Neuro-fuzzy Techniques Used for Steady State Modeling of *p*H Neutralization Process

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This paper presents an artificial intelligence approach on modeling highly nonlinear processes with application to pH neutralization process. The hybrid neuro-fuzzy technique is applied to model the titration curve from a weak acid with a strong base. This titration curve has three major parts that describe the system behavior: above the equivalence point, near equivalence point and under equivalence point. Process gain has an important variation due to its high nonlinearity. The ANFIS method provides a good solution in modeling this nonlinear titration curve. The resulted model can be used to control the pH neutralization process. The results are promising and can be further developed for the other-input output channels of the pH neutralization process (acid volume – pH, acid concentration – pH, base concentration -pH).

Keywords: ANFIS; pH neutralization; Nonlinear Model

The Adaptive Network based Fuzzy Inference System (ANFIS) method is used to model complex nonlinear systems, with a behavior that can be described by rules. The artificial intelligence techniques have imposed as modeling and forecasting methods in different fields. The ANFIS hybrid technique provides good solutions in designing a railway decision support system [1], in modeling the evaporation process in high reservoir [2], in predicting wheat grain yield [3], in power plant generation forecasting [4], in modeling groundwater level fluctuations [5], in evapotranspiration modeling [6], in rainfall–runoff modeling [7], in municipal water consumption modeling [8], in estimating of mean monthly air temperatures [9] and in forecasting automobile sales [10].

The neuro-fuzzy approach on *p*H neutralization process started with the proposal of a simplified fuzzy model based of the identified rule-base derived by using three network-based self-organizing algorithms: unsupervised self-organizing counter-propagation network, supervised self-organizing counter-propagation network, and self-growing adaptive vector quantization [11].

In [12] it is presented a dynamic modeling of *p*H neutralization process using Fuzzy Dynamic Neural approach. The proposed architecture is specific to *p*H chemical reactor and the simulation results proved a realistic dynamic nonlinear modeling.

The main goal of *p*H neutralization process modeling is the best control scheme for *p*H control. A fuzzy adaptive *p*H controller is presented in [13], tested through simulations and experimental studies. In [14] Pishvaie and Shahrokhi propose a new approach of fuzzy modeling of titration curves offering two control algorithms. They demonstrate the efficacy of proposed approach via simulation and experimental study.

In [15] Zanil et al. propose a hybrid model (based on the combination of neuro-fuzzy identification technique and first principle model) to identify the on-line *p*H characteristic of a neutralization plant.

In this paper is presented a neuro-fuzzy method of modeling the titration curve in the case of weak acid with strong base. The resulted model can be used to control the *p*H neutralization process.

Steady state characteristic of pH neutralization process: titration curve

In order to obtain the theoretical titration curve for acetic acid with sodium hydroxide input data are necessary (reaction volumes, molar mass etc.). To calculate the needed reaction volumes the following assumptions are made:

-molar mass of reagent solutions $M_{CH3COO}H$ = 60.05 g / mol, M_{NaOH} = 39.997 g / mol;

-molar concentrations of reaction solutions $[CH_3COOH]$; $[NaOH]$; $[CH_3COO^-]$ (mol / L);

-the volume of the solution to be neutralized V_a – acid volume (mL); V_b – base volume (mL);

-initial acid moles M_a=0.1M; added base moles M_b=0.2M;

-acid/base type (weak monoprotic acid, strong base);

-logarithmic acid dissociation constant pK_a (for acetic acid pK_a=4.75, K_a = 1.8 . 10^{-5}; for sodium hydroxide K_b = 5.6 . 10^{-10});

-ionic product for water e K_w = 10^{-14}.

For calculating the *p*H after titrating until equivalence point with a specified amount of NaOH it is used the relation [16]:

$$[CH_3COOH] = \frac{M_a V_a - M_b V_b}{V_a + V_B}\ ; \qquad (1)$$

where $[CH_3, COOH]$ – molar concentration of acetic acid solution.

After reacting with NaOH, a part of acetic acid is transformed into its conjugate base, acetate CH_3COO^-. The acetate concentration is computed with [16]:

$$[CH_3COO^-] = \frac{M_b V_b}{V_a + V_B}. \qquad (2)$$

The molar concentration of acid and its conjugate base can be used in Henderson–Hasselbalch equation to generate the *p*H:

$$pH = pK_a + \lg\left(\frac{[CH_3COOH]}{[CH_3COO^-]}\right). \qquad (3)$$

The strong nonlinearity appear where *p*H has a sharp rise comparing to the volume of titrated sodium hydroxide and this comes near equivalence point. The equivalence point is located where the solution has the same moles number for acetic acid and sodium hydroxide. It is very

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important the added sodium hydroxide volume at equivalence point:

$$M_a \cdot V_a = M_b \cdot V_b,\ V_{eq} = V_b = \frac{M_a \cdot V_a}{M_b} \quad (4)$$

For 50 mL of acetic acid with 0.1M the resulted sodium hydroxide volume is 25 mL, corresponding to a *p*H=8.79, because the *p*H at the equivalence point is determined by the titrand's conjugate form, the acetate. After the equivalence point, it is necessary to determine the water ionic product K_w, the hydroxide concentration $[OH^-]$ and hydronium ion concentration $[H_3O^+]$. The *p*H is calculated with:

$$[OH^-] = \frac{M_b V_b - M_a V_a}{V_a + V_B},\ [H_3O^+] = \frac{K_w}{[OH^-]},\ pH = -\lg([H_3O^+]). \quad (5)$$

In table 1 is presented the *p*H variation related to sodium hydroxide titrated. The acid volume, initial acid moles, added base moles are kept constant (V_a=50, M_a=0.1M, M_b=0.2M).

There are three sections that describe the titration curve: above equivalence point, near equivalence point and under the equivalence point. For the plot there are necessary five points:

-the first inflection point, situated at the beginning of reaction and representing Ka - 1 (*p*H = 3.76, for V_b = 2.5 mL).

-the second inflection point, placed before equivalence point for K_a + 1, (*p*H = 5.76, for a V_b = 25 mL)..

-the equivalence point (*p*H=8.79, for a V_b = 25 mL;

-for a V_b = 40-mL). The resulted titration curve is presented in figure 1.

The steady state behaviour is highly nonlinear due to the strong variation of *p*H process gain. The ANFIS approach can provide an alternative to conventional modeling methods. The paper presents the ANFIS approach used to model the titration curve from literature

ANFIS approach in modeling weak acid with strong base titration curve

The ANFIS method was developed to compensate the disadvantages of fuzzy logic systems (high time consuming in designing and adapting a consistent, continuous and complete rule base and also trial-error methods in tuning membership functions parameters). For fuzzy based systems there are no standard methods of transforming human knowledge and expertise into a rule base. A solution is completing fuzzy inference systems (FIS) with artificial neural networks (ANN) in order to enhance FIS capabilities with those of ANN. In this way is obtained the hybrid ANFIS with an architecture proposed by Jang in 1993 [17], (fig. 2).

Table 1

*p*H VARIATION IN CASE OF TITRATING 50 mL ACETIC ACID (0.1 M CONCENTRATION) WITH SODIUM HYDROXIDE (0.2 M CONCENTRATION)

V_b	[acetic acid]	[acetate]	$[OH^-]$	$[H_3O^+]$	pH
0	0.100	0	0.0013	7.559E-12	2.8785
5	0.073	0.018	-	-	4.1579
10	0.050	0.033	-	-	4.5839
15	0.031	0.046	-	-	4.9361
20	0.014	0.057	-	-	5.3621
22	0.008	0.061	-	-	5.6253
24	0.002	0.064	-	-	6.1402
25	0	0.066	0.0000	-	8.7880
26	-	-	0.0026	3.8E-12	11.4202
28	-	-	0.0077	1.3E-12	11.8861
30	-	-	0.0125	8E-13	12.0969
35	-	-	0.0235	4.25E-13	12.3716
40	-	-	0.0333	3E-13	12.5229
45	-	-	0.0421	2.375E-13	12.6243
50	-	-	0.0500	2E-13	12.6990
100	-	-	0.1000	1E-13	13.0000

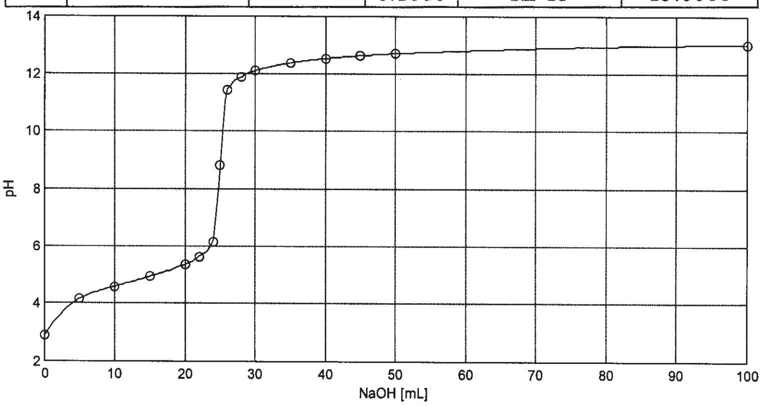

Fig. 1. Titration curve for weak acid with strong base

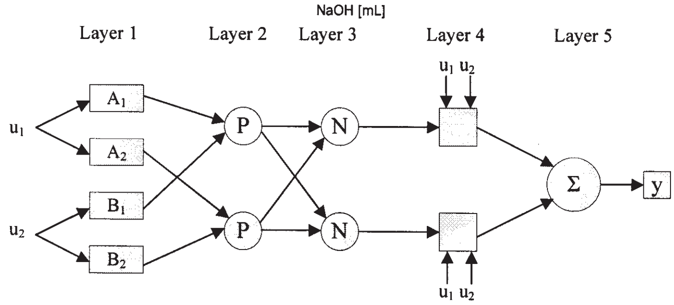

Fig. 2. ANFIS architecture

A fuzzy inference system is formed by five functional blocks: a fuzzification block that transforms a crisp value into a fuzzy set, a defuzzification block that converts a fuzzy set into a crisp value (based on Mamdani or Takagi Sugeno models), the database block with the description of membership functions for input and output variables, a rule base block with the rules defined for FIS, and the decision block that performs the inference operations on the rules. The main advantages of a fuzzy system are the fact that it does not require a mathematical model of the process, the process description with rules emulates human thinking, the interpretations of the results is simple and rule based. The ANN does not require a mathematical model of the process (like FIS) and have learning/adapting capabilities (not provided by FIS). A neuro-fuzzy system is capable to learn new rules or membership functions, to optimize the existing ones. The starting point is the training data in creating the rule base and membership functions. There are three possible situations:

-the rule base is empty and the ANFIS creates rules until the problem is solved. It is possible that the resulted rule base is inconsistent and oversized with negative consequences on time consuming;

-the rule base is complete and the proper training lead to some rule elimination. Sometimes the result has a smaller number of rules than needed and the resulted rule base must be checked for consistency;

-the initial rule base has an fixed number of rules. Through learning old rules are replaced with new ones in order to maintain system size.

In each situation the rule base must be checked for completeness, consistency and continuity.

In figure 2 the fixed nodes are represented with circles while the adaptive nodes are squares. The proposed architecture has five layers. The Takagi Sugeno models are more efficient from computing effort perspective and results interpretation. For a two inputs $u = [u_1\ u_2]^T$ one output *y* system the fuzzy rules are:

Rule 1: if u_1 is A_1 and u_2 is B_1 then $y = f_1u_1 + g_1u_2 + q_1$,
Rule 2: if u_1 is A_2 and u_2 is B_2 then $y = f_2u_1 + g_2u_2 + q_2$,

where A_1 and B_1 are the fuzzy sets associated to u_i inputs, and f_i, g_i and q_i are parameters that will be determined after training process.

Layer 1: The membership degree of an input variable to a fuzzy set is defined through membership functions. The *i*-node function is:

$$O_i^1 = \mu_{A_i}(u_1),\ i = \overline{1,2}, \tag{6}$$

$$O_i^1 = \mu_{B_i}(u_2),\ i = \overline{3,4}. \tag{7}$$

where membership functions can have any analytical form. At this layer are formed the premise parameters.

Layer 2: Each node from this layer is denoted with P, the output being the product of input signals:

$$O_i^2 = w_i = \mu_{A_i}(u_1)\cdot\mu_{B_i}(u_2),\ i = \overline{1,2}. \tag{8}$$

Layer 3: The fixed *i*-node makes a normalized sum of the inputs:

$$O_i^3 = \overline{w_i} = \frac{w_i}{w_1 + w_2},\ i = \overline{1,2}. \tag{9}$$

Layer 4: The adaptive *i*-node computes the contribution of *i* rule to ANFIS output:

$$O_i^4 = \overline{w_i}y_i = \overline{w_i}(f_iu_1 + g_iu_2 + q_i),\ i = \overline{1,2}. \tag{10}$$

The computed parameters are called consequence parameters.

Layer 5: The fixed node makes the summation of all inputs:

$$O_i^5 = \sum_{i=1}^{2}\overline{w_i}y_i = \frac{w_1y_1 + w_2y_2}{w_1 + w_2}. \tag{11}$$

ANFIS applies a hybrid learning algorithm formed by combining gradient method used to identify premise parameters with least square method used to generate consequence parameters. The learning algorithm task is tuning the premises (the parameters associated with membership functions) and the consequences in order that ANFIS response match the training data. At feedforward propagation step from hybrid learning, the system output reaches layer 4, and the consequence parameters are formed with least square method. At backpropagation step, the error signal is fed back and the premise parameters are updated through gradient method.

Applying the ANFIS method to the titration curve obtained in the previous section can be done with no prior designed fuzzy inference system. The rule base is empty and the chosen method to generate the new fuzzy inference system is clustering method.

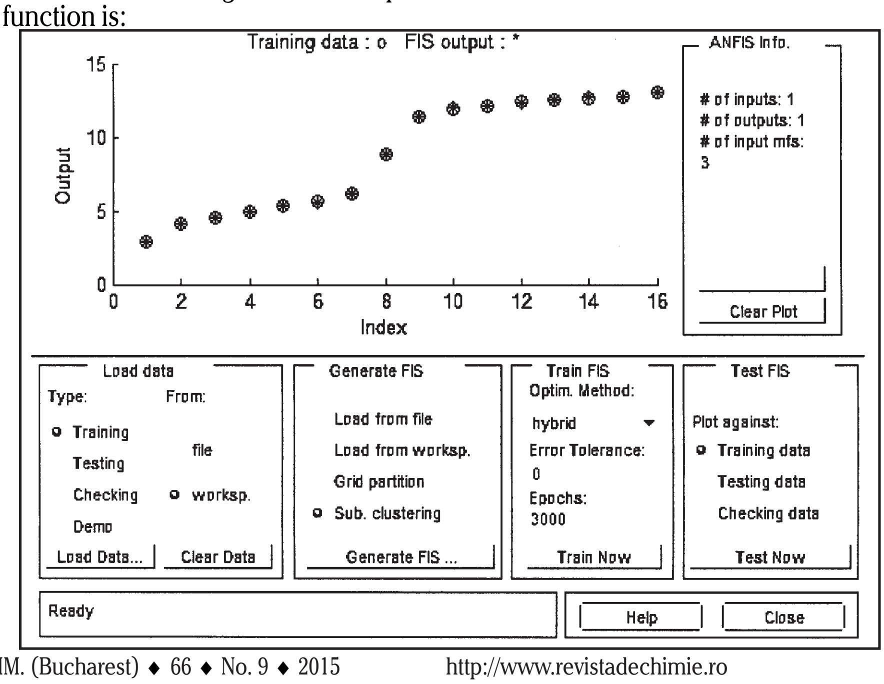

Fig. 3. Training data for clustering method.

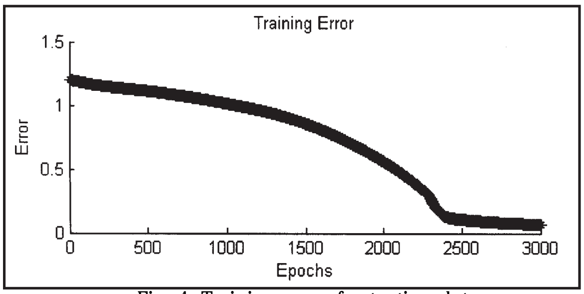

Fig. 4. Training error for testing data.

The training error is represented in figure 4. After 3000 epochs the stopping criteria for error tolerance.

Conclusions

This titration curve has three major parts that describe the system behaviour: above the equivalence point, near equivalence point and under equivalence point. Process gain has an important variation due to its high nonlinearity. The ANFIS method provides a good solution in modeling this nonlinear titration curve. The resulted model can be used to control the *p*H neutralization process. The results are promising and can be further developed for the other- input output channels of the *p*H neutralization process (acid volume – *p*H, acid concentration – *p*H, base concentration -*p*H).

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