

# Modeling and Identification of pH Processes

Jose L. Rodriguez  
Dept. de Ingenieria Mecanica  
Universidad Nacional Experimental del Tachira  
San Cristobal, Edo. Tachira, Venezuela  
jlorodriguez@ieee.org

Kenneth A Loparo  
Department of Electrical Engineering and  
Computer Sciences  
Case Western Reserve University  
Cleveland, OH 44106-7070, USA  
kal4@po.cwru.edu

**Abstract**—This paper presents in a complete and detailed manner the modeling of pH processes. The model is strictly based in the physical balance equations of mass and charge. The model exactly represents the balance equation, it is proven that polyprotic substances can be represented uniquely by a combination of monoprotic substances equivalent to the real acids, bases and salts that compose the solution. A general differential algebraic equation model is derived for the CSTR arrangement. Observability conditions for the solution inside the CSTR are derived using a reduced model and based on these observability conditions a minimal description for the chemical solution is derived. The balance equation is shown to be monotone, hence the solution of this equation is unique and well defined for each value of pH. This establishes the validity of nonlinear feedback linearization techniques which require the inverse of the static nonlinearity. Two identification methods are proposed: the nonnegative least squares algorithm to find the influent concentrations when the dissociation constants pK's are known or to find a set of fictitious concentrations that best represent an unknown model using a fixed and ample set of fictitious pK's. The nonlinear optimization algorithm operating in cascade with the nonnegative least squares algorithm determines the set of pK's and respective concentrations that best approximate the influent composition.

## I. INTRODUCTION

Control of  $pH$  is a very difficult and complex task because in many cases the slope of the process nonlinearity can be very steep around the setpoint and small changes in the influent concentration can result in extreme changes in  $pH$ .

The preferred arrangements for  $pH$  control are the Continuously Stirred Tank Reactor (CSTR), Batch and In-Line.

This paper focuses on the modeling and identification of  $pH$  processes in a CSTR configuration.

The main contribution of this work is the extension of the model description to include multiple fictitious monoprotic substances to exactly represent the entire *balance equation*. This approach yields a *balance equation* that is a good approximation for any neighborhood size around the setpoint. It is also shown that the states (concentration) of weak components can be observed if

their dissociation constants are in the excitation region and they are different. It is further shown that this memoryless nonlinearity is strictly monotone around the setpoint. Consequently, the inverse is well-defined and is also an explicit function of the control action, making its use in nonlinear feedback control the natural choice for attacking this problem.

Chemical based models are available as a result of the works of McAvoy [1]; P. Jutila et al [2], Gustafsson and Waller [3] and [4], Gustafsson et al [5]; Wright and Kravaris [6] and Levie [7], among many others.

This paper begins by deriving a model for a chemical solution of any number of acids, bases or salts. The monoprotic simplification of polyprotic substances is discussed. A compact balance equation is proposed and examples of the new notation are presented. A differential algebraic equation model describing the  $pH$  process in a CSTR is proposed. Observability conditions for the chemical solution states are developed. Implications on monotonicity and uniqueness are discussed. A minimal description based on the observability conditions and the monoprotic simplification is proposed. A structure to include multiple reagents is established. An identification approach for the influent concentrations and components is proposed. Finally, conclusions are presented.

## II. PH CHEMISTRY

In this section a balance equation describing a chemical solution is obtained using the fundamental equations of chemical equilibrium and conservation.

### A. Notation

$H_{(n_a - \mathcal{Z}_a)} A^{\mathcal{Z}_a -}$  : acid molecule ( $\mathcal{Z}_a = 0$ ).

$B(OH) A_{(n_b - \mathcal{Z}_b)}^{\mathcal{Z}_b +}$  : base molecule ( $\mathcal{Z}_b = 0$ ).

$H_2O$  : water molecule.

$H^+$  : hydrogen ion (proton).

$OH^-$  : hydroxyl ion.

$\mathcal{Z}$  : formal charge.

$K$  : dissociation constant.

$pK = -\log(K)$

$n_a$  : number of dissociations for an acid.

$n_b$  : number of dissociations for a base.

*Remark 1:* If the formal charge:  $Z_a > 0$  and  $Z_b > 0$ , the acid molecule becomes its conjugate base and the basic molecule becomes its conjugate acid, respectively.

## B. Conservation equations

A vessel containing water mixed with several chemical substances will be studied.

*Assumptions:* Constant temperature, ions involved are completely soluble and salts do not precipitate.

Since all the ions involved are soluble (by assumption), the study will focus on the individual dissociations of each component, this approach is valid because properties such as total mass and total charge are invariant.

Given several polyprotic acids or its conjugate bases,  $\sum_{k=1}^{N_a} [H(n_{a,k} - Z_{a,k}) A^{Z_{a,k}-}]_{0,k}$  and several polyprotic bases or its conjugate acids  $\sum_{k=1}^{N_b} [B(OH)_{(n_{b,k} - Z_{b,k})}^{Z_{b,k}+}]_{0,k}$ . Where the conjugate acids or bases could come from the dissolution of salts.

Where:

$[ ]_0$  : Nominal or market concentration.

$N_a$  : Number of acids present in solution.

$N_b$  : Number of bases present in solution.

$n_{a,k}$  : Number of dissociations of the  $k^{th}$  acidic component.

$n_{b,k}$  : Number of dissociations of the  $k^{th}$  basic component.

The equations of dissolution, dissociation reactions, conservation of molecular mass and charge yield

$$\sum_{k=1}^{N_b} \mathcal{X}_{b,k} (\mathcal{D}_{b,k} - Z_{b,k}) - \sum_{k=1}^{N_a} \mathcal{X}_{a,k} (\mathcal{D}_{a,k} - Z_{a,k}) + \alpha = 0 \quad (1)$$

Where:

$$\mathcal{X}_a \triangleq H(n_a - Z_a) A^{Z_a -}$$

$$\mathcal{X}_b \triangleq B(OH)_{(n_b - Z_b)}^{Z_b +}$$

$$\alpha \triangleq 10^{-pH} - 10^{pH - pK_w}$$

## III. MONOPROTIC SIMPLIFICATION

This section will show that the dissociation factor ( $\mathcal{D}$ ) of a polyprotic substance can be represented uniquely by the linear combination of several dissociation factors ( $\mathcal{D}$ ) of fictitious monoprotic (equivalent) substances.

Most of the analysis will be focused on acids, but the results can be easily extended to bases.

### Monoprotic acids and bases

Fact:

$$\mathcal{D}_a \triangleq \mathcal{D}_a = \frac{1}{1 + 10^{pK_a - pH}} \quad (2)$$

$$\mathcal{D}_b \triangleq \mathcal{D}_b = \frac{1}{1 + 10^{pH - pK_{ab}}} \quad (3)$$

The dissociation factor of a base can be expressed in terms of an acid by noticing that  $\mathcal{D}_b = 1 - \mathcal{D}_a$  if  $pK_{ab} = pK_a$

### Diprotic acids and bases:

In the case of diprotic acids and bases it is possible to show that under certain conditions they can be represented exactly by two monoprotic acids or bases, respectively. Consider

$$\mathcal{D}_a = \frac{10^{pH - pK_{a,1}} + (2) 10^{2pH - pK_{a,1} - pK_{a,2}}}{1 + 10^{pH - pK_{a,1}} + 10^{2pH - pK_{a,1} - pK_{a,2}}} \quad (4)$$

Simplifying (4)

$$\mathcal{D}_a = \frac{1}{1 + 10^{pK_{a,1} - pH}} + \frac{1}{1 + 10^{pK_{a,2} - pH}} \quad (5)$$

By adding the right hand side (*rhs*) of (5) and matching term by term with the *rhs* of (4) a feasible solution for monoprotic simplification can be obtained when

$$K_{a,1} \geq 4K_{a,2} \quad (6)$$

The result in terms of  $pK_a$  is:

$$pK_{a,2} - pK_{a,1} \geq 0.60206 \quad (7)$$

Because the difference between the  $pK_a$ 's in most diprotic substances is greater than 3.0 (Rodriguez [8]), then it is reasonable that this monoprotic simplification is valid from a practical prospective.

A similar result is given by Gustafsson et al [5], but there was no discussion about the validity of this simplification from the physical constraints.

In conclusion  $\mathcal{D}_a = \mathcal{D}_{a,1} + \mathcal{D}_{a,2}$ .

The dissociation factor of a base can be obtained by  $\mathcal{D}_b = 2 - \mathcal{D}_a$  if  $pK_{a,1} = pK_{ab,2}$  and  $pK_{a,2} = pK_{ab,1}$ .

### Triprotic acids and bases

In the case of triprotic acids and bases, it is also possible to show that under certain conditions they can be represented exactly by three monoprotic acids or bases, respectively. Consider

$$\mathcal{D}_a = \frac{\sum_{j=1}^3 j 10^{jpH - \sum_{k=1}^j pK_{a,k}}}{1 + \sum_{j=1}^3 10^{jpH - \sum_{k=1}^j pK_{a,k}}} \quad (8)$$

Simplifying (8)

$$\mathcal{D}_a = \sum \frac{1}{1 + 10^{pK_{a,j} - pH}} \quad j = 1, 2, 3 \quad (9)$$

By adding the right hand side (*rhs*) of (9) and matching term by term with the *rhs* of (8) an explicit solution for the minimal difference between two consecutive  $pK_a$ 's in order that a meaningful monoprotic substitution of a triprotic acid exists is not easy to obtain. However, numerically solving the cubic equation gives a minimal difference that depending on the distribution of

the  $pK_a$ 's, varies between 0.47713 and 0.60206. From a practical point of view this substitution is usually valid because the minimal difference between  $pK_a$ 's for several common substances is greater or equal to 0.65 (Rodriguez [8]).

The dissociation factor of bases can be obtained by  $\mathcal{D}_b = 3 - \mathcal{D}_a$  if  $pK_{a,1} = pK_{ab,3}$ ,  $pK_{a,2} = pK_{ab,2}$  and  $pK_{a,3} = pK_{ab,1}$ .

In summary, using the monoprotic simplification, polyprotic substances can be represented as follows:

$n_{b,k}$ -protic base:

$$\mathcal{D}_{b,k} = n_{b,k} - \sum_{j=1}^{n_{b,k}} \frac{1}{1 + 10^{pK_{ab,k,j} - pH}} \quad (10)$$

$n_{a,k}$ -protic acid:

$$\mathcal{D}_{a,k} = \sum_{j=1}^{n_{a,k}} \frac{1}{1 + 10^{pK_{a,k,j} - pH}} \quad (11)$$

#### IV. BALANCE EQUATION

The *balance equation* for the acids and bases present in the solution is given by

$$T_B - T_A + \alpha = 0 \quad (12)$$

where:

$$T_B = \sum_{k=1}^{N_b} \mathcal{X}_{b,k} \left( n_{b,k} - \sum_{j=1}^{n_{b,k}} \mathcal{D}_{b,j,k} - \mathcal{Z}_{b,k} \right) \quad (13)$$

$$T_A = \sum_{k=1}^{N_a} \mathcal{X}_{a,k} \left( \sum_{j=1}^{n_{a,k}} \mathcal{D}_{a,k,j} - \mathcal{Z}_{a,k} \right) \quad (14)$$

Define:

$X_b$  : vector derived from  $\mathcal{X}_b$  where each entry in  $X_b$  is an element of  $\mathcal{X}_b$  replicated  $n_{b,k} - 1$  times.

$Z_b$  : vector derived from  $\mathcal{Z}_b$  where each entry in  $Z_b$  is an element of  $\mathcal{Z}_b$  replicated  $n_{b,k} - 1$  times and divided by  $-n_{b,k}$ .

$N_b = \sum_{k=1}^{N_b} n_{b,k}$  : the dimension of  $X_b$ .

$S_b$  :  $N_b \times 1$  vector with all its entries equal to one, that identifies basic components.

$X_a$  : vector derived from  $\mathcal{X}_a$  where each entry in  $X_a$  is an element of  $\mathcal{X}_a$  replicated  $n_{a,k} - 1$  times.

$Z_a$  : vector derived from  $\mathcal{Z}_a$  where each entry in  $Z_a$  is an element of  $\mathcal{Z}_a$  replicated  $n_{a,k} - 1$  times and divided by  $n_{a,k}$ .

$N_a = \sum_{k=1}^{N_a} n_{a,k}$  : the dimension of  $X_a$ .

$S_a$  :  $N_a \times 1$  vector with all its entries equal to zero, that identifies acidic components.

Using this new notation, (12) can be written as:

$$(-D_b + S_b + Z_b)^T X_b + (-D_a + S_a + Z_a)^T X_a + \alpha = 0 \quad (15)$$

Defining the vectors:

$$X = \begin{bmatrix} X_b \\ X_a \end{bmatrix}, \quad Z = \begin{bmatrix} Z_b \\ Z_a \end{bmatrix}, \quad pK = \begin{bmatrix} pK_{ab} \\ pK_a \end{bmatrix}$$

$$D = \begin{bmatrix} D_b \\ D_a \end{bmatrix}, \quad \text{where } D_k = \frac{1}{1 + 10^{pK_k - pH}}$$

$$S = \begin{bmatrix} S_b \\ S_a \end{bmatrix}, \quad N = N_b + N_a$$

Equation (15) is written as:

$$-D^T X + (S + Z)^T X + \alpha = 0 \quad (16)$$

Define

$$\gamma = (S + Z)^T X \quad (17)$$

Notice that  $X$  is a nonnegative vector of the *nominal concentrations* and is invariant with respect to  $pH$ , then  $\gamma$  is a nonnegative constant as long as the *nominal concentrations* of the basic components remain constant. Equation (16) can be written as

$$-D^T X + \gamma + \alpha = 0 \quad (18)$$

1) *Notation Summary:*

- $X$  : vector of concentrations where each entry of  $\mathcal{X}$  is replicated  $n - 1$  times in  $X$ ; being  $n$  the number of possible dissociations for each multiprotic component. Besides, if a component has the structure  $T(P)_n$  with molar concentration  $\delta M$  (where  $\delta$  is a constant and  $M$  stands by "molar"), the ion concentration is  $\delta M$  w.r.t. the  $T^{\pm n}$  ion and  $n\delta M$  w.r.t. the  $P^{\pm}$  ion ([9], pp. 212)
- $pK$  : vector with the dissociation constants of all the substances in the solution.
- $Z$  : formal charge vector, where each entry of  $\mathcal{Z}$  is replicated  $n - 1$  times and divided by  $n$  for acids and by  $-n$  for bases.
- $S$  : vector with all entries equal to one for basic components and to zero for acidic components.

*Remark 2:* This model that includes salts was validated solving the examples: 7.10, 7.11, 7.12, 7.14 and the exercise 56 from [10].

#### Notational Example

A set of solutions is given in Table I, such set can be written using the notation proposed in this work as is shown in Table II.

### V. CSTR MODELING

#### A. Description

The CSTR arrangement can be described as a tank which receives influent flow (process stream) and reagent flow (control stream), which are mixed inside the tank, and the resulting mixture is discharged into the effluent stream.

The influent flow can be the result of the mixing of several streams, each one with known or unknown

TABLE I  
NOMINAL SUBSTANCES

N°	Substance	$pK_a$ (o $pK_{ab}$ )	Condition
1	0.1 M NaOH	17.00	base
2	0.1 M Ca(OH) <sub>2</sub>	12.600 11.570	base
3	0.1 M HNO <sub>3</sub>	-1.444	acid
4	0.1 M H <sub>3</sub> PO <sub>4</sub>	2.125 7.208 12.000	acid
5	0.1 NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	9.255 2.125 7.208 12.000	salt
6	0.1 (NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	9.255 2.125 7.208 12.000	salt

TABLE II  
DESCRIPTION IN TERMS OF THE PROPOSED NOTATION

N°	X	pK	S	Z
1	0.1	17.00	1	0
2	0.2	12.60	1	0
	0.2	11.57	1	0
3	0.1	-1.44	0	0
4	0.1	2.13	0	0
	0.1	7.21	0	0
	0.1	12.00	0	0
5	0.1	9.26	1	-1
	0.1	2.13	0	1/3
	0.1	7.21	0	1/3
	0.1	12.00	0	1/3
6	0.3	9.26	1	-1
	0.1	2.13	0	3/3
	0.1	7.21	0	3/3
	0.1	12.00	0	3/3

components, and even if the components are known it is possible that the concentrations of the components are unknown and time-variant.

The reagent flow can switch between acid and base reagents, based upon the setpoint (desired  $pH$  of the effluent) and the incoming  $pH$ .

### B. Assumptions

- 1) Constant temperature.
- 2) Water density is constant.
- 3) Level control is perfect or level is measurable.
- 4) Perfect mixing.
- 5) Ionic reactions are instantaneous in comparison to other dynamic effects.
- 6) No precipitates are formed.

### C. State/output map

The equation describing the system state/output map is given by (18). Separating (18) in terms of the influent

and reagent contributions, an equation more useful for identification and control purposes is obtained.

$$\text{Reagent: } X_r = \begin{bmatrix} X_{b,r} \\ X_{a,r} \end{bmatrix}, \quad pK_r = \begin{bmatrix} pK_{ab,r} \\ pK_{a,r} \end{bmatrix}$$

$$D_r = \begin{bmatrix} D_{b,r} \\ D_{a,r} \end{bmatrix}, \quad Z_r = \begin{bmatrix} Z_{b,r} \\ Z_{a,r} \end{bmatrix}, \quad S_r = \begin{bmatrix} S_{b,r} \\ S_{a,r} \end{bmatrix}$$

$$\text{Influent: } X_i = \begin{bmatrix} X_{b,i} \\ X_{a,i} \end{bmatrix}, \quad pK_i = \begin{bmatrix} pK_{ab,i} \\ pK_{a,i} \end{bmatrix}$$

$$D_i = \begin{bmatrix} D_{b,i} \\ D_{a,i} \end{bmatrix}, \quad Z_i = \begin{bmatrix} Z_{b,i} \\ Z_{a,i} \end{bmatrix}, \quad S_i = \begin{bmatrix} S_{b,i} \\ S_{a,i} \end{bmatrix}$$

Using this notation, (18) can be written as:

$$(-D_i + S_i + Z_i)^T X_i + (-D_r + S_r + Z_r)^T X_r + \alpha = 0 \quad (19)$$

### D. Dynamics

$$\frac{dh}{dt} = \frac{F_r + F_i - F_e}{A} \quad (20)$$

$$\frac{dX_r}{dt} = \frac{F_r C_r - (F_i + F_r) X_r}{Ah} \quad (21)$$

$$\frac{dX_i}{dt} = \frac{F_i C_i - (F_i + F_r) X_i}{Ah} \quad (22)$$

Where:

$F_r$ : reagent flow (control action).

$F_i$ : influent flow.

$F_e$ : effluent flow.

$A$ : tank sectional area.

$h$ : tank level.

$X_r$ : concentration vector inside the tank caused by the reagent stream.

$X_i$ : concentration vector inside the tank caused by the influent stream.

## VI. OBSERVABILITY

Model-based approaches have proven to be the best way to control  $pH$ ; however, in most of the  $pH$  industrial applications there is incomplete knowledge of the influent composition or concentration, and the observability property of the realization is important.

Some authors have concluded that the realization (19)-(22) is not observable; however, in the following analysis it will be shown that under certain assumptions the realization is observable.

**Assumptions:**

- 1) The  $pH$  is measurable.

- 2) The reagent components and their concentrations ( $C_r$ ) are known.
- 3) The reagent flow ( $F_r$ ) is known because is the control signal.
- 4) The cross sectional area of the tank ( $A$ ) is known.
- 5) The level ( $h$ ) and influent flow ( $F_i$ ) are measurable.

The conclusion derived in Rodriguez and Loparo[11], is that the vector  $X$  is observable provided that all the dissociation factors  $D_j$  are linearly independent on a time interval  $[t_0, t_f]$ .

Linear independence of the dissociation factors in a physical sense means that each component must be weak and with different  $pK_j$ . The observability of  $X$  provides a minimal description of the system.

### VII. MONOTONICITY AND UNIQUENESS

Equation (19) reveals some interesting properties. Because the balance equation (19) is the linear combination of several monotone decreasing functions plus a nonnegative scalar,  $\gamma = (S_i + Z_i)^T X_i + (S_r + Z_r)^T X_r$ , then is also a monotone function with a unique solution for each concentration of reagent added. The implication of this observation is that this equation is invertible and could be used for feedback linearization control.

### VIII. MINIMAL DESCRIPTION

Equation (19) shows that the *balance equation* is the linear combination of the function  $\alpha$ , several dissociation factors,  $D$  and a scalar  $\gamma$ . This description can be reduced by eliminating all the elements that are linearly dependent according to the following criteria:

- 1) Components with varying but equal  $D_k$ 's ( $pK_k$ 's are equal) can be reduced to a single component, and the *nominal concentrations*,  $X_k$ 's, of the components that are removed are added to the *nominal concentration*,  $X_k$ , of the single component.
- 2) Components in which  $D_k$  is constant and equal to zero (strong bases) can be removed from the set of candidates (the *nominal concentrations* of these components are included in the parameter  $\gamma$ ).
- 3) Components in which  $D_k$  is constant and equal to one (strong acids) can be removed from the set of candidates; however, their corresponding concentrations must be subtracted from  $\gamma$ .

Once all these elements have been removed the remaining system defines a "minimal description" of the process. Notice that this static minimal description is defined by the reagent excitation, which means that for a very small  $pH$  region the dimension of the description will be the smallest, and in a certain sense incomplete.

This representation is called minimal because the number of elements in this representation are necessary and sufficient to model the balance equation in the region of excitation.

### IX. MULTIPLE REAGENT

Consider that  $C_r$  in (21) has the form:

$$C_r = \mathbf{C}_r S \quad (23)$$

where

$$\mathbf{C}_r = \begin{bmatrix} C_{r,1} & 0 & \cdots & 0 & 0 \\ 0 & C_{r,2} & \cdots & 0 & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \cdots & C_{r,n_r-1} & 0 \\ 0 & 0 & \cdots & 0 & C_{r,n_r} \end{bmatrix} \quad (24)$$

and

$$S = [ 0 \quad \cdots \quad 1 \quad \cdots \quad 0 ]^T \quad (25)$$

In this structure  $\mathbf{C}_r$  is a matrix that includes  $n_r$  different reagents separated by columns. The reagent in use is selected by the position of the one entry in vector  $S$ . Any reagent  $C_{r,j}$ ,  $j = 1, 2, \dots, n_r$  is a vector with multiple components. Equation (21) can be written as:

$$\frac{dX_r}{dt} = \frac{F_r \mathbf{C}_r S - (F_i + F_r) X_r}{Ah} \quad (26)$$

### X. IDENTIFICATION

In order to identify the influent concentrations,  $X_i$ 's, and the influent dissociation constants,  $pK_i$ 's (if the influent is completely unknown) a standard performance function is defined as  $J = \frac{1}{2} \sum_{k=1}^N e_k^2$ , where  $e_k$  is the error in the computation of the balance equation. From (19)  $e_k$  is computed as

$$e_k = y_k - \hat{y}_k = \alpha_k - \mathbb{D}_{r,k}^T X_{r,k} + \gamma_i - D_{i,k}^T X_i \quad (27)$$

where  $\mathbb{D}_{r,k} \triangleq D_{r,k} - S_r - Z_r$  is a known vector with reagent data and  $\gamma_i \triangleq (S_i + Z_i)^T X_i$  is an unknown scalar and  $X_i$  is an unknown vector.

Equation (27) can be arranged as

$$e_k = y_k - \varphi_k^T \theta = [\alpha_k - \mathbb{D}_{r,k}^T X_{r,k}] - \begin{bmatrix} -1 \\ D_{i,k} \end{bmatrix}^T \begin{bmatrix} \gamma_i \\ X_i \end{bmatrix} \quad (28)$$

Function  $J$  can be optimized in terms of  $\gamma_i$  and  $X_i$  using a nonnegative least square algorithm because these parameters come into (28) in linear fashion.

If the influent is completely unknown, the optimal  $pK_i$ 's that define the  $D_i$ 's can also be found by using a nonlinear optimization algorithm in cascade with the nonnegative least square method. Functions *lsqnonneg.m* and *fmincon.m* from MATLAB<sup>®</sup> where used for this purpose.

### Discussion about this identification approach

- 1) If the dissociation constants of the influent are known, the *lsqnonneg* method should be used for identifying the concentrations of the influent. Simulations shown that such an approach provides excellent convergence with very few samples.
- 2) If the influent is completely unknown and the *lsqnonneg* method is used with an ample fixed fictitious dissociation constant description for the influent, the solution obtained is generally acceptable if the separation of the fixed dissociation constants selected is small. The convergence to the solution is fast and the matching with the real *titration curve* is acceptable.
- 3) If the influent is completely unknown and the *fmincon* method is used even with a sparse dissociation constant description, the solution obtained is good because in this case the *lsqnonneg* method finds the best set of concentrations and at the same time the *fmincon* method finds the best set of dissociation constants that match the curve.

### XI. CONCLUSIONS

This paper presents a derivation of the general nonlinear differential algebraic equation model for the CSTR configuration. Conditions for observability of the states are obtained (i.e. all the components have to be weak acids or bases with different dissociation constants). The balance equation is shown to be monotone. Because of the monotonicity of the balance equation, the solution of this equation is unique and well defined for each value of *pH*. This establishes the validity of nonlinear feedback linearization techniques which require the inverse of the static nonlinearity. Although these facts about *pH* modeling have been assumed to be true for quite some time, this paper has proved their validity in a rigorous manner.

Using multiple components to represent the solution allows the balance equation to be represented in the complete region defined for the *pH* values that can be obtained for a certain reagent excitation. This representation allows for the implementation of bi-directional identification and control and for the use of multiple components. In this case, the system can be controlled aggressively, while at the same time buffering can be introduced to reduce the sensitivity of the controlled system around the *pH* setpoint.

Two identification methods were proposed: the non-negative least squares (*lsqnonneg*) algorithm to find the actual concentrations when the dissociation constants (*pK*'s) are known or to find a set of fictitious concentrations that best represent an unknown model

using a fixed and ample set of fictitious *pK*'s. The nonlinear optimization algorithm (*fmincon*) operating in cascade with the *lsqnonneg* algorithm determines the set of influent *pK*'s and respective concentrations. The identification procedure guarantees that the model converges to an accurate description. The nonnegative restriction allows to preserve properties such as monotonicity, eliminating problems caused by noise in other identification approaches.

### XII. ACKNOWLEDGMENTS

The authors gratefully acknowledge the contribution of the Universidad Nacional Experimental del Tachira and reviewers' comments.

### XIII. REFERENCES

- [1] T.J. McAvoy, E. Hsu and S. Lowenthal, Dynamics of pH in controlled stirred tank reactor, *Ind. Eng. chem. Process Des. Develop.* 1972, 11, 68-70.
- [2] P. Jutila, P. J. Orava and B. Salmelin, A physico-chemical model and simulation of pH-process in continuous stirred tank reactors, *Mathematics and Computers in Simulation* 1981, XXIII, 99-106.
- [3] T. K. Gustafsson and K. V. Waller, Dynamic modeling and reaction invariant control of pH, *Chem. Eng. Sci.* 1983, 38, 389-398.
- [4] T.K. Gustafsson and K. V. Waller, Myths about pH and pH control, *AIChE J.* 1986, 32, 335-337.
- [5] T.K. Gustafsson, B. O. Skrifvars, K. V. Sandstrom and K. V. Waller, Modeling of pH for control. *Ind. Eng. Chem. Res.* 1995, vol. 34, pp. 820-827.
- [6] R. A. Wright and C. Kravaris, Nonlinear control of pH processes using the strong acid equivalent. *Ind. Eng. Chem. Res.* 1991, vol. 30, pp. 1561-1572.
- [7] R. de Levie, General expressions for acid-base titrations of arbitrary mixtures. *Anal. Chem.* 1996, vol. 68, pp. 585-590.
- [8] J. L. Rodriguez, *Modeling, Identification and Predictive Control of pH Processes*, Thesis, Case Western Reserve University, 1999.
- [9] J. L. Rosenberg and L. M. Epstein, *Química General*, seventh edition, series Schaum, McGraw-Hill, México, 1988.
- [10] S. S. Zumdahl, *Chemical Principles*, second edition, D.C. Heath and Company, 1995.
- [11] J. L. Rodriguez and K. A. Loparo, "A Minimal Description for pH Processes" in *40th IEEE Conference on Decision and Control*, Orlando, Florida, 2001, pp. 3679-3680.