Nonlinear pH Control Using a Three Parameter Model

Jietae Lee and Ho-Cheol Park

Abstract: A two parameter model of a single fictitious weak acid with unknown dissociation constant has been successfully applied to design a neutralization system for many multi-component acid streams. But there are some processes for which above two parameter model is not satisfactory due to poor approximation of the nonlinearity of pH process. Here, for better control of wide class of multi-component acid streams, a three parameter model of a strong acid and a weak acid with unknown dissociation constant is proposed. The model approximates effectively three types of largest gain variation nonlinearities. Based on this model, a nonlinear pH control system is designed. Parameters can be easily estimated since their combinations appear linearly in the model equations and nonlinear adaptive control system may also be constructed just as with the two parameter model.

Keywords: nonlinear pH control, three parameter model

I. Introduction

The acidity of an aqueous solution which is measured with a pH sensor, plays a very important role in various physical, chemical and biological processes. For example, neutralization is required for a biological treatment of wastewater stream. The control of the pH level is known as a difficult problem due to its severe nonlinearity. The nonlinearity of a pH process is represented with the titration curve and is usually considered as a gain variation. Fig. 1 shows three typical titration curves for which conventional linear controllers suffer from poor performances or instability due to large gain variations.

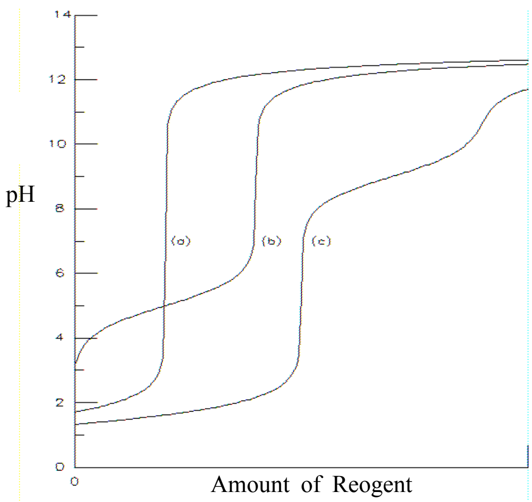

Fig. 1. Three typical titration curves having the most severe gain variation. (a) strong acid-strong base system, (b) weak acid-strong base system, (c) strong acid, weak acid-strong base system.

Many nonlinear control methods which use empirical models or rigorous physicochemical models of McAvoy et al.[1] and Gustafsson and Waller[2] are available. Shinskey [3] introduced a nonlinear controller with piecewise linear gains to compensate the nonlinearity of the process. Goodwin et al.[4] developed an adaptive linearizing controller for neutralization of a strong acid process.

Reccently nonlinear control methods based on the two parameter model of a weak acid process have beeen proposed by some authors and applied to practical multi-component processes successfully. The model consists of two unknown parameters of acid concentration and dissociation constant which can be estimated from the titration curve of feed stream or some steady-state operation data. Parrish and Brosilow[5] applied their nonlinear inferential control methodology to this model. Williams et al.[6] proposed a method to obtain the unknown two parameters by injecting the strong base at two points of a special in-line process and designed a nonlinear model based controller based on this model. Li et al.[7] applied the nonlinear internal model control method. Lee et al.[8] used this model to design a nonlinear adaptive control system[9] utilizing the linearity of unknown parameters in the model. Simulation and experimental studies show that these nonlinear control methods give very good control performances for practical multi-component acid processes even though they are based on one weak acid model.

Wright and Kravaris[10] introduced a first order model by reducing the general reaction invariant model of pH processes and presented an excellent nonlinear control method. Their controller requires an information about the steady-state titration curve. Since the controller is robust for the variation of the titration curve, a rough titration curve is sufficient in practice. Here, as a practical parameterization of Wright and Kravaris model or an extension of the above two parameter model, we propose a three parameter model of a strong acid and a weak acid process. The model can approximate effectively three most severe nonlinear titration curves in Fig. 1. Furthermore three unknowns can be arranged to be linear as in the two parameter model, so that they are easily estimated from the titration curve. A nonlinear adaptive control system can be also constructed with this model just like the way of the two parameter model of Lee et al.[8] Corresponding linearizing control system is designed here and its performances are investigated.

II. Three parameter model

Consider a continuous stirred tank mixer in Fig. 2, in

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which the process stream is neutralized by a strong base

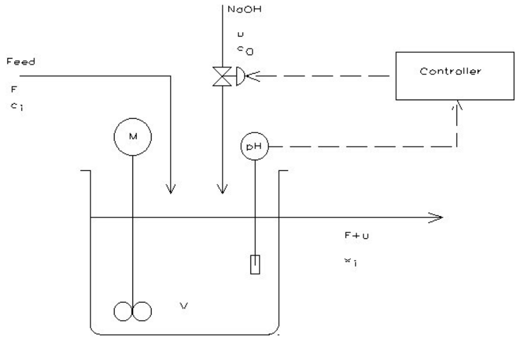

Fig. 2. Continuous stirred tank neutralization system.

such as sodium hydroxide (NaOH). Although the process stream may contain various species, it is assumed to consist of one strong acid and one weak acid. Assuming constant tank volume and perfect mixing, the following model equation can be obtained[1]:

$$\begin{aligned} V\frac{dx_0}{dt} &= uc_0-(F+u)x_0 \\ V\frac{dx_{11}}{dt} &= Fc_{11}-(F+u)x_{11} \\ V\frac{dx_{12}}{dt} &= Fc_{12}-(F+u)x_{12} \end{aligned} \tag{1}$$

$$\begin{aligned} & z^3+(K_a+x_0-x_{11})z^2 \\ & +(K_ax_0-K_ax_{11}-K_ax_{12}-K_w)z-K_aK_w=0 \\ & pH=-\log_{10}(z) \end{aligned} \tag{2}$$

where

c_0, x_0 = total ion concentration of a strong base in the titrating and effluent streams,

c_{11}, x_{11} = total ion concentration of a fictitious strong acid in the process and effluent streams,

c_{12}, x_{12} = total ion concentration of a fictitious weak acid in the process and effluent streams,

K_a = dissociation constant of the fictitious weak acid,

K_w = dissociation constant of water,

z = concentration of the hydrogen ion in the effluent stream,

and V, F and u are volume of the mixer, the influent flow rate and the titrating flow rate, respectively.

Since all equations in (1) are distinct and structurally similar, they can be reduced as[10]:

$$\begin{aligned} & V\frac{dx}{dt}=-Fx+(1-x)u \\ & x_0(t)=c_0x(t)+e_0(t) \\ & x_{11}(t)=c_{11}(1-x(t))+e_{11}(t) \\ & x_{12}(t)=c_{12}(1-x(t))+e_{12}(t) \end{aligned} \tag{3}$$

where $e_0(t)$, $e_{11}(t)$ and $e_{12}(t)$ are due to mismatches in initial values of the states $x_0(t)$, $x_{11}(t)$ and $x_{12}(t)$, and their magnitudes decay exponentially to zero. Equation (2) becomes

$$\begin{aligned} & z^3+(K_a-c_{11})z^2-(K_ac_{11}+K_ac_{12}+K_w)z-K_aK_w \\ & +x((c_0+c_{11})z^2+K_a(c_0+c_{11}+c_{12})z) \\ & +(e_0-e_{11})z^2+(e_0-e_{11}-e_{12})K_az=0 \end{aligned} \tag{4}$$

The model represented by equations (3) and (4) with $e_0=e_{11}=e_{12}=0$ is used to design a control system. It contains three unknown parameters c_{11}, c_{12} and K_a (all other constants such as V and F are assumed known since they are constant or can be measured easily). Their effects on the titration curve are shown in Fig. 3. That is, the above model can approximate effectively three highly nonlinear titration curves in Fig. 1. Combination of the three unknown parameters, K_a, c_{11} and $K_a(c_{11}+c_{12})$ appear linearly in equation (4) as:

$$\begin{aligned} & [z^2-K_w+c_0xz,\ (x-1)z^2,\ (x-1)z] \\ & \begin{bmatrix} K_a \\ c_{11} \\ K_a(c_{11}+c_{12}) \end{bmatrix} \\ & =[-z^3+K_wz-c_0xz^2]+(\text{error terms}) \end{aligned} \tag{5}$$

So estimation and adaptation of the parameters can be included easily with the least squares method.

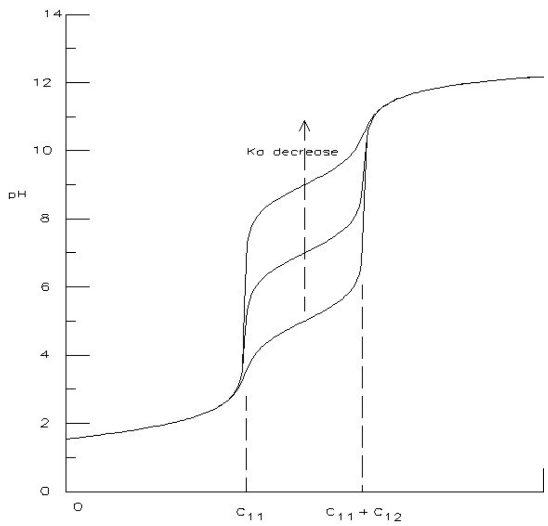

Fig. 3. Titration curves of the three parameter model.

III. Nonlinear control system design

Many control methods are available for the process with model equations (3) and (4). Here a linearizing control method is used as shown in Fig. 4. The state variable x is calculated from equation (4) with the measured pH as

$$\begin{aligned} x &= \phi(\mathrm{pH}) \\ &= -[z^2+(K_a-c_{11})z-(K_ac_{11}+K_ac_{12}+K_w) \\ &\quad -K_aK_w/z]/[(c_0+c_{11})z+K_a(c_0+c_{11}+c_{12})], \\ z &= 10^{-\mathrm{pH}} \end{aligned} \tag{6}$$

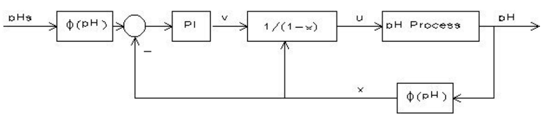

Fig. 4. Linearizing control system.

The proportional and integral (PI) controller is used as

$$u = \frac{1}{1-x}\left(K_c(x_s-x)+\frac{K_c}{\tau_i}\int_0^t (x_s-x)dt\right), \quad x_s=\phi(\mathrm{pH}_s) \tag{7}$$

where K_c and τ_i are the controller gain and integral time, respectively. The two PI controller parameters are chosen as

$$K_c = 1.414\omega V - F, \quad \tau_i = K_c/[\omega^2 V] \tag{8}$$

so that two closed-loop poles of the linear system about the state x are at ω 0.707 ± 0.707j). Faster responses can be obtained by increasing ω at the expense of higher sensitivity to modeling error.

IV. Simulation

A process where phosphoric acid (H_3PO_4) is titrated by the sodium hydroxide (NaOH) is simulated. The process can not be approximated very well by the two parameter model. To simulate the behavior of the pH process, we used full order model as in Wright and Kravaris.[10] In solving the nonlinear titration equation, we used the reliable bisection method. Integral windup was avoided simply by freezing the integration when input u exceeds the upper and lower limits. Parameters used in the simulation are given in Table 1. Titration curves of the process, the two parameter model and the three parameter model are shown in Fig. 5. Fig. 6 and 7 show responses of control systems based on the two parameter model and the three parameter model. The two parameter model system shows an oscillation around the set point pHs=5 due to high loop gain and time delay effect

Table 1. Parameters used in simulation of the phosporic process.

V : 5 L
F : 0.0188 L/s
u : [0 0.0552 L/s]
sampling time : 5 s
Feed: 0.025 mol/L H_3PO_4 solution
dissociation constant = 7.11×10^{-3} , 6.34×10^{-8}, 4.2×10^{-13}
Disturbances:
0.005 mol/L NaOH is added in feed stream between 400 and 500 seconds.
0.03 mol/L HCI is added in feed stream between 1200 and 1300 seconds.
Model:
two parameter model: c_{12}=0.05mol/L, $K_a=2.0\times10^{-7}$ (c_{11}=0)
three parameter model: c_{11}=0.025 mol/L, c_{12}=0.025 mol/L, $K_a=6.34\times10^{-8}$
Controlller tuning parameter, ω 0.1

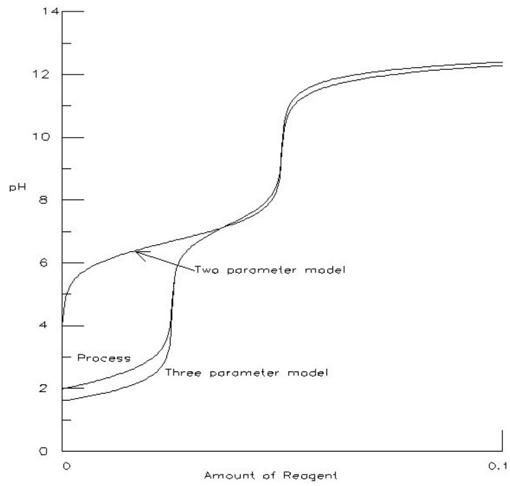

Fig. 5. Titration curves of the process, the two parameter model and the three parameter model used in simulation.

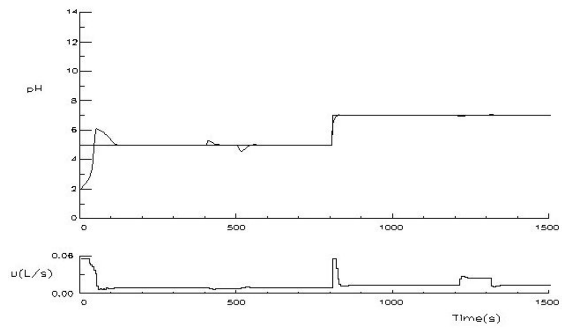

Fig. 6. Simulation results of the control system with three parameter model.

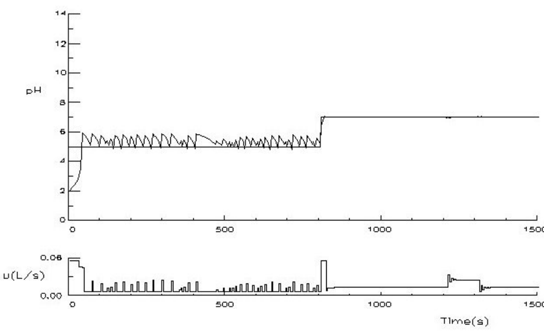

Fig. 7. Simulation results of the control system with two parameter model.

of sample and hold. It was removed by decreasing the sampling time as in Fig. 8. However, since very small sampling time is economically impractical and real processes also have unmodeled dynamics due to such as slow sensor dynamics and imperfect mixing, control system based on the two parameter model may be inadequate. Fig. 9 shows the effect of mismatches of the feed flow rate, F, where 0.0066 L/s is used for controller design which is different from that of process (0.0188 L/s). Many other situations are also simulated and we can see that control systems based on the three parameter model are robust for parameters variations and various mismatches between the process and model.

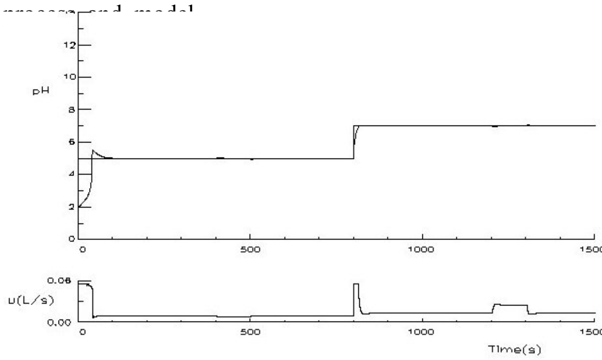

Fig. 8. Simulation results of the control system with two parameter model for small integration step.

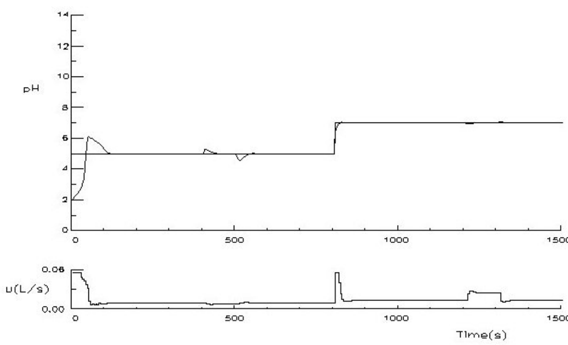

Fig. 9. Simulation results of the control system with three parameter model when different feed flow rate is used for controller design.

V. Experiments

Two different pH processes are experimented. One is the same as the process used in the simulation study. Second is a practical multi-component process. As a pH sensor, Signet 8700 pH transmitter is used, which has manufacturer's specifications of 5 seconds response time for 63% of step response, 0.1 pH accuracy, an automatic temperature compensation and 4-20mA output. Titrating flow is adjusted by the solenoid valve with 5 second pulse width modulated signal. Other instruments are IBM PC/286 and home-made interface cards of resolution 12 bits.

Table 2. Parameters for the first experiment of phosporic process.

run 1 :
Feed: 0.025 mol/L H_3PO_4 solution
Disturbances:
50 ml of 0.15 mol/L NaOH is added instantaneously at 450 and 1180 seconds.
100 ml of 0.20 mol/L HCl is added instantaneously at 980 second.
Model:
three parameter model: c_{11}=0.025 mol/L, c_{12}=0.025 mol/L, K_a=6.34x10^{-8}
run 2:
Feed: unknown H_3PO_4 and HCl mixture
Disturbances:
100 ml of 0.15 mol/L NaOH is added instantaneously at 600 second.
100 ml of 0.20 mol/L HCl is added instantaneously at 980 second.
Model:
three parameter model: the same as run 1

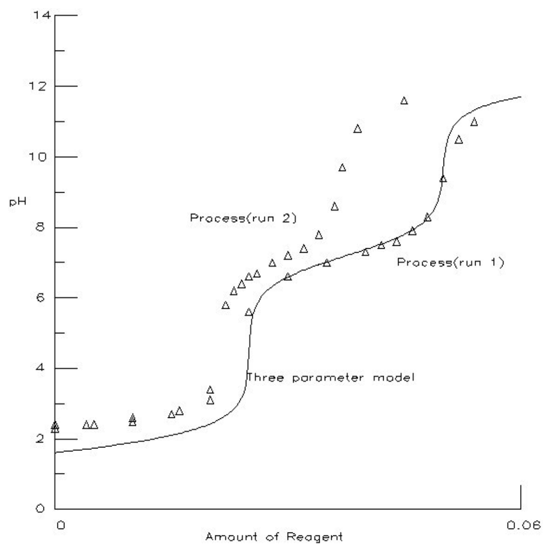

Fig. 10. Titration curves of the process and the three parameter model in the experiment 1.

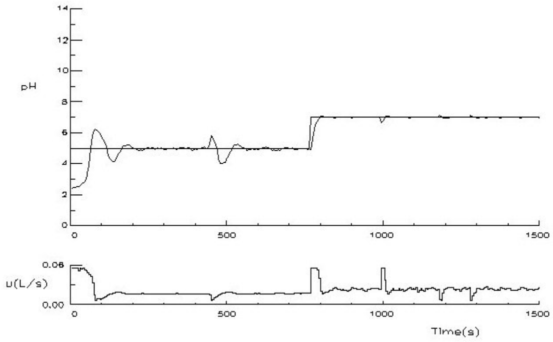

Fig. 11. Experimental results of the control system with three parameter model: run 1.

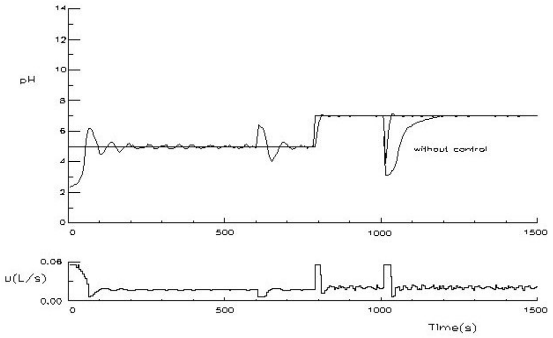

Fig. 12. Experimental results of the control system with three parameter model: run 2.

Experiment 1: First, a phosphoric stream is titrated with a sodium hydroxide solution. Model parameters are obtained from the titration curve of the process phosphoric stream. Control performances for set point changes and instantaneous addition of a strong base and an acid are experimented. Second, the feed stream is diluted and corrupted with a strong acid, HCl. The model used is still the same as the first run. The same disturbances are introduced. Parameters different from the Table 1 are shown in Table pH Titration curves are shown in Fig. 10. There are significant mismatches in titration curves between the process and model for the second run. Experimental results are shown in Fig. 11 and 12. Effects of disturbance without control is also shown in Fig. 12. Fluctuations around the set point 5 seem mainly due to the unmodeled sensor dynamics and time delay effect of sampling.

Table 3. Parameters for the second experiment of multi -component process.

Amount of Reagent

run 1: Feed: 0.013 mol/L H_3PO_4 and 0.016 mol/L CH_3COOH solution Disturbances: 50 ml of 0.15 mol/L NaOH is added instantaneously at 340, 390 and 1280 seconds. 100 ml of 0.20 mol/L HCl is added instantaneously at 860 second. Model: three parameter model: c_{11}=0.012 mol/L, c_{12}=0.027 mol/L, K_a=1.0x10^{-6} run 2: Feed: the same as in run 1 Disturbances: 50 ml of 0.15 mol/L NaOH is added instantaneously at 260 and 980 seconds. 100 ml of 0.20 mol/L HCl is added instantaneously at 380 and 980 seconds. Model: two parameter model: c_{12}=0.038 mol/L, K_a=8.0x10^{-7} (c_{11}=0)

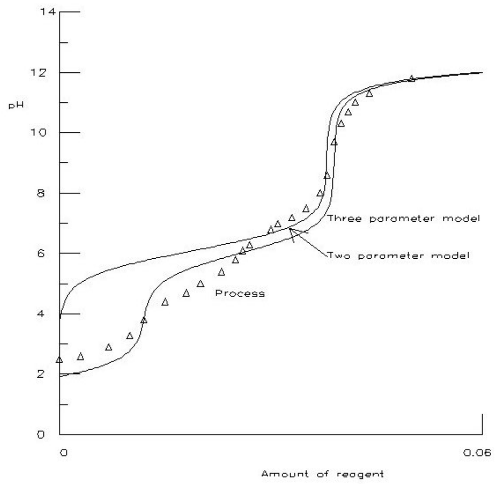

Fig. 13. Titration curves of the process, the two parameter model and the three parameter model in the experiment 2.

Experiment 2: A mixture of the phosphoric acid and the acetic acid is titrated by the sodium hydroxide solution. Parameter values are shown in Table 3. Model parameters are obtained graphically from the titration curve of the process by trial and error, which are shown in Fig. 13. Approximation by the three parameter model was better. Both controllers based on the two parameter model and the three parameter model provided excellent control performances, which are shown in Fig. 14 and 15.

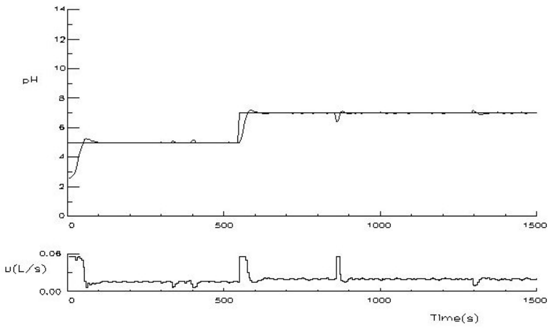

Fig. 14. Experimental results of the control system with three parameter model: run1.

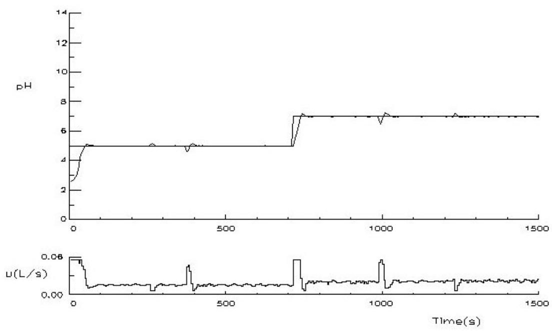

Fig. 15. Experimental results of the control system with two parameter model: run2.

VI. Conclusion

A three parameter model is proposed, which can approximate nonlinearity of many pH processes well while maintaining simplicity of the two parameter model such as linearity among model parameters. Simulation and experiments show that the control system with the three parameter model can be applied to a large class of pH processes. Parameters can be obtained form a steady-state titration curve. Since combinations of parameters appear linearly in the model equations, with the on-line parameter estimating scheme by the well-known least squares method, a nonlinear adaptive control system may also be constructed with this three parameter model.

VII. Nomenclature

c_0, c_{11}, c_{12} = fictitious total ion concentration of the titrating strong base, the process strong acid, and the process weak acid, respectively, [mol/L]

e_0, e_{11}, e_{12} = error due to mismatches in initial states

F = flow rate of the process stream, [L/s]

K_a = dissociation constant of a fictitious weak acid, [mol/L]

K_c, τ_i = controller gain and integral time of the PI controller

K_w = dissociation constant of water, 10^{-14}

pH, pH_s = $-\log_{10}z$ and its set point varible

t = time, [s]

u = flow rate of the titrating stream, [L/s]

V = volume of the mixing tank, [L]

x = normalized total ion concentration in the effluent stream (system state)

x_0, x_{11}, x_{12} = effluent fictitious total ion concentration of the titrating strong base, the process strong acid, and the process weark acid, respectively, [mol/L]

z = total ion concentration of hydrogen ion in effluent stream, [mol/L]

ϕ ·) = steady-state relation between x and pH

ω = natural frequency for the linearized closed-loop system, [1/s]

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