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Der Chemica Sinica, 2011, 2(6):325-330

Der Chemica Sinica
Pelagia Research Library
ISSN: 0976-8505
CODEN (USA) CSHIA5

Potentiometric analysis of mixtures of acids or bases

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ABSTRACT

Earlier proposed a general approach using data mV/mL from a potentiometric titration is tested for the quantitative determination of mixtures of mono- and poly-protic substances. The method is based on the treatment of the primary data with nonlinear regression procedure using commercial software which gives directly the analytical result. A general formula valid for every type of acid base titration (even mixtures of mono- and poly-protic substances) is used as a direct input with the applied software. Along with the analytical concentration, some specific parameters of the analyzed system are also determined (pK-values, E_o', pK_w). The primary data mV/mL are transferred into pH/mL data using a self-calibration procedure, hence no preliminary pH-calibration of the glass electrode cell is necessary. The applicability of the method is proven to be correct by the analyses of a number of mixtures of mono- and poly-protic substances. The method is applied also in non-aqueous solvents and a number of sparingly soluble in water organic acids and bases have been determined successfully.

Keywords: chemometrics; potentiometry; self pH calibration; acid-base constants; non-aqueous titrimetry.

INTRODUCTION

Acids and bases are conveniently determined by potentiometric titrimetry. Serious difficulties arise when complicated mixtures are analyzed and especially in the case of overlapping pK-values. Using different graphical and numerical methods [1] many attempts were proposed to solve this problem in the last decades. It seems that mainly two computer aided approaches were applied successfully to solve this issue. They are based on the so called *hard-* and *soft-modelling*. The *hard-modelling* approach is founded on strictly theoretical base, including precise treatment of mass balance equations [2-6]. The *soft-modelling* approach [7-13]) is based on the similarity of behaviour of a series of standard solutions with known composition, near to that of the analyzed solution, their successive pH-metric titration and data treatment.

The present study is related to the *hard-modelling* approach. Based on the mass balance concept, acid-base equilibrium constants and constancy of activity factors a single equation $V = f(h)$,

derived in an earlier paper [14], valid for the determination of every combination of acids and bases (monoprotic, polyprotic substances, their mixtures etc.), covering thus the whole spectrum of acid-base titration analyses. The method is also verified for the case of close or overlapping pK-values.

MATERIALS AND METHODS

Chemicals and reagent

Methanol – p.a. and potassium chloride – p.a. (Merck, Darmstadt, Germany) were used without purification. Water-methanol mixture (40:60) was prepared by weight (± 0.1%) with redistilled water. Hydrochloric acid and sodium hydroxide (0.1mol L^{-1}) in water and water-methanol mixture were prepared by dilution of certified volumetric solutions with carbon-dioxide free redistilled water. The solution of hydrochloric acid was standardized with TRIS (tris(hydroxymethyl)-aminomethane) and those of sodium hydroxide with standard solution of hydrochloric acid. All chemicals investigated, corresponded to p.a. purity and were used without purification.

Measurements

The potentiometric titrations were carried in thermo stated vessel 25^{o}C, by means of 713 Metrohm pH-meter, equipped with Metrohm combined electrode ref. 6.0228.000 Pt1000 with temperature sensor and auto burette “Radiometer” ABU 80. The ionic strength was supported with KCl (I = 0.2 mol L^{-1}).

The determination of poly- and mono-protic mixtures with overlapping pK – values

In order to illustrate the proposed method in practice first a relatively simple system of two bases with close pK-values ($\Delta pK \approx 1$) will be discussed, namely an equimolar mixture of TRIS (pK_a=8.00) and IMIDAZOLE [15] (pK_a=6.98; the values of these acid constants are borrowed from [16]). It is obvious that the resulting titration curve will have a smooth sigmoidal course, without any hint of inflexion in the middle (see the equivalent point 1 in Figure 1).

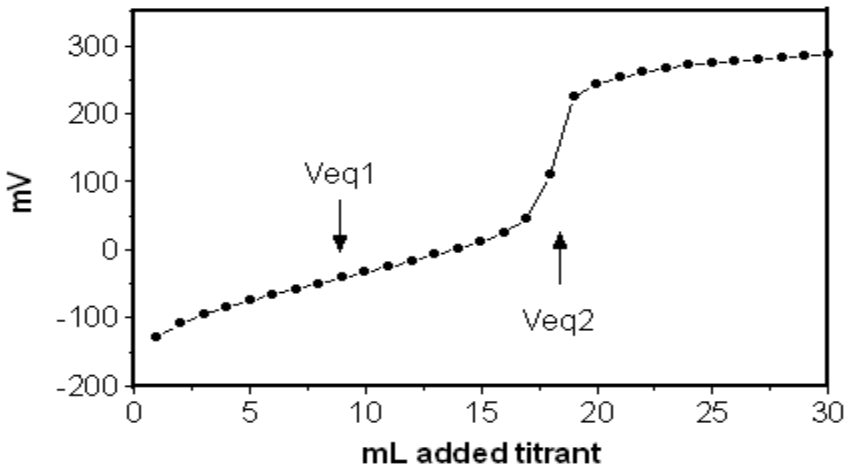

Figure 1: Potentiometric titration curve of equimolar mixture of TRIS and IMIDAZOLE; (Data from Table 1)

Applying formula (1) from [14], for the present case (M=2); m1, n1=1 and m2, n2=1 (two mono-functional bases) one obtains two equations which are inserted as input of the DataFit program

$$Y = V_0 * \left(\left(F1 \right) - K_w / \left(F1 \right) + B_{1,1} * b_{1,1} * \left(F1 \right) / \left(1 + b_{1,1} * \left(F1 \right) \right) + B_{2,1} * b_{2,1} * \left(F1 \right) / \left(1 + b_{2,1} * \left(F1 \right) \right) \right) / \left(C_t + K_w / \left(F1 \right) - \left(F1 \right) \right) \quad (1)$$

and

$$F1 = 10^{\left(\left(X - E_0' \right) / S \right)} \qquad (F1 = h; X = E) \quad (2)$$

where, $B_{m,n}$ are the analytical concentrations of the two bases

$b_{m,n}$ are the respective base constants

The other symbols are the same as in equations (1) and (3) in [14].

As starting values in the regression procedure, the proton stability constants $\beta_{m,n}$ ($b_{1,1}$ and $b_{2,1}$) can be borrowed from literature [16] or preferably put to regression together with the two searched parameters $B_{1,1}$ and $B_{2,1}$. The values of the parameters V_o, K_w, S and C_t are precisely known, that is why they are put as constants.

The discussed equimolar mixture TRIS-IMIDAZOLE was analyzed by means of potentiometric titration with a standard solution of hydrochloric acid. The experimental data V, mL/E, mV and the conditions of this titration are presented in Table 1.

Table 1: Experimental data V, mL/E, mV from potentiometric titration of an equimolar mixture of TRIS (0.01003 mol L^{-1}) and IMIDAZOLE (0.00993 mol L^{-1})

V, mL	E, mV	V, mL	E, mV	V, mL	E, mV
1.00	-127.6	11.00	-25.1	21.00	253.1
2.00	-108.3	12.00	-16.6	22.00	260.3
3.00	-95.1	13.00	-7.9	23.00	265.9
4.00	-84.5	14.00	1.3	24.00	270.4
5.00	-75.2	15.00	11.9	25.00	274.1
6.00	-66.5	16.00	25.2	26.00	277.2
7.00	-58.0	17.00	44.9	27.00	280.1
8.00	-49.7	18.00	110.8	28.00	282.6
9.00	-41.5	19.00	224.2	29.00	284.8
10.00	-33.3	20.00	242.7	30.00	286.8

Table 2: OUTPUT from computer treatment (ProgramDataFit)

Equation ID: twomonofunctbasesMV
Solver type: Nonlinear
Number of nonlinear iterations performed = 6
Residual Sum of Squares (Absolute) = 1.50E-02
Adjusted coefficient of multiple determination (R^2) = 0.99999
Regression Variable Results

	Variable Value	Standard Deviation (SD)	Accuracy Error %
A1	0.01006 ($B_{o,1}$)	± 0.00014	+ 0.4 %
A2	0.009948 ($B_{o,2}$)	± 0.00014	+ 0.2 %
B1	1.19 10^8 ($b_{1,1}$) (pK_a = 8.07)	± 0.02 10^8	
B2	1.00 10^7($b_{2,1}$) (pK_a =7.00)	± 0.02 10^7	
E_0'	404.67	± 0.05	

The data from Table 1, were used as an input in DataFit program fixing the following parameters V_o =100.0 mL; $C_{t\,(HCl)}$ = 0.1110 mol L^{-1}; S = 59.16 mV moL^{-1} (corresponding to 25^oC theoretical value) and K_w = 1.2 10^{-14} (ionic strength 0.2). The output of the computer calculations is shown in Table 2.

As seen from Table 2, the analytical results for TRIS and IMIDAZOLE in this mixtures are determined with good accuracy (error +0.4 % for TRIS and +0.2 % for IMIDAZOLE) and precision (1 % for both). The adjusted coefficient of multiple determination R^2, which is a measure for the response of the regression model described with equation (1) and (2), shows a highly good correlation between model and experiment (R^2) = 0.99999. The acid-base constants of both protolytes are found with good accuracy and precision: pK_a=8.07±0.01 (TRIS) and pK_a=7.00±0.01 (IMIDAZOLE). Some influence of the ionic strength is observed, when compared with the thermodynamic values (cited above). A special attention deserves the standard deviation of E_0', which shows that the *auto pcH-calibration procedure* is functioning highly correct (SD =±0.05 E_0'; SD = ± 0.001 pcH).

In order to examine further the proposed method, a number of other mixtures with overlapping pK values were also analyzed (see Table 3). Summary of the obtained results in water is presented in Table 3A. In the Table 3B some examples of sparingly soluble in water substances determined in a MeOH – H_2O (40:60 w/w) medium are also given.

Table 3: Determination of mixtures of mono- and poly-protic substances in water and some poly- protyc substances in non aqueous medium

A. ***Analytical determinations in water***

Substance	m, mg taken	m, mg found	% found	Error, %	R^2	$\sum\Delta^2$
Formic acid **Acetic acid**	47.4 60.6	47.5 60.8	100.2 100.3	+0.2 +0.3	0.9999_5	$6.10.10^{-2}$
Tartaric acid **Boric acid**	148.6 62.0	149.6 61.8	100.7 99.70	+0.7 -0.3	0.9999_6	$6.25.10^{-2}$
Tartaric acid **Maleic acid**	75.0 116.9	74.4 117.6	99.20 100.6	-0.8 +0.6	0.9999_9	$0.17.10^{-2}$
Malonic acid **Oxalic acid**	104.1 126.6	103.2 125.2	99.12 98.89	-0.9 -1.1	0.9999_9	$0.10.10^{-2}$
Boric acid **Oxalic acid** **Phosphoric acid**	62.2 126.5 115.3	62.6 126.1 115.2	100.6 99.68 99.95	+0.6 -0.3 -0.08	0.9999_9	$9.06.10^{-2}$

B. Analytical determinations in MeOH – H_2O (40:60 w/w)

Substance	m, mg taken	m, mg found	% found	Error, %	R^2	$\sum\Delta^2$
Phtalic acid	165.3	163.9	99.15	- 0.9	0.9999_8	$2.51.10^{-2}$
Quinine	281.6	281.0	99.79	- 0.2	0.9999_4	$4.65.10^{-2}$
Ethylenediamine	62.6	61.9	98.88	- 1.1	0.9999_7	$6.10.10^{-2}$
Pheniramine Maleate	287.4	285.6	99.37	-0.6	0.9999_6	$6.67.10^{-3}$

The combinations are chosen arbitrarily. As seen a relatively good precision and accuracy is achieved with the all results.

RESULTS AND DISCUSSION

As compared to previous investigations, the present study seems to be the most straightforward method for analyses for mixtures of acids and bases. In fact the analytical determination is performed without whatever preparations of the sample and the titration assembly, using the mV/mL mode of titration with the only one precondition, that the composition of the sample is previously known. The computer treatment makes use of a general valid equation [14] applying a commercial software product DataFit. After the calculations the analytical result is obtained directly, associated with important statistical characteristics. Among the standard deviation and the confidential interval, many other important features of the analyzed system are also available. Two of them: the adjusted coefficient of multiple determination (R^2) and the residual sum of squares ($\Sigma\Delta^2$) serve as a sure criterion confirming the validity the chosen model. A practical rule has been drawn that R^2 should be greater then 0.99999 and $\Sigma\Delta^2 \leq 10^{-2}$ in order to accept the determination as reliable. This rule is observed in all examples given in the experimental part of this paper. The acid-base constants of the analyzed components are also obtained, which may serve as an additional proof for the presence of the substances in the tested sample. The constancy of the value E_0' is a reliable measure for the correct behaviour of glass electrode cell (in both water and non-aqueous media). In most of the cases the standard deviation of E_0' was found to be better as ± 0.4 mV corresponding to ± 0.007 pcH units. The proposed procedure itself can serve as a reliable method for determination of acid-base constants in both water and non-aqueous media. The analytical determination of many samples is a proof that the proposed method can be applied in complicated mixtures of protolytes with overlapping pK–values.

CONCLUSION

The main advantage of the present method is the easy access with the applied software DataFit, simple input, no intermediate interventions during the calculations; instant, sure and unequivocal result even with rough starting parameters. The use of the applied software does not require a profound knowledge of computer programming. Other advantages are: the lack of whatever preparation before starting the potentiometric titration with the glass electrode cell; the use of non aqueous solvents in the case of sparingly soluble substances; the determination of acid-base constants as a by-product of the calculations may serve in some extent as a qualitative criterion for the presence of an analyzed protolyte.

REFERENCES

[1] T. Michałowski, M. Toporek, M.Rymanowski, *Talanta*, **2005**, 65, 1241.
[2] N. Ingri, L.G. Sillén, *Pure Appl. Chem.*, **1968**, 17, 55.
[3] D. Dyrssen, D. Jagner, F. Wengelin; Computer Calculation of Ionic Equilibria and Titration Procedures: With Specific Reference to Analytical Chemistry, Almqvist & Wiksell, Stockholm, **1968**.
[4] F. Ingman, A. Johansson, S. Johansson, R. Karlsson, *Analytica Chimica Acta*, **1973**, 64**,** 113.
[5] F. İslamoğlu, H. Yüksek, M. Özdemir, *Der Chemica Sinica*, **2011**, 2 (3), 117.
[6] R. Thanavelan, G. Manikandan, G. Ramalingam, V. Thanikachalam, *Der Chemica Sinica*, **2011**, 2 (4), 90.
[7] R.R. Brereton, *Analyst*, **2000**, 125**,** 2125.
[8] W. Lindberg, B. Kowalski, *Analytica Chimica Acta*, **1988**, 206**,** 125.
[9] Y. Ni, *Analytica Chimica Acta*, **1998**, 367**,** 145.
[10] M. Akhond, J. Tashkourian, B. Hemmateenejad, *J. Anal. Chem. (Moscow)*, 2**006**, 61**,** 804.
[11] X.H. Song, J. Xu, R.Q. Yu, *Microchimica Acta*, **1993**, 111**,** 199.

[12] V. Martínez, M.I. Maguregui, R.M. Jiménez, R.M. Alonso, *J. Pharm. Biomed. Anal.*, **2000**, 23**,** 459.
[13] P. Mittal, V. Uma, K.G. Ojha, *Der Chemica Sinica*, **2010**, 1 (3), 146.
[14] V. Maslarska, J. Tencheva, O. Budevsky, *Anal. Bioanal. Chem.*, **2003**, 375**,** 217.
[15] K. Shalini, P. Kumar Sharma, N. Kumar, *Der Chemica Sinica*, **2010**, 1 (3), 36.
[16] A. Martell, L.G. Sillén; Stability Constants of Metal-Ion Complexes. Special Publication No 25; Suppl. No 1 to Special Publ No 17, 2nd edition, The Chemical Society, Burlington House, London, **1971**.