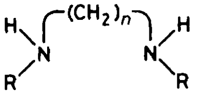
A Thermometric Titrimetric Study of the Complexation of Alkaline-earth Metals by Linear Poly(aminocarboxylic) Acids

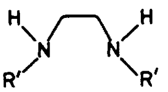
Gavin Ewin *
Coal Research Laboratory, B.P. Aust. Ltd., Port Melbourne, Victoria 3207, Australia
John O. Hill
Department of Inorganic and Analytical Chemistry, La Trobe University, Bundoora, Victoria 3083, Australia

Thermometric titrimetry has been employed to determine K, $\Delta H^{\ominus}$, and $\Delta S^{\ominus}$ data for the complexation reaction in aqueous solution of ethylenediamine-*NN'*-diacetic acid, trimethylenediamine-*NN'*-diacetic acid, ethylenediamine-*NN'*-di-α-propionic acid, and *NN'*-dimethylethylenediamine-*NN'*-diacetic acid with alkaline-earth metal cations. Factors influencing the thermodynamic stability of these complexes are discussed.

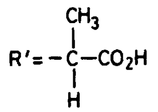
Thermometric titrimetry has been applied to study the solution thermodynamics of a variety of metal complexation reactions especially those associated with small K values.[1-8] Stability constants relating to alkaline-earth metal complexes of poly(aminocarboxylic) acids have previously been derived by conventional pH titration methods [9,10] and in a few cases, the enthalpy of complexation has been derived from the temperature dependence of the relevant stability constant.[11] The poly(aminocarboxylic) acid ligands, (1)—(4), studied in the present work are shown below. Stability constant, and enthalpy and entropy of protonation are reported for these ligands and stability constants, and enthalpy and entropy of complexation in aqueous solution are reported for the corresponding Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} complexes. The stability constant data for these complexes are rationalised in terms of the magnitude of the related enthalpy and entropy of complexation.



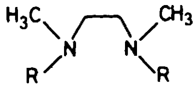
(1; *n*=2)
(2; *n*= 3)
R = – CH_2CO_2H



(3)



$$R' = -\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}-CO_2H$$



(4)
R = – CH_2CO_2H

Experimental

Calorimeter and Accessories.—A Tronac (model 450) thermometric titrimetric system was used. The calorimeter was a rapid-response, glass vacuum Dewar of 100 cm^3 maximum capacity. The burette capacity was 6 cm^3 and the measured titrant delivery rate was 1.0335 ± 0.0011 cm^3 min^{-1}. The thermostat was maintained at 298.0 ± 0.001 K by employing a Tronac (model 1040) precision temperature controller. Potential *versus* time measurements were made using a Systron Donner (model 7005A) digital voltmeter in conjunction with a Systron Donner (model 5103B) Digital Printer and Digital Clock (model 8210). The precision in time and potential difference measurements was ±0.01 min and ±0.01 mV respectively. The overall sensitivity with respect to energy measurement was 2 600 mV K^{-1}. Such sensitivity was achieved by amplifying the thermistor bridge output by a factor of 100 using a low-level, chopper-stabilised, differential amplifier (Utah Electronics).

Calibration. The precision of the thermometric titration system was determined using the well-defined thermochemical system, pyridine–acetic acid. The thermodynamic parameters for the protonation of pyridine are known [12-15] and in the presence of acetic acid, the competing dissociation of acetic acid results in an overall log K of 0.4 for the calorimetric reaction. Pyridine (90 cm^3, 0.01163 mol dm^{-3}) was titrated with 0.2015 mol dm^{-3} aqueous acetic acid (6 cm^3). Log K and the dissociation enthalpy for acetic acid were taken as 4.756 and −0.042 kJ mol^{-1} (298 K) respectively.[12] The derived thermodynamic data for the pyridine–acetic acid system based on five determinations are as follows: log K 5.18 ± 0.06, lit.[12,15] 5.17; ΔH -20.64 ± 0.47, lit.[12-14] −20.84 kJ mol^{-1}; and ΔS 29.9 ± 1.6, lit.[12] 29.1 J K^{-1} mol^{-1}.

Calorimetric Procedure.—The general procedure involves three separate calorimetric experiments: protonation and dilution of the aqueous poly(aminocarboxylate) ligand (L^{2-}) and titration of the ligand with a Group 2A metal cation (M^{2+}) in aqueous solution.[16]

Protonation. Only the first protonation of these ligands is significant in terms of the magnitude of the heat effect. The relevant protonation constant was derived by standard pH measurements at an ionic strength, I, of 0.1 mol dm^{-3} using sodium perchlorate, previously dried at 413 K for 48 h. pH Determinations were made at 298 K using a Radiometer PHM64 pH meter with a combined glass electrode. The system was standardised at 298 K before and after each pH determination using 0.01 mol dm^{-3} sodium borate (pH 9.180) and saturated calcium hydroxide (pH 12.450) standard buffer solutions prepared by published procedures.[17] The Davis equation [18,19] was used to derive a mean hydrogen-ion activity coefficient at 0.7815. Species concentrations were derived using an iterative technique [20] assuming the existence of the equilibria $H^+ + L^{2-} \rightleftharpoons HL^-$ and $H_2O \rightleftharpoons H^+ + OH^-$ (K_w); K_w was taken as 1.04×10^{-14} mol^2 dm^{-6}.[21]

Protonation enthalpies were determined by thermometric titration of *ca.* 0.02 mol dm^{-3} Na_2L solution ($I = 0.1$ mol dm^{-3}) (90 cm^3) with 0.1 mol dm^{-3} $HClO_4$ (6 cm^3). Species concentrations at each selected data point were derived using an iterative technique based on the existence of the two equilibria used previously. The protonation enthalpy was derived by a least-squares analysis of the calculated reaction heat data. The heat of formation of water was taken as 55.919 kJ mol^{-1}.[22] Linearity of the corrected thermogram is a further check on the accuracy of the protonation stability constant since inaccurate log *K* values lead to over correction for the hydrolysis reaction.

Dilution. Dilution enthalpies were determined by thermometric titration of 0.1 mol dm^{-3} $NaClO_4$ (90 cm^3) with *ca.* 0.2 mol dm^{-3} Na_2L solution. The data were corrected for the effect of ionic strength variation on the protonation of the titrant using an extended version of the Debye–Hückel equation.[23] Species concentrations at each selected data point were derived using an iterative technique [24] based on the existence of two equilibria in solution: $H^+ + OH^- \rightleftharpoons H_2O$ and $H^+ + L^{2-} \rightleftharpoons HL^-$.

Complexation. The general thermometric titration involves the titration of 0.01 mol dm^{-3} metal perchlorate solution (90 cm^3) with *ca.* 0.2 mol dm^{-3} ligand solution (6 cm^3); both solutions are initially at 298 K. The 0.01 mol dm^{-3} aqueous metal solutions (titrate) were adjusted to $I = 0.1$ mol dm^{-3} using $NaClO_4$. Metal concentrations were determined by atomic absorption spectrophotometry and by ethylenediaminetetra-acetic acid titration. For systems necessitating a competitive calorimetric reaction (M^{2+}-*NN′*-dimethylethylenediamine-*NN′*-diacetate) the titrate was a 0.01 mol dm^{-3} aqueous solution of the corresponding metal complex of ethylenediamine-*NN′*-diacetic acid, adjusted to $I = 0.1$ mol dm^{-3}. The titrant was an approximately 0.2 mol dm^{-3} aqueous solution of the disodium salt of a poly(aminocarboxylic) acid. Observed reaction heats were corrected for dilution, stirring, thermistor heating, and heat loss using the procedure detailed by Christensen and co-workers.[23,25,26] Data analyses for calorimetric reactions whereby log $K < 4$ and for those whereby log $K > 4$ are based on reaction sequences (i)—(iv) and (i)—(vii) respectively, where A = ethylenediamine-*NN′*-diacetate.

$$M^{2+} + L^{2-} \rightleftharpoons ML \tag{i}$$

$$H_2O \rightleftharpoons H^+ + OH^- \tag{ii}$$

$$H^+ + L^{2-} \rightleftharpoons HL^- \tag{iii}$$

$$M^{2+} + OH^- \rightleftharpoons M(OH)^+ \tag{iv}$$

$$MA + L^{2-} \rightleftharpoons ML + A^{2-} \tag{v}$$

$$MA \rightleftharpoons M^{2+} + A^{2-} \tag{vi}$$

$$H^+ + A^{2-} \rightleftharpoons HA^- \tag{vii}$$

Corrections for the heat change due to side reactions were applied using known or separately determined log *K* and ΔH data for these reactions. Corrections due to the heat of formation of $M(OH)^+$ species, equation (iv), were calculated using literature values for enthalpies of formation of these species: $\Delta H[Ca(OH)^+]$ 4.98, $\Delta H[Sr(OH)^+]$ 4.81, and $\Delta H[Ba(OH)^+]$ 7.32 kJ mol^{-1} respectively;[27] $\Delta H[Mg(OH)^+]$ was estimated by Nancollas and Park [19] to be 11.72 kJ mol^{-1}. The extent of metal-ion hydrolysis was calculated using published equilibrium constants.[19,28] Under the conditions of the titration, typical concentrations of HL^-, $M(OH)^+$, and H^+ are less than 10^{-3}, 10^{-5}, and 10^{-10} mol dm^{-3} respectively. Thus heat contributions resulting from the formation of species H_2L and $M(OH)(HL)$ are negligible. Further, the assumption that the extent of the second protonation of these ligands is insignificant is partially compensated by the method of determination of the first protonation enthalpy.

Log *K* and ΔH data were calculated using an iterative method: log *K* is assumed and the corresponding average ΔH for the reaction is used to calculate a series of *Q* values (reaction heat in Joules) which are compared to the experimental *Q* values over 30 data points during the titration; the resulting error square sum is then minimised by systematic variation of log *K*.

Table 1. Thermodynamic data (298 K) for protonation of some poly(aminocarboxylates)

Ligand	log *K*	ΔH/kJ mol^{-1}	ΔS/ J K^{-1} mol^{-1}
(1) Ethylenediamine-*NN′*-diacetic acid	9.4	-34.69 ± 0.04	63.6 ± 0.2
(2) Trimethylenediamine-*NN′*-diacetic acid	9.9	-39.41 ± 0.10	56.4 ± 0.4
(3) Ethylenediamine-*NN′*-di-α-propionic acid	9.5	-28.28 ± 0.08	86.3 ± 0.4
(4) *NN′*-Dimethylethylenediamine-*NN′*-diacetic acid	9.8	-25.61 ± 0.17	101.0 ± 0.5

Overall estimates of precision associated with thermodynamic data obtained by this method are log *K*, ±0.1; ΔH, ±0.4 kJ mol^{-1}; and ΔS, ±1.0 J K^{-1} mol^{-1}. Full details of calculation procedures, error analysis, and computer software have been published.[16]

Syntheses.—All chemicals used were of reagent grade.

Ethylenediamine-NN′-*diacetic acid.* The method of Haydock and Mulholland [29] was employed. Yield 25%, m.p. 219 °C (decomp.) [lit.[29] 218 °C (decomp.)] (Found: C, 40.8; H, 7.0; N, 15.9; O, 36.3. Calc. for $C_6H_{12}N_2O_4$: C, 40.9; H, 6.9; N, 15.9; O, 36.3%).

Trimethylenediamine-NN′-*diacetic acid.* The general method of Haydock and Mulholland [29] was employed. Yield 20%, m.p. 241—242 °C. Thermogravimetric analysis confirmed the product as a monohydrate (Found: C, 40.2; H, 7.7; N,13.5; O, 38.6. Calc. for $C_7H_{16}N_2O_5$: C, 40.4; H, 7.7; N, 13.5; O, 38.5%). I.r. spectrum: 3 510, 3 220, 2 700, 2 450, 1 640, 1 580, 1 472 (doublet), 1 375, 1 320, 1 264, 1 240, 1 172, 1 109, 1 040, 919 (doublet), 780, 700, 581, and 447 cm^{-1}. ^1H N.m.r. spectrum (D_2O): δ 2.34 (2 H, multiplet), 3.30 (4 H, triplet), 3.75 p.p.m. (4 H, singlet).

NN′-*Dimethylethylenediamine*-NN′-*diacetic acid.* The method of Legg and Cooke [30] was employed with modification of the reaction period to 24 h which increased the yield of the acid as the barium salt from 29 to 64%, m.p. 223 °C (Found: C, 46.7; H, 7.9; N, 13.5; O, 31.1. Calc. for $C_8H_{16}N_2O_4$: C, 47.1; H, 7.9; N, 13.7; O, 31.3%).

Ethylenediamine-NN′-*di-α-propionic acid.* The method of Schoenberg *et al.*[31] was employed, m.p. 284—286 °C (lit.[31] 256—258 °C, lit.[32] 260—265 °C (Found: C, 46.9; H, 8.0; N, 13.5; O, 31.5. Calc. for $C_8H_{16}N_2O_4$: C, 47.1; H, 7.9; N, 13.7; O, 31.3%).

Microanalysis data were provided by the Australian Microanalytical Service, CSIRO, Melbourne. Infrared spectra, range 4 000—250 cm^{-1} (KBr discs) were obtained using a Perkin-Elmer 457 spectrophotometer. N.m.r. spectra were obtained using a Varian T60 n.m.r. spectrometer and $SiMe_4$ as internal reference. Thermogravimetry data were obtained using a Rigaku-Denki (Thermoflex) Thermal Analysis system, a 10 mg sample mass, a heating rate of 10 °C min^{-1}, and a dynamic nitrogen atmosphere.

Results and Discussion

Thermodynamic data (298 K) relating to the protonation of four poly(aminocarboxylates) are summarised in Table 1 and similar data relating to the complexation in aqueous

Table 2. Thermodynamic data (298 K) [a] for complexation (aqueous solution) of Group 2A metal cations with linear poly(aminocarboxylic) acids

	Mg^{2+}			Ca^{2+}			Sr^{2+}			Ba^{2+}		
Ligand	log K	ΔH	ΔS	log K	ΔH	ΔS	log K	ΔH	ΔS	log K	ΔH	ΔS
(1) Ethylenediamine-*NN'*-diacetic acid	4.3	12.3	124.0	2.9	0.3	57.6	2.3	3.4	54.8	1.2	6.8	46.3
(2) Trimethylenediamine-*NN'*-diacetic acid	3.4	10.5	99.0	2.4	3.8	57.9	1.3	2.9	34.9	1.3	2.5	33.6
(3) Ethylenediamine-*NN'*-di-α-propionic acid	3.2	23.3	139.9	2.1	8.7	77.0		[b]			[b]	
(4) *NN'*-Dimethylethylenediamine-*NN'*-diacetic acid	5.2	8.5	128.0	6.0	−4.8	99.0	3.3	−2.7	54.0	2.5	−3.8	34.9

[a] Units: ΔH kJ mol^{-1}, ΔS J K^{-1} mol^{-1}. [b] No reaction observed.

solution of some Group 2A metal cations with these ligands are given in Table 2. For ethylenediamine-*NN'*-diacetic acid, various published log K data for protonation exist: log K 9.57 (298 K) ($I = 0.1$ mol dm^{-3}, KNO_3);[33] 9.46 (303 K) ($I = 0.1$ mol dm^{-3}, KCl);[34] 9.62 (298 K) ($I = 0.1$ mol dm^{-3}, KNO_3);[35] 9.58 (298 K) ($I = 0.1$ mol dm^{-3}, KNO_3);[36] and 9.695 (298 K) ($I = 1.0$ mol dm^{-3}, $NaClO_4$).[37] These data were obtained by conventional pH titration and are in good agreement with log $K = 9.4$ (298 K) ($I = 0.1$ mol dm^{-3}, $NaClO_4$) obtained by titration calorimetry. No stability constant data exist relating to the protonation of trimethylenediamine-*NN'*-diacetic acid. For ethylenediamine-*NN'*-di-α-propionic acid, Irving *et al.*[38] have reported log K (protonation) as 9.58 (293 K) ($I = 0.1$ mol, dm^{-3}, KCl) as derived by pH titration. For *NN'*-dimethylethylenediamine-*NN'*-diacetic acid, Ockerbloom and Martell[39] have reported log K (protonation) as 9.882 (303 K) ($I = 0$) and have also derived the corresponding protonation enthalpy as −28.66 kJ mol^{-1} (303 K) ($I = 0$) based on the temperature variation of the protonation constant. These data compare favourably with log $K = 9.8$ and ΔH (protonation) $= -25.61$ kJ mol^{-1} (298 K) ($I = 0.1$ mol dm^{-3} $NaClO_4$) as derived by titration calorimetry.

Trends are apparent with respect to the protonation constants of the poly(aminocarboxylate) species studied. The acid strength decreases as the carbon chain length of the parent diamine increases and as electron-donating alkyl groups are attached to the nitrogen donor atoms or to the terminal carbon atom of the carboxylic acid residue.

For the Group 2A metal complexes of poly(aminocarboxylic) acids, Irving *et al.*[38] have reported that only Mg^{2+} and Ca^{2+} complex with ethylenediamine-*NN'*-di-α-propionic acid which is confirmed by the present work. For the Mg^{2+} complex, Irving *et al.*[38] reported log $K = 2.8 \pm 0.1$ (293 K) ($I = 0.1$ mol dm^{-3} KCl) which is in good agreement with log $K = 3.2 \pm 0.07$ (298 K) ($I = 0.1$ mol dm^{-3}, $NaClO_4$) obtained by thermometric titrimetry. Ockerbloom and Martell[39] have reported log $K = 5.72$, $\Delta H = 4.0$ kJ mol^{-1}, and $\Delta S = 130$ J K^{-1} mol^{-1} for the Mg^{2+} complex of *NN'*-dimethylethylenediamine-*NN'*-diacetic acid. Agreement of these data with the corresponding data obtained by thermometric titrimetry is excellent except for the complexation enthalpy. It is difficult to assess the accuracy of the previous data since the method by which the complexation enthalpy was derived is not stated.

If the thermodynamic data summarised in Table 2 are considered collectively various trends are apparent. For ligands (1)—(3) (Table 2), the log K of complexation decreases in the order $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$. Thus the stability of the complexes decreases as the effective size of the co-ordinated cation increases and this decrease in stability appears to be entropy controlled; the magnitude of the ΔS term reflects the degree of dehydration of the cation upon complexation. No reaction occurs between Sr^{2+} and Ba^{2+} and ligand (3) which possibly reflects the steric effect of the ligand α-CH_3 groups preventing complexation of this ligand with the larger cations which is reflected in the relatively large endothermic complex reaction with Mg^{2+} and Ca^{2+}. For ligand (4) the enthalpy of complexation is negative for the larger cations and hence the magnitude of the corresponding $\Delta G^\ominus$ is not predominantly reflecting an entropy effect. The exothermicity of the complexation reaction reflects an increase in donor strength of the ligand resulting from the electron-donating inductive effect of the N-CH_3 groups of the ligand.

Thus these linear poly(aminocarboxylic) acids show selectivity between alkaline-earth metal cations. Such selectivity can be rationalised in terms of the relative magnitudes of the enthalpy and entropy of complexation. In the case of *NN'*-dimethylethylenediamine-*NN'*-diacetic acid, cationic size is not a controlling factor since selectivity towards Ca^{2+} is shown. Future design of poly(aminocarboxylic) acids may result in a ligand superior to ethylenediaminetetra-acetic acid for the selective complexation of alkaline-earth metals.

References

1 G. W. Ewing, ' Instrumental Methods of Chemical Analysis, 4th edn., McGraw-Hill, New York, 1975, pp. 448—453.
2 E. J. Greenhow, *Chem. Rev.*, 1977, **77**, 835.
3 J. Barthel, ' Thermometric Titrations,' Wiley, New York, 1975.
4 H. J. V. Tyrrell and A. E. Beezer, ' Thermometric Titrimetry,' Chapman and Hall, London, 1968.
5 J. J. Christensen and R. M. Izatt, in ' Physical Methods in Advanced Inorganic Chemistry,' eds. H. A. O. Hill and P. Day, Wiley, New York, 1968.
6 L. S. Bark and S. M. Bark, ' Thermometric Titrimetry,' Pergamon, Oxford, 1969.
7 L. D. Hansen, R. M. Izatt, and J. J. Christensen, ' New Developments in Titrimetry,' ed. J. Jordan, Dekker, New York, 1974.
8 P. W. Carr, *Crit. Rev. Anal. Chem.*, 1972, **3**, 491.
9 F. J. C. Rossotti and H. Rossotti, ' The Determination of Stability Constants,' McGraw-Hill, New York, 1961.
10 E. Gells and G. H. Nancollas, *Trans. Faraday Soc.*, 1956, **52**, 98.
11 G. H. Nancollas, ' Interactions in Electrolyte Solutions,' Elsevier, Amsterdam, 1966.
12 J. J. Christensen, D. P. Wrathall, and R. M. Izatt, *Anal. Chem.*, 1968, **40**, 175.
13 L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Am. Chem. Soc.*, 1960, **82**, 3831.
14 D. C. Levi, W. S. McEwan, and J. H. Wolfenden, *J. Chem. Soc.*, 1949, 760.
15 R. K. Murman and F. Basolo, *J. Am. Chem. Soc.*, 1955, **77**, 3484.
16 G. Ewin, Ph.D. Thesis, La Trobe University, Melbourne, Australia, 1978.
17 R. G. Bates, ' Determination of pH,' Wiley, New York, 1963, p. 123.

18 C. W. Davis, 'Ion Association,' Butterworths, London, 1962.
19 G. H. Nancollas and C. Park, *Inorg. Chem.*, 1968, **7**, 58.
20 A. J. Bard and D. M. King, *J. Chem. Educ.*, 1965, **42**, 127.
21 W. J. Moore, 'Physical Chemistry,' 3rd edn., Prentice Hall, New Jersey, 1962, p. 365.
22 D. J. Eatough, J. J. Christensen, and R. M. Izatt, *J. Chem. Thermodyn.*, 1975, **7**, 417.
23 D. J. Eatough, J. J. Christensen, and R. M. Izatt, *Thermochim. Acta*, 1972, **3**, 219.
24 S. Cabani and P. Gianni, *J. Chem. Soc. A*, 1968, 547.
25 J. J. Christensen, J. Ruckman, D. J. Eatough, and R. M. Izatt, *Thermochim. Acta*, 1972, **3**, 203.
26 D. J. Eatough, R. M. Izatt, and J. J. Christensen, *Thermochim. Acta*, 1972, **3**, 233.
27 F. G. R. Gimblett and C. B. Monk, *Trans. Faraday Soc.*, 1954, **5**, 965.
28 'Stability Constants,' eds. L. G. Sillen and A. E. Martell, Special Publ. No. 17, The Chemical Society, London, 1964.
29 D. B. Haydock and T. P. C. Mulholland, *J. Chem. Soc. C*, 1971, 2389.
30 J. I. Legg and D. W. Cooke, *Inorg. Chem.*, 1965, **4**, 1576.
31 L. N. Schoenberg, D. W. Cooke, and C. F. Liu, *Inorg. Chem.*, 1968, **7**, 2386.
32 H. Irving, R. Shelton, and R. Evans, *J. Chem. Soc.*, 1958, 3540.
33 S. Charberek and A. E. Martell, *J. Am. Chem. Soc.*, 1952, **74**, 6228.
34 L. C. Thompson, *J. Inorg. Nucl. Chem.*, 1962, **24**, 1083.
35 G. Degischer and G. H. Nancollas, *Inorg. Chem.*, 1970, **9**, 1259.
36 L. Sharma and B. Prasad, *J. Indian Chem. Soc.*, 1969, **46**, 241.
37 I. Grenthe and G. Gardhammer, *Acta Chem. Scand.*, 1974, **28**, 125.
38 H. Irving, R. Shelton, and R. Evans, *J. Chem. Soc.*, 1958, 3540.
39 N. E. Ockerbloom and A. E. Martell, *J. Am. Chem. Soc.*, 1956, **78**, 267.

Received 13*th July* 1982; *Paper* 2/1194