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MULTIPARAMETRIC CURVE FITTING—XI

POLET COMPUTER PROGRAM FOR ESTIMATION OF FORMATION CONSTANTS AND STOICHIOMETRIC INDICES FROM NORMALIZED POTENTIOMETRIC DATA

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Summary—The FORTRAN computer program POLET(84) analyses a set of normalized potentiometric titration curves to find a chemical model, *i.e.*, the number of species present and their stoichiometry, and to determine the corresponding stability constants $\log \beta_{pqrs}$ and unknown stoichiometric indices p, q, r, and s of up to quaternary $M_pL_qY_rH_s$ complexes. The program belongs to the ABLET family, based on the LETAG subroutine, and can use an algorithmic and/or heuristic minimization strategy, or a beneficial combination of both. The data, a set of potentiometric titration curves plotted as volume and potential, are converted into normalized variables (formation function, pH) and then a computer-assisted search for a chemical model by POLET(84) is applied. The procedure for efficient application of POLET(84) in an equilibrium analysis is described and the program is validated by use of literature and simulated data. The reliability of the chemical model and its parameters is established by the degree-of-fit achieved, and the closeness of the stoichiometric indices to integral values.

The formation function Z has traditionally been used in analysis of potentiometric titration data. The algorithms developed by Sillén and co-workers[1-8] are still widely accepted as the most accurate method of determining a chemical model, *i.e.*, the number of complexes, and their stability constants and stoichiometry. Since then, many computer programs have been written for the analysis of potentiometric titration data, such as MINIQUAD,[9] SCOGS,[10] ACBA,[11] PSEQUAD,[12] TITFIT,[13] MARFIT,[14] MUCOMP,[15] ESTA,[16] but none of these accommodates a straight determination of the stoichiometric indices p, q, r of $M_pL_qH_r$ complexes. Various programs applied in potentiometric study of solution equilibria have been critically surveyed.[17-21]

All the programs mentioned above search for the most probable chemical model by the trial-and-error method, and the stability constants and compositions of the complexes are estimated by the curve-fitting technique. If a particular fit being examined is considered false, another set of complexes of different stoichiometry is tried and so on, until the best fit to the data is found. Such treatment needs considerable computer time and an examination of all possible combinations of species is sometimes impossible. When p and q for M_pL_q, for example, each have a limiting value of 10, a large number of individual species is possible.

The program POLET (version 1984) directly determines the stoichiometric coefficients and stability constants of the complexes by means of the recently published ESI method.[22] The species are divided into two groups: "certain" species of known stoichiometry for which only the stability constants are to be estimated, and "uncertain" species of completely unknown stoichiometry (or with at least some indices unknown) for which both the stability constants and stoichiometric indices are estimated simultaneously. The program is a member of the ABLET family[23] and can use either an algorithmic or heuristic strategy, or a combination of both. Like MRLET[24] and PRCEK,[25] the POLET(84) estimates the stoichiometric indices by multiparametric curve fitting and the chemical model selected is then validated by the statistical analysis of residuals.

THEORY

Chemical model

The complex-formation equilibria of n basic components, for example, $n = 4$, may be described by the general reaction and stability constant:

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$$pM + qL + rY + sH = M_pL_qY_rH_s \quad (1)$$

$$\beta_{pqrs} = [M_pL_qY_rH_s]/[M]^p[L]^q[Y]^r[H]^s = c_{pqrs}/m^p l^q y^r h^s \quad (2)$$

with the mass-balance equations

$$c_M = m + pS \quad (3)$$

$$c_L = l + qS \quad (4)$$

$$c_Y = y + rS \quad (5)$$

$$c_H = h + sS \quad (6)$$

where

$$S = \sum_{i=1}^{n_c} \beta_{pqrs,i} m^{p_i} l^{q_i} y^{r_i} h^{s_i} \quad (7)$$

and $c_M, \ldots, c_H$ are the total analytical concentrations of the four basic components and m, l, y, h are the free equilibrium concentrations.

For the more common ternary ($n = 3$) and binary ($n = 2$) equilibria, the complexes $M_pL_qH_r$ or M_pL_q will be referred to as the (p, q, r) or (p, q) species. When protons are split off, the hydroxo species $M_pL_q(OH)_r$ are treated as protonated species with negative r value, *i.e.*, $M_pL_qH_{-r}$ and the corresponding Z function is then also negative if no other equilibrium occurs.

The formation function Z

The primary data of the potentiometric titration curve, with original variables $(V_H, E_H)_{M,L}$ must be converted into the normalized variables $(Z, pH)_{M,L}$. The free equilibrium concentration of the basic component H is measured potentiometrically:

$$E = E^0 + (RT/nF)\ln h + E_j \quad (8)$$

where E_j is the liquid-junction potential and Z is the average number of component entities H bound per M or L,

$$Z \equiv Z_{H/M} = (c_H - h)/c_M = rS/c_M \quad (9)$$

and

$$Z \equiv Z_{H/L} = (c_H - h)/c_L = rS/c_L \quad (10)$$

for the $M_pL_qH_r$ complexes in the model.

Regression analysis

Regression analysis of (Z, pH) curves consists of the estimation of chosen unknown parameters, *i.e.*, the stability constants β_{pqrs} and stoichiometric indices p, q, r and s of up to quaternary $M_pL_qY_rH_s$ complexes by minimizing the difference between the experimental and calculated values of Z. The dependent variable Z represents the average number of moles of protons bound per mole of M (if the program key KV = 1) or of L (if the program key KV = 2) and is easily calculated from the original titration data. For NB titration curve points described by data-pairs $\{Z, pH\}$, the sum of the squared residuals

$$U = \sum_{i=1}^{NB} w_i (Z_{exp,i} - Z_{calc,i})^2 = \text{minimum} \quad (11)$$

is minimized; w_i is the statistical weight, usually taken as unity, and $Z_{calc,i}$ is calculated according to equations (9) and (10) for the current estimation of the parameters.

POLET(84) estimates the stability constants of polynuclear and/or mixed complexes of any system with one metal and two ligands or two metals and one ligand. When an ion-selective electrode is used to indicate the free concentration of component X (where X stands for M or L or Y), the basic component H being indicated potentiometrically may be replaced by that component X. The mixed hydroxo-species $M_pL_q(OH)_r$ are treated as protonated species with negative r values, but negative Z values also mean proton-deficient species. It is impossible to distinguish between a bound OH^- group and a proton split off from a water molecule.

The choice of basic ligand component is up to the user. For example, L can stand for any protonated form of a ligand of up to a tetrabasic acid LH_4, and the four dissociation constants of LH_4 might be supplied in the input if they are already known and there is no request to refine them.

POLET(84) uses the pit-mapping algorithm LETAG, and does the minimization heuristically (steps controlled by the operator) or algorithmically (steps controlled by the program). A combined strategy, heuristic control followed by algorithmic, is beneficial in the first part of the minimization, when the user must decide whether it is sufficient to know the location of some local minimum or whether a global minimum is required. The user has to supply here initial guesses of the parameters to be refined, the minimization steps, and an organizational framework to control the process from iteration to iteration. Final refinement can then be managed algorithmically. Parameters which may reach a negative value must be specified in the input.

POLET(84) consists of three specific units, the INPUT block, the RESIDUAL-SQUARE SUM block and the MAIN block, along with six permanent blocks of ABLET system described previously.[23]

The INPUT block reads the input data $\{Z, pH\}$ by format-free reading subroutines, and the dissociation constants $pK_{a1}, \ldots, pK_{aj}$ of the j-basic ligand acid (if $j \neq 0$) and the side-reaction coefficients $\alpha_{L(H)}$ are then calculated. These coefficients are used in calculation of the initial estimates of the free equilibrium concentrations of all the complexes in a given equilibrium system, $[M_pL_qY_rH_s]_j$; $j = 1, \ldots, n_c$. The free concentrations m, l, y and h are calculated by the subroutine COGS adapted from Perrin and Sayce[26] and modified according to Ginzburg.[27]

The RESIDUAL-SQUARE-SUM block calculates, in subroutine UBBE, the calculated $Z_{calc,i}$ value for each point, starting from the total concentrations of the basic components and the free concentrations

computed by COGS for the current estimates of the parameters, p, q, r and s, and β_{pqrs}.

The MAIN part contains a function as written in the description of ABLET.[23] The OUTPUT block was extended to include printer-plotting of the distribution diagrams for all complex species in the chemical model.

EXPERIMENTAL

Equilibrium analysis by POLET(84)

(1) *Potentiometric equilibrium titration.* Data collection is performed as a potentiometric "equilibrium titration",[8] where usually c_M and c_L are kept constant in the equilibrium solution and c_H is varied by addition of acid from a burette; $c_H = (V_H c_{H,T} + V_0 c_{H,0})/(V_0 + V_H)$ where $c_{H,0}$ and $c_{H,T}$ are the total concentrations of protons in the titrand and titrant, and V_0 is the initial volume of titrand and V_H the volume of titrant added from the burette. Suitable electrodes are used to measure $[H^+]$ to obtain data pairs $(c_H, [H^+])_{M,L}$ over a wide concentration range of M and L; the "inert medium method"[28] or the "self medium method"[29–32] can be used.

(2) *Conversion of primary* (V_H, E_H) *into normalized* (Z, pH) *data.* A calibration titration of a strong acid with a strong base is done to determine three parameters: the standard potential E^0 of the electrode cell used, the Nernst coefficient 2.303 (RT/nF) and the ionic product of water pK_w, by application of the regression program MAGEC.[33] With these three parameters and the Nernst equation the primary data $(V_H, E_H)_{M,L}$ are converted into normalized quantities $(Z, pH)_{M,L}$. This conversion can be done by computer program TRAVE[34] or by pocket-calculator.

(3) *The number of species by factor analysis of* (Z, pH) *data.* The number of complex species in solution may be determined by a factor analysis with program SPECIES[35] from a set of potentiometric titration curves, each containing n_s points and measured for n_x total concentrations of M or L to give finally the $(n_s \times n_x)$ matrix Z by finding the rank of matrix Z. The number of species in equilibrium is equal to the rank of matrix Z. However, for a simple mononuclear system the number of species can be estimated from the number of inflection points on the $Z = f(pH)$ curves.

(4) *MESAK treatment of data.* The MESAK treatment[36] is used to limit the number of ternary complexes (p, q, r) from which the final combination giving the "best" fit may be selected. MESAK can give valuable information about the average composition of the complexes, $\bar{p}$, $\bar{q}$, and $\bar{r}$. Such treatment can thus give initial information about the principle species in a solution, and its use is for guidance only.

(5) *Determination of chemical model.* After data conversion and preliminary data analysis by MESAK, the final selection of the true chemical model from several proposed models is performed with POLET. The complex species are divided into the "certain species" of known stoichiometry (usually, but not necessarily the principal species of the equilibrium mixture) for which only the stability constants are to be estimated, and the "uncertain species" of partly known stoichiometry for which both the stability constants and some stoichiometric coefficients are to be estimated simultaneously. Use is made of combined, heuristic, and finally algorithmic strategy in the LETAG minimization process.

Three strategies for chemical model search are possible:

(*i*) species are tested by the trial-and-error method and only stability constants are refined;
(*ii*) for uncertain species with some unknown indices the stability constants are refined simultaneously with selected indices by the ESI approach;
(*iii*) for the most probable chemical model found a final refinement of stability constants and stoichiometric indices is performed; for a true model the parameters are not changed significantly by refinement and the refined indices should be close to integer values.

Of course, the indices for the basic components for which the free and/or total concentrations have not been varied during collection of titration data cannot be estimated, *e.g.*, when the pH is kept constant in a titration the number of protons r in $M_pL_qH_r$ cannot be determined.

Computation

Potentiometric data analysis by POLET(84) was done with the EC 1033 (500 K) computer in The Department of Computing Techniques, J. E. Purkyně University, CS-611 37 Brno and in The Computing Centre, College of Chemical Technology, CS-532 10 Pardubice, Czechoslovakia. A listing of POLET(84), specimen data and detailed manual are available on request.

DISCUSSION

The major objective of this project was to provide a computing tool for investigating chemical models on the basis of estimating the stoichiometry of various complexes in a complex-forming system by analysis of potentiometric data. To illustrate the performance of POLET(84) a set of simulated data was used first. Table 1 shows the POLET output in shortened form. Two hydrolysed species, $Bi(OH)$ and $Bi_6(OH)_{12}$, described by the stability constants $\log \beta_{1,-1} = -1.58$ and $\log \beta_{6,-12} = 0.33$, were selected and for six different concentrations of Bi^{3+} ions and 8 values of the different variable pH for each concentration, precise values of the dependent variable Z were calculated. With a selected value of the instrumental standard deviation $s_{inst}(Z)$, random errors were generated and imposed on the precise Z values. With the simulated data in Table 1, statistical analysis of the generated errors proved a Gaussian normal distribution of random errors by statistical values describing this error set.

Before minimization was started, complex $M_1(OH)_1$ was chosen as the "certain species" with known stoichiometry, and complex $M_6(OH)_{12}$ as the "uncertain species" for which the stoichiometry was to be estimated. Minimization was started heuristically from the initial guess of the parameters to be estimated, $(\log \beta_{6,-12})^{(0)} = 2.0$., $p_2^{(0)} = 2.0$ and $r_2^{(0)} = -3.0$, and the other parameters were kept at the values initially guessed, $(\log \beta_{1,-1})^{(0)} = -1.58$, $p_1^{(0)} = 1.0$ and $r_1^{(0)} = -1.0$. The minimization terminated with the estimates $\log \beta_{6,-12} = 0.3643 \pm 0.0456$, $p_2 = 6.051 \pm 0.094$ and $r_2 = -12.094$. Statistical analysis of the residuals proved the parameters found were sufficiently reliable, as all the statistical characteristics describing the residual set had the same values as those of the generated errors. When even incorrect values of both stoichiometric coefficients were used in the initial guess, POLET found the true values of p and r.

POLET(84) was further validated by the use of some literature titration data. Sasaki[37] studied the CrO_4^{2-}–H^+ equilibria by potentiometric titration with use of the glass electrode, and from a set of (Z, pH) data concluded there were two protonation

Table 1. Validation of POLET(84) by the simulated data set of Bi^{3+} hydrolysis: for two hydrolytic species, Bi(OH) ("certain complex") and $Bi_6(OH)_{12}$ ("uncertain complex") the (Z, pH) data were simulated: conditions: $\log \beta_{1,-1} = -1.58$, $\log \beta_{6,-12} = 0.33$ and $s_{inst}(Z) = 0.01$

Parameter	Numerical values: Selected for simulation	Initial guess	Refined estimation
Kept at a constant value:			
$(\log \beta_{pr})_1$	−1.58	−1.58	−1.58
p_1	1.0	1.0	1.0
r_1	−1.0	−1.0	−1.0
Refined:			
$(\log \beta_{pr})_2$	0.33	−2.0	0.3643 ± 0.0456
p_2	6.0	2.0	6.0510 ± 0.0944
r_2	−12.0	−3.0	−12.0940 ± 0.1899

	Variables			Simulation		Refinement	
i	pH	c_M	Z_{accur}	Error	Z_{exp}	Z_{calc}	Residual
1	0.00	0.0010	−0.025665	−0.009245	−0.0349	−0.0257	−0.0092
2	0.20	0.0010	−0.040080	−0.000098	−0.0402	−0.0401	−0.0001
3	0.40	0.0010	−0.062074	0.021240	−0.0408	−0.0621	0.0212
4	0.60	0.0010	−0.094920	0.000784	−0.0941	−0.0949	0.0008
5	0.80	0.0010	−0.142581	−0.008168	−0.1507	−0.1426	−0.0082
6	1.00	0.0010	−0.214157	0.003395	−0.2108	−0.2138	0.0031
7	1.50	0.0010	−1.456644	0.003001	−1.4536	−1.4535	−0.0001
8	2.00	0.0010	−1.905545	0.005408	−1.9001	−1.9036	0.0034
9	0.00	0.0050	−0.025590	−0.005515	−0.0311	−0.0256	−0.0055
10	0.20	0.0050	−0.040079	−0.007127	−0.0472	−0.0401	−0.0071
11	0.40	0.0050	−0.062877	0.000559	−0.0615	−0.0621	0.0006
12	0.60	0.0050	−0.095591	0.011835	−0.0838	−0.0956	0.0118
13	0.80	0.0050	−0.231336	0.008999	−0.2223	−0.2299	0.0076
14	1.00	0.0050	−0.945959	0.013832	−0.9321	−0.9446	0.0125
15	1.50	0.0050	−1.849614	−0.010417	−1.8600	−1.8481	−0.0120
16	2.00	0.0050	−1.975067	−0.001604	−1.9767	−1.9737	−0.0030
17	0.00	0.0100	−0.025587	0.008234	−0.0174	−0.0256	0.0082
18	0.20	0.0100	−0.040079	0.009674	−0.0304	−0.0401	0.0097
19	0.40	0.0100	−0.062182	0.008625	−0.0536	−0.0622	0.0086
20	0.60	0.0100	−0.115114	0.009703	−0.1054	−0.1147	0.0093
21	0.80	0.0100	−0.665716	0.007558	−0.6582	−0.6654	0.0073
22	1.00	0.0100	−1.363112	0.006533	−1.3566	−1.3625	0.0059
23	1.50	0.0100	−1.914916	0.010549	−1.9044	−1.9136	0.0093
24	2.00	0.0100	−1.985988	−0.000731	−1.9867	−1.9846	−0.0021
25	0.00	0.0250	−0.025590	−0.002978	−0.0286	−0.0256	−0.0030
26	0.20	0.0250	−0.040128	0.005527	−0.0346	−0.0401	0.0055
27	0.40	0.0250	−0.072272	0.000462	−0.0718	−0.0721	0.0003
28	0.60	0.0250	−0.533428	−0.030596	−0.5636	−0.5343	−0.0293
29	0.80	0.0250	−1.290659	−0.011390	−1.3020	−1.2914	−0.0106
30	1.00	0.0250	−1.690188	0.007523	−1.6827	−1.6899	0.0071
31	1.50	0.0250	−1.960133	−0.000719	−1.9609	−1.9588	−0.0020
32	2.00	0.0250	−1.993483	0.002612	−1.9909	−1.9921	0.0013
33	0.00	0.0500	−0.025593	−0.011159	−0.0368	−0.0256	−0.0112
34	0.20	0.0500	−0.041633	−0.000825	−0.0425	−0.0416	−0.0009
35	0.40	0.0500	−0.246769	−0.005953	−0.2527	−0.2481	−0.0046
36	0.60	0.0500	−1.060399	0.004531	−1.0559	−1.0627	0.0069
37	0.80	0.0500	−1.586509	−0.003288	−1.5898	−1.5869	−0.0029
38	1.00	0.0500	−1.823634	0.006896	−1.8167	−1.8230	0.0062
39	1.50	0.0500	−1.977581	−0.003577	−1.9812	−1.9763	−0.0048
40	2.00	0.0500	−1.996346	−0.006328	−2.0027	−1.9950	−0.0077
41	0.00	0.1000	−0.025805	0.010394	−0.0154	−0.0258	0.0104
42	0.20	0.1000	−0.083661	−0.004300	−0.0880	−0.0840	−0.0039
43	0.40	0.1000	−0.769383	0.004190	−0.7652	−0.7735	0.0083
44	0.60	0.1000	−1.442235	−0.000197	−1.4424	−1.4440	0.0015
45	0.80	0.1000	−1.763447	0.000463	−1.7630	−1.7633	0.0003
46	1.00	0.1000	−1.900189	−0.004241	−1.9044	−1.8994	−0.0050
47	1.50	0.1000	−1.987427	−0.011020	−1.9984	−1.9861	−0.0123
48	2.00	0.1000	−1.997958	0.006222	−1.9917	−1.9966	−0.0048

$S_{error}(Z) = 0.0089$	$S_{resid}(Z) = 0.0088$
Error mean = 8.18E-4	Residual mean = 5.48E-4
Mean error = 0.0066	Mean residual = 0.0066
Standard deviation = 0.0086	Standard deviation = 0.0085
Skewness (should be 0) = −0.463	Skewness (should be 0) = −0.445
Curtosis (should be 3) = 4.808	Curtosis (should be 3) = 4.487
Hamilton R-factor, % = 0.721	Hamilton R-factor % = 0.712

Table 2. Comparison of (Z, pH) data analysis of CrO_4^{2-}–H^+ system by POLET(84), projection map method used by Sasaki,[37] and LETAGROP-Z + ETA; input data taken from Sasaki[37]

Parameter	POLET(84)	Projection map	LETAGROP-Z + ETA
$\log \beta_{11}$	6.0092 ± 0.0014	5.89 ± 0.02	5.9086 ± 0.0019
$\log \beta_{22}$	13.9892 ± 0.0018	13.98 ± 0.04	14.0012 ± 0.0028
q_1	1.0156 ± 0.0003	1	1
r_1	1.0054 ± 0.0005	1	1
q_2	1.9995 ± 0.0004	2	2
r_2	1.9994 ± 0.0007	2	2
$s(Z)$	0.00266	0.00719	0.00431
Residual mean	−3.15E-3	5.08E-3	2.64E-4
Mean residual	0.0020	0.0059	0.0034
Standard deviation	0.0026	0.0072	0.0043
Skewness (should be 0)	−0.202	1.411	0.445
Curtosis (should be 3)	4.781	2.494	2.914
Hamilton R-factor, %	0.424	1.161	0.696

constants, $\log \beta_{11} = 5.89 \pm 0.02$ and $\log \beta_{22} = 13.98 \pm 0.04$. These data were first analysed by the projection map method with program PROKA and then the resulting normalized data (Z, pH) by the POLET(84) program. Low values of the residuals and the Hamilton R-factor indicated that a good degree-of-fit was achieved and the parameter estimation was reliable (Table 2).

The complex-forming system of vanadium(V) and tartrate to form M_2LH and $M_4L_2H_4$ complexes and the aggregates M_3 and M_4 was used to illustrate the determination of stability constants only. Here, M

Table 3. $Z = f$(pH) data analysis of vanadate(V)–tartrate system by POLET(84) and a comparison of some results with those obtained by LETAGROP-ETITR program: values of $\log \beta_{011} = 3.685$ and $\log \beta_{012} = 6.36$ taken from Bartušek and Šustáček,[40] total concentration in mole/l.

pH	c_M	c_L	Z	pH	c_M	c_L	Z
7.26	0.0199	0.146	0.1375	7.17	0.0199	0.145	0.182
7.08	0.0195	0.144	0.2385	6.99	0.0193	0.142	0.322
6.89	0.0189	0.139	0.438	6.79	0.0185	0.136	0.577
6.69	0.0181	0.133	0.710	6.58	0.0178	0.131	0.812
7.24	0.020	0.0983	0.0959	7.06	0.0198	0.0971	0.168
6.98	0.0196	0.0961	0.226	6.89	0.0193	0.0947	0.311
6.79	0.0189	0.0927	0.438	6.69	0.0184	0.0904	0.588
6.59	0.018	0.0883	0.735	7.04	0.0201	0.0493	0.079
6.955	0.020	0.049	0.111	6.875	0.0198	0.0487	0.1535
6.79	0.0196	0.0481	0.224	6.695	0.0192	0.0472	0.333
6.595	0.0188	0.046	0.477	6.485	0.0183	0.0488	0.646
6.92	0.0051	0.0373	0.107	6.83	0.0051	0.0373	0.145
6.75	0.0051	0.0372	0.200	6.66	0.0050	0.0370	0.288
6.56	0.005	0.0368	0.419	6.46	0.0050	0.0366	0.568
6.355	0.0050	0.0363	0.710	6.26	0.0491	0.0362	0.818
6.80	0.0051	0.0249	0.108	6.72	0.0051	0.0248	0.147
6.64	0.0051	0.0248	0.208	6.55	0.0050	0.0247	0.305
6.45	0.0050	0.0245	0.448	6.35	0.0050	0.0243	0.610
6.245	0.0050	0.0242	0.749	6.605	0.0051	0.0124	0.099
6.525	0.0051	0.0124	0.150	6.44	0.0050	0.0124	0.222
6.345	0.0050	0.0123	0.341	6.245	0.0050	0.0122	0.496
6.14	0.0050	0.0121	0.657				

Species by POLET(84)		Species by LETAGROP-ETITR	
	$\log \beta_{pqr}$	$\log \beta_{pqr}$	*Reference*
M_3	7.360 ± 0.016	7.20	38
M_4	9.67 ± 0.14	10.15	38
$M_4L_2H_4$	39.80 ± 0.01	39.750 ± 0.008	39
M_2LH	11.805 ± 0.020	11.820 ± 0.020	39
$U \times 10^3$, $s(Z)$	6.56, 0.01267	8.60, 0.014	39
Residual mean	2.0E-3		
Mean residual	0.0096		
Standard deviation	0.0124	Not calculated	
Skewness (should be 0)	0.658		
Curtosis (should be 3)	2.520		
Hamilton R-factor, %	2.862		

stands for the vanadate anion. The equilibria are complicated by competitive hydrolysis of vanadium(V). In alkaline medium the species MOH and M_2OH prevail, and in neutral medium M_3 and M_4 ionic aggregates predominate.

Six potentiometric titrations for two total vanadium(V) concentrations (5 and 20m*M*) and six tartrate concentrations (12.5, 25, 37.5, 50, 100 and 150m*M*) in the pH range from 6.1 to 7.1 were performed by addition of mineral acid to a mixture of vanadate and tartrate (Table 3). The titration data were converted into ($Z_{H/M}$, pH) variables and analysed by POLET(84). Of the six stability constants, two were kept at constant values, log $\beta_{011} = 3.685$ and log $\beta_{012} = 6.360$, while the remaining four were refined, the resulting estimates being log $\beta_{300} = 7.3604 \pm 0.0164$, log $\beta_{400} = 9.6735 \pm 0.1430$, log $\beta_{211} = 11.8049 \pm 0.0196$, log $\beta_{424} = 39.7951 \pm 0.0196$ with SIGY [*i.e.*, $s(Z)$, *cf.* Meloun and Čermák[23]] = 0.01267. On the assumption that the experimental error of Z, $s_{inst}(Z)$, was 0.01 for the given experimental arrangement, the refined parameters were considered reliable. The degree-of-fit also proved there was sufficient refinement of the parameters. The polyvanadate stability constants found were in satisfactory agreement with those obtained by Brito *et al.*[39] from a quite independent data set by using LETAGROP-ETITR.

Other examples of application of POLET(84) can be found[17,18,42] and the use of direct stoichiometry estimation by the ESI approach has been demonstrated in a comparison of three programs, POLET(84), LETAGROP-ETITR and MINIQUAD, applied to the complexation systems of molybdate–malic acid, molybdate–citric acid and borate–malic acid.[42]

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