$$H_2Y^{2-} \rightleftharpoons HY^{3-} + H^+$$

$$HY^{3-} \rightleftharpoons Y^{4-} + H^+$$

$$M^{2+} + Y^{4-} \rightleftharpoons MY^{2-}$$

$$MY^{2-} + H^+ \rightleftharpoons MHY^-$$

The principal complexation reaction is therefore ion association of metal cation and protonated Y^{4-} anion

$$M^{2+} + HY^{3-} \rightleftharpoons MHY^-$$

As the fourth hydrogen of H_3Y is only weakly acidic [24], a solution of the tetrasodium salt is partially hydrolysed; thus the system contains some HY^{3-} in addition to the Y^{4-} and NaY^{3-} species. When a metal is added, the HY^{3-} is either partially or completely reconverted to Y^{4-} as the Y^{4-} originally present in solution combines with the metal ion. Thus a heat effect due to the reaction

$$HY^{3-} + OH^- \rightleftharpoons Y^{4-} + H_2O$$

is superimposed on the heat of reaction of the metal ion with Y^{4-}.

Despite the complex nature of the overall complexometric process, the overall reaction heat correlates linearly with the total cation concentration present over the range investigated, and a lower concentration limit of $\approx 2 \times 10^{-5}$ mol dm^{-3} can be determined by the thermometric titrimetry method.

The interference effect of a series of metal ions on the complexation of Al^{3+}, Cd^{2+}, Pb^{2+} and Zn^{2+} by $EDTA^{4-}$ is given in Tables 6–9 respectively.

TABLE 6

Al^{3+}–$EDTA^{4-}$ (pH = 8.7): cation interference effect

Cation	$-\Delta T$ (mV)	$\bar{C}_p$ (kJ mV^{-1})	Q_R or Q'_R $\times 10^{-4}$ (kJ)	Q'_R/Q_R
Al^{3+} [a]	0.00190	0.21566	4.09754	–
Ca^{2+}	0.00195	0.21581	4.20830	1.03
Cd^{2+}	0.00075	0.21754	1.63155	0.40
Cu^{2+}	0.00095	0.21632	2.05504	0.50
Fe^{3+}	0.00110	0.21425	2.35675	0.58
Mg^{2+}	0.00175	0.21952	3.84160	0.91
Mn^{2+}	0.00115	0.21944	2.52356	0.62
Pb^{2+}	0.00080	0.21692	1.73536	0.42
Zn^{2+}	0.00150	0.21371	3.20565	0.78

[a] $[Al^{3+}] = 10^{-4}$ mol dm^{-3}.

TABLE 7

Cd^{2+}–$EDTA^{4-}$ (pH = 8.7); cation interference effect

Cation	ΔT (mV)	$\bar{C}_p$ (kJ mV^{-1})	$-Q_R$ or $-Q'_R$ $\times 10^{-4}$ (kJ)	Q'_R/Q_R
Cd^{2+} [a]	0.00170	0.21283	3.61811	–
Al^{3+}	0.00075	0.21754	1.63155	0.45
Ca^{2+}	0.00185	0.21575	3.99137	1.10
Cu^{2+}	0.00160	0.21455	3.43280	0.95
Fe^{3+}	0.00145	0.21353	3.09619	0.86
Mg^{2+}	0.00140	0.21487	3.00818	0.83
Mn^{2+}	0.00180	0.21752	3.91536	1.08
Pb^{2+}	0.00175	0.21722	3.80135	1.05
Zn^{2+}	0.00400	0.21951	8.78040	2.42

[a] $[Cd^{2+}] = 10^{-4}$ mol dm^{-3}.

This interference study reveals overall the extent to which mixed cation systems can be determined sequentially by EDTA, and the corresponding enthalpy data, given in the form of Q'_R/Q_R, can be rationalised in terms of the relevant stability constant [17] of the metal–EDTA complexes involved. Thus, in cases where Q'_R/Q_R is close to unity, there is minimal interference effect, the relevant stability constants [17] are well separated and sequential complexation of the relevant metal ions occurs. Examples of this category include: Al^{3+}/Ca^{2+} (log K values are 16.8, 11.0); Al^{3+}/Mg^{2+} (log K values are 16.8, 9.1); Cd^{2+}/Ca^{2+} (log K values are 16.3, 11.0); Cd^{2+}/Pb^{2+} (log K values are 16.3, 17.3); Pb^{2+}/Ca^{2+} (log K values are 17.3, 11.0); Pb^{2+}/Fe^{3+} (log K values are 17.3, 25.4); and Zn^{2+}/Cu^{2+} (log K values are 16.3, 17.9). Conversely, in cases where Q'_R/Q_R deviates significantly from unity, a

TABLE 8

Pb^{2+}–$EDTA^{4-}$ (pH = 8.7); cation interference effect

Cation	ΔT (mV)	$\bar{C}_p$ (kJ mV^{-1})	$-Q_R$ or $-Q'_R$ $\times 10^{-4}$ (kJ)	Q'_R/Q_R
Pb^{2+} [a]	0.00190	0.21904	4.00786	–
Al^{3+}	0.00075	0.21699	1.62743	0.41
Ca^{2+}	0.00180	0.21414	3.85452	0.96
Cd^{2+}	0.00200	0.21568	4.31360	1.08
Cu^{2+}	0.00205	0.21500	4.40750	1.10
Fe^{3+}	0.00175	0.22131	3.87293	0.97
Mg^{2+}	0.00150	0.21848	3.27720	0.82
Mn^{2+}	0.00140	0.21616	3.02624	0.76
Zn^{2+}	0.00215	0.21933	4.71560	1.18

[a] $[Pb^{2+}] = 10^{-4}$ mol dm^{-3}.

TABLE 9

Zn^{2+}–$EDTA^{4-}$ (pH = 8.7): cation interference effect

Cation	ΔT (mV)	$\bar{C}_p$ (kJ mV^{-1})	$-Q_R$ or $-Q'_R$ $\times 10^{-4}$ (kJ)	Q'_R/Q_R
Zn^{2+} [a]	0.00130	0.21151	2.74963	–
Ca^{2+}	0.00155	0.21430	3.32165	1.21
Cd^{2+}	0.00470	0.21561	1.01337	0.37
Cu^{2+}	0.00115	0.21502	2.47273	0.90
Fe^{3+}	0.00100	0.21470	2.14700	0.78
Mg^{2+}	0.00110	0.21271	2.33981	0.85
Mn^{2+}	0.00150	0.21626	3.24309	1.18
Pb^{2+}	0.00140	0.21554	3.01756	1.00

[a] $[Zn^{2+}] = 2 \times 10^{-4}$ mol dm^{-3}.

considerable interference effect results; the relevant metal–EDTA complex stability constants [17] are of a similar order of magnitude and hence simultaneous complexation of these metal ions occurs in solution. Examples in this category are: Al^{3+}/Cd^{2+} (log K values are 16.8, 16.3); Cd^{2+}/Zn^{2+} (log K values are 16.3, 15.5); Pb^{2+}/Al^{3+} (log K values are 17.3, 16.8); and Zn^{2+}/Pb^{2+} (log K values are 16.3, 17.3). Owing to the overall complexity of these systems, these two categories of behaviour are not clearly separated, but, with reference to the first category of systems, the scope of the thermometric titrimetric determination of metal ions by EDTA in aqueous media is revealed.

REFERENCES

1 G. den Boef, Fresenius' Z. Anal. Chem., 311 (1982) 232.
2 R.G. Charles, J. Am. Chem. Soc., 76 (1954) 5854.
3 R.A. Care and L.A.K. Staveley, J. Chem. Soc., (1956) 4571.
4 G. Schwarzenbach and H. Flaschka, Die Komplexometrische Titration, 5th edn., Ferdinand Enke Verlag, Stuttgart, 1965.
5 A.P. Brunetti, G.H. Nancollas and P.N. Smith, J. Am. Chem. Soc., 91 (1969) 4680.
6 G. Degischer and G.H. Nancollas, Inorg. Chem., 9 (1970) 1259.
7 S. Boyd, A. Bryson, G.H. Nancollas and J. Torrance, J. Chem. Soc., (1965) 7353.
8 G.C. Kuyler and G.H. Carey, Talanta, 17 (1970) 907.
9 J. Bassett, R.C. Denney, G.H. Jeffery and J. Mendham, Vogel's Textbook of Quantitative Inorganic Analysis, 4th edn., Longman, London, 1978.
10 S. Richards, B. Pedersen, J.V. Silverton and J.L. Hoard, Inorg. Chem., 3 (1964) 27.
11 M.J. Jamor, T.A.A. Hamor, M.D. Lind and J.L. Hoard, Inorg. Chem., 3 (1964) 34.
12 G.S. Smith and J.L. Hoard, J. Am. Chem. Soc., 81 (1959) 556.
13 G. Schwarzenbach, R. Gut and G. Anderegg, Helv. Chim. Acta, 37 (1954) 937.
14 W.C.E. Higginson, J. Chem. Soc., (1962) 2761.
15 T.R. Bhat and M. Krishnamurthy, J. Inorg. Nucl. Chem., 25 (1963) 1147.

16 J.K. Grime (Ed.), Analytical Solution Calorimetry, Vol. 79 in Chemistry Analysis—A Series of Monographs on Analytical Chemistry and its Applications (P.J. Elving and J.D. Winefordner (Eds.)), Wiley–Interscience, New York, 1985.
17 J.J. Christensen, D.J. Eatough and R.M. Izatt, Handbook of Metal–Ligand Heats and Related Thermodynamic Properties, 2nd edn., Marcel Dekker, New York, 1975.
18 P.T. Priestley, Analyst (London), 88 (1963) 194.
19 P.T. Priestley, W.S. Sebborn and R.F.W. Selmann, Analyst (London), 90 (1965) 589.
20 J.C. Wasilewski, P.T.S. Pei and J. Jordan, Anal. Chem., 36 (1964) 2131.
21 J. Jordan, R.A. Henry and J.C. Wasilewski, Microchem. J., 10 (1966) 260.
22 J. Jordan and T.G. Alleman, Anal. Chem., 29 (1957) 9.
23 F.F. Carini and A.E. Martell, J. Am. Chem. Soc., 74 (1952) 5745.
24 F.F. Carini and A.E. Martell, J. Am. Chem. Soc., 75 (1953) 4810.
25 F.F. Carini and A.E. Martell, J. Am. Chem. Soc., 76 (1954) 2153.
26 H.J.V. Tyrrell and A.E. Beezer, Thermometric Titrimetry, Chapman and Hall, London, 1968.
27 K. Doi and M. Tanaka, Anal. Chim. Acta, 71 (1974) 464.
28 K. Doi, Anal. Chim. Acta, 74 (1975) 357.
29 T. Moeller and S. Chu, J. Inorg. Nucl. Chem., 28 (1966) 153.
30 K.B. Yatsimirskii and G.A. Karacheva, Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol., 1 (1958) 13.
31 D.L. Wright, J.H. Holloway and C.N. Reilley, Anal. Chem., 37 (1965) 884.
32 R. bin Ahmad, J.O. Hill and R.J. Magee, Thermochim. Acta, 71 (1977) 25.
33 R. bin Ahmad, J.O. Hill and R.J. Magee, Thermochim. Acta, 98 (1986) 127.