A Method of Digital Simulation for Acid-Base Titration Curves

Myung-Zoon Czae*, Suw Yong Ly, Taekee Hong†, and Myung-Hoon Kim‡

Department of Chemistry, Hanyang University, Seoul 133-791, Korea
†Department of Chemical Engineering, Hansio University, Choongnam Seosan 352-820
‡Department of Chemical Sciences, Old Dominion University, Norfolk, VA 23529
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Digital Simulation, the term used to describe any procedure of establishing a model (mathematical, dynamic) and deriving a solution numerically⁵, provides a powerful means of studying problems associated with (1) model will be difficult if not impossible to solve analytically, and (2) derived analytical result (even when is adequate) occurs in very complicated form that still requires extensive evaluation; thereby in some cases it is more convenient to use simulation to obtain results directly from a model with specific values rather than to perform the numerical evaluation of the analytical solution⁵.

The potentiometric titration-curve problem is one of the typical cases involved in all of these two features. The exact description (solution) of the titration curves (ionic equilibrium problems) implies the calculation of roots of high-degree polynomial equations solvable only by numerical computation⁵. Moreover, derived (analytical) titration curve equations (and those describing parameters, such as titration error, sharpness index, etc) are complicated and expressed in inverted-variable forms⁵. As a result, approaches based on the artifice of approximations, segmentation, linear plot, and of inverting-the-variables have been employed in many practical applications⁵—¹⁰.

A desirable goal in theoretical titration-curve problem is an autonomous computation scheme that closely follows the practical titration procedure. This purpose might be achieved by digital simulation technique that we employ in this note. It is important to note that the "digital simulation", a technique used here, has to be distinguished from the "numerical computation" on which most of the previous workers relied. Simulation program solves (calculate pH) the problem step by step by observation of the performance, over time (successive stages of titrant additions), of a dynamic model of the titration system. Simulation procedure is therefore perfectly logical and consistent with experimental practice. Moreover, if the information were derived by simulation, the behavior of the system under various conditions (Ka, concentration) would be determined, and any conclusions about the nature of the behavior would be drawn from these results. In this context, this kind of study (real simulation) on titration curves seems not to have been attempted.

We have developed a computer program that simulates the titration curves for the titration of monoprotic acids with a strong base. The simula-
tion program coded in Fortran 77 (put fully in Appendix for readers' application) consists of MAIN and SUBROUTINE BISECTION (Sequence Number, SN, ABT00470-00750). The later locates the roots of the model FN(X) defined as in SN ABT00880-00890, where X refers to hydrogen ion concentration [H⁺]. The variable name statements are obvious referring the following titration curve equation (eq 1) with familiar notations. The mathematical expression describing the titration curves is given by a third-degree polynomial in [H⁺], after V mL addition of Cₗ M strong base to a Vₛ mL of Cₛ M acid during the titration

\[
F([H^+] = [H^+]^3 + \left( K_a + \frac{K_w}{1+f} \right) [H^+]^2 \\
+ \left( \frac{K_a C}{1+f} - \frac{K_w C}{1+f} \right) [H^+] \\
- K_w = 0
\]  

(1)

with titration fraction \( f = C_v/V_v \), \( C_i = C_s = C \), and added volume correction is made. This equation is solved numerically by the bisection algorithm which is prefer to Newton-Raphson method used in the numerical computing scheme for the plot of titration curve (polyprotic acid with a monobasic strong base). By employing bisection method, we can avoid the necessity of the following points in which Newton-Raphson method involved; (1) initial guess for [H⁺] at the first point of the titration usually is made using approximation, (2) computing differentiation of the \( F(X) \), and (3) worrying about the convergence problem (test).

The program was run on a PC 386 equipped with 387 math coprocessor.

Several conclusions pertinent to the \( pK_a \) can be drawn from the simple results, Fig. 1 and 2. Foremost is the gradual approach of the titration curves each other, that begins with \( pK_a \) value of about zero, as \( pK_a \) value decreases (becomes stronger). They overlapped eventually into one (see inset in Fig. 1) when \( pK_a \) value reaches to 1.4, which would be the \( pK_a \) value for the leveled acid H₂O⁺ dissociation. Hence with regard to the \( pK_a \) values of strong acids such as HCl in aqueous solution, the guess or putting in \(-4\), \(-7\), or \(-3\) seems to be pointless. Further analytical application and evaluation will be reported in subsequent papers.

In conclusion, the present work describes a Fortran program that simulates titration curves in the titrations of acids with a strong base without using any artifices employed in previous works. The bisection algorithm for solving the third-degree polynomial in [H⁺] has advantages over that of Newton-Raphson. The results obtained directly by the simulation indicate that the strong acids

**Fig. 1.** Simulated titration curves as a function of \( pK_a \) of the titrand acids with \( C_i = C_s = C = 0.1 M \); inset, segments of the curves in enlarged scale, shows the asymptotic approach to the curve for \( pK_a = 1.4 \).

**Fig. 2.** Three-dimensional plot of the simulated titration curves with \( pK_a \) variation (\( C = 0.1 M \)).
are all leveled to the same strength of hydronium ion, $pK_a = -1.4$ which is in good agreement with established value (around $-1.5$)\textsuperscript{14}.

**APPENDIX**

C ABT FORTRAN:

C ABT FORTRAN: THIS IS FOR TITRATION OF WEAK ACID WITH A STRONG BASE

C THE CUBIC EQUATION FOR THE HYDROGEN ION CONCENTRATION IS SOLVED

C WITH THE BISECTION METHOD (WITH CONCENTRATION CORRECTION DUE TO

C THE VOLUME INCREASE)

C PROGRAM MAIN

IMPLICIT REAL*8(A-H, K, O-Z)
COMMON/AREA1/CNA(40, 500), HH(40, 500), FV(40, 500), HA(40, 500)
* PH(40, 500), KAD(40), FC(40, 500), PKAD (40), PLC(40)
* VCAO(40, 500), CNAD(40), KBD(40), KEQD(40), PHD(40, 500), PLKEQD(40)
COMMON/AREA2/ VCAO, KA, KW, CAL, KB, KEQ
COMMON/AREA3/ CNAO, CAO, VCAO, VC, VCI, PKAD
COMMON/AREA4/ CNAO, CAO, VCAO, VC, VCI, FC(40, 500), PKAD (40), PLC(40)
FUNCTION KEQD(40), PHC(40, 500), FC(40, 500), PKAD (40), PLC(40)
FUNCTION FC(40, 500), FC(40, 500), PKAD (40), PLC(40)

* SUBROUTINE BISECTYPEN, A, B, N, I, J, I)
IMPLICIT REAL*8 (A-H, K, O-Z)
COMMON/AREA1/ CNA(40, 500), HH(40, 500), FV(40, 500), HA(40, 500)
* PH(40, 500), KAD(40), FC(40, 500), PKAD (40), PLC(40)
COMMON/AREA2/ VCAO, KA, KW, CAL, KB, KEQ
COMMON/AREA3/ CNAO, CAO, VCAO, VC, VCI, PKAD

C -

STOP
END

SUBROUTINE BISECTFN, A, B, N, I, J, I)
IMPLICIT REAL*8 (A-H, K, O-Z)
COMMON/AREA1/ CNA(40, 500), HH(40, 500), FV(40, 500), HA(40, 500)
* PH(40, 500), KAD(40), FC(40, 500), PKAD (40), PLC(40)

CALL BISECTFN, A, B, N, I, J, I)
CNA(40, 500) = CNAD(40, 40, 40, 40)
PHD(J, D = DLOG10(HH(J, D))
PKAD(J) = DLOG10(KAD(J))
COMMON/AREA/ CNAI
COMMON/AREA/ CNAO, CAO, VCAO.
VC, VCI, FCI
KW=1.0D-14
CAI=CAO*VCAO/(VCAO-VCAO)
CNAI=CNAO*VCNAI/(VCAO-VCAO)
FN=X*X*X+(KA+FCI*CNAI/(1+FCI) # X*X+(KA+FCI*CNAI/(1+FCI)
-KA*CNAI/
*(1+FCI)-KW)*X-KA*KW
RETURN
END

인용문헌
7. M. D. Seymour, J. W. Clayton Jr., and Q. Ferna