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Heat effects due to mixing (dilution) the mixed acid solutions—Application of neural networks to approximate and generalize experimental data

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ABSTRACT

The feed-forward neural networks have been used to approximate the specific molar enthalpy and the specific molar heat capacity of the mixed acid solutions. The nets have been trained with experimental data taken from the literature, so the values of the specific molar enthalpy and the specific molar heat capacity at the reference temperature $T = 0\,^\circ C$ could be successively estimated for any composition of the mixed acid. Two principal methods have been considered and tested. In the first method two independent neural nets have been employed: the net NN-H, which approximates separately the specific molar enthalpy and the net NN-C, to approximate the specific molar heat capacity, respectively. In the second method only one net is employed (the net NN-HC), which simultaneously approximates both the specific molar enthalpy and the specific molar heat capacity. Then following both mentioned methods, the trained neural nets have been used to model the heat effects due to dilution of mixed acid solutions, carried out at various conditions – i.e. at any temperature and composition. Using these nets, both, the integral and the differential enthalpy balance can be carried out, so the smart and accurate method to model the mixed acid dilution has been elaborated. The proposed methods and their prediction accuracy have been successfully verified with our own experimental data carried out in the RC1 reaction calorimeter.

1. Introduction

Nitration of organic compounds is widely employed and plays an important role in the chemical industry. Usually, it is carried out with use of the so-called mixed acid, which contains: sulfuric acid, nitric acid and water – where the sulfuric acid acts as the catalyst. During preparation of mixed acid solutions as well as performance the nitration process the sulfuric acid is being diluted, so a large amount of heat is generated. Therefore, a proper description of physico-chemical properties of mixed acid solutions is required for accurate characterization and designing both, the preparation of mixed acid solutions as well as the nitration process itself.

As nitration carried out with the mixed acid solutions is well known from many years, there is a lot of available data to estimate heat effects due to dilution of mixed acid solutions [1–4]. Regretfully, these data are usually collected as tables and/or plots, which make a designing of the dilution process inconvenient and usually inaccurate due to interpolation of required data. Even more recent studies suffer from the lack of a good method of data approximation – e.g. see papers [5,6].

It should be pointed out, that at some operating conditions the heat effect due to dilution of mixed acid is comparable to that due to the nitration reaction progress, so an accurate heat balance over the reactor is crucial for safe and effective performance of the reactor. This is particularly important for safety of industrial nitration processes – e.g. in a case of quenching of nitration reaction with addition of water, when the heat generated due to dilution of mixed acid present in the reactor can significantly increase the temperature of the reacting mixture and even provoke the thermal runaway. Problems of performance of nitration reactions and safety aspects of these processes are still widely reported and discussed in the literature of subject [7–14].

In this study the neural networks are used to approximate the specific enthalpy and the specific heat capacity of mixed acid solutions, so modeling of heat effects due to dilution of these solutions can be carried out, as the neural networks supply a smart and accurate method to approximate any experimental data sets. Others widely employed methods of experimental data approximation, which are based mainly on application of polynomial expressions, splines, etc., give in comparison to neural nets less flexible and

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Nomenclature

A	heat exchange surface area [m^2]
A_a	heat exchange surface area for heat losses through the reactor cover [m^2]
B	neuron threshold value (bias)
$C_{p,n}$	molar specific heat capacity of the mixture of given composition [$J\,mol^{-1}\,K^{-1}$]
$C_{p,m}$	mass specific heat capacity of the mixture of given composition [$J\,kg^{-1}\,K^{-1}$]
$H_{i,n}$	specific molar enthalpy of the *i*th liquid portion [$J\,mol^{-1}$]
$H_{i,m}$	specific mass enthalpy of the *i*th liquid portion [$J\,kg^{-1}$]
H_R	specific molar enthalpy of the mixture after mixing completion [$J\,mol^{-1}$]
H_{dos}	the specific molar enthalpy of solution of fixed composition which is dosed into the vessel [$J\,mol^{-1}$]
H_R	the molar specific enthalpy of solution present in this vessel [$J\,mol^{-1}$]
$\dot{m}_{dos}$	mass dosing rate [$kg\,s^{-1}$]
m_i	mass of *i*th component in the reactor vessel [kg]
$\dot{n}_{dos}$	molar dosing rate [$mol\,s^{-1}$]
n_i	number of moles each of liquid portion taken for mixing [mol]
$n_R = \sum_{i=1}^{2} n_i$	the total number of moles present in a vessel after mixing,
$Q_{dil,\mathrm{int}}$	total (integrated) heat effect due to mixing (dilution) [J]
$\dot{Q}_{dilution}$	heat flow generated due to a dilution (mixing) [W]
$\dot{Q}$	heat flow measured or determined in the reaction calorimeter [W]
P	number of learning patterns,
rms	root means square error (Eq. (14)),
T	temperature [°C]
U	overall heat transfer coefficient [$W\,m^{-2}\,K^{-1}$]
U_a	overall heat transfer coefficient for heat losses through the reactor cover [$W\,m^{-2}\,K^{-1}$]
w_i	mass fraction of the *i*th component in the solution
W_i	synaptic weight to the *i*th input signal
x_i	molar fraction of each *i*th mixture component
x_1 and x_2	components of the input signals vector **X**,
y	component of the output signal vector **Y**,
φ and γ	complex functional dependencies (see Eqs. (10) and (11), respectively),

Subscripts

a	ambient
accu	accumulated
cal	calibration
dos	dosed
ex	exchanged
loss	loosed
m	mass
n	molar
str	stirrer
R	reactor

general results [15,16]. Even for the considered case, the polynomial regression has been used to estimate the partial molar enthalpies for dilution of mixed acids solutions [4,12]. Although an accuracy of approximation obtained with polynomials is very good, it is practically impossible to find a single polynomial, which is able to approximate data with a sufficient accuracy within the whole range of concentrations. Only with artificial neural networks (ANN) rules following behavior of any experimental data set can be easily detected, even when explicit expressions describing investigated complex experimental functional dependencies are not known [15,17,20]. In the literature of subject still new and exciting neural networks applications in chemical engineering are observed, even for complex reacting systems [15,17–20].

The approach employing neural networks – proposed, described and tested below – makes possible a smart and accurate designing of the dilution of mixed acid process.

2. Modeling of heat effect due to mixing (dilution)

In general, heat effect due to dilution can be described by formulation an integral (macroscopic) or a differential enthalpy balance.

For mixing of two portions of the mixed acid solutions of different composition, an integral enthalpy balance can be formulated, which at isothermal conditions ($T = T_R$) reads as follows:

$$\left[\sum_{i=1}^{2} n_i \cdot H_i\right]_{T=T_R} + Q_{dilution} = [n_R \cdot H_R]_{T=T_R} \tag{1}$$

At any temperature *T*, the specific molar enthalpy of any mixture of given composition (say the mixed acid solution of composition: x_W, x_S, x_N) – H can be estimated as:

$$H(x_W, x_S, x_N, T) = H_{ref}(x_W, x_S, x_N, T_{ref}) + \int_{T_{ref}}^{T} C_p(x_W, x_S, x_N, T) \cdot dT \tag{2}$$

where H_{ref} is the specific molar enthalpy of mixed acid solution of the same composition but at the reference temperature T_{ref} is expressed according to the general relationship:

$$H_{ref} = f(x_W, x_S, x_N, T_{ref}) \tag{3}$$

In Eqs. (2) and (3) the molar fraction of each *i*th mixture component (here W – water, S – sulfuric acid, N – nitric acid, respectively) is noted as x_i [–].

For mixing with a continuous dosing of the solution of a constant composition, a differential enthalpy balance for the mixture can be formulated, which at the isothermal conditions reads as follows:

$$\dot{n}_{dos} \cdot H_{dos}(T_R) + \dot{Q}_{dilution}(T_R) = \frac{d[n_R \cdot H_R(T_R)]}{dt} \tag{4}$$

For the considered continuous addition the molar balance for the mixture can be expressed as:

$$\frac{dn_R}{dt} = \dot{n}_{dos} \tag{5}$$

so rearrangement of Eq. (4) leads to the expression:

$$\dot{Q}_{dilution}(T_R) = n_R \cdot \frac{dH_R(T_R)}{dt} + \dot{n}_{dos} \cdot [H_R(T_R) - H_{dos}(T_R)] \tag{6}$$

in which the differential term can be estimated as:

$$\frac{dH_R(T_R)}{dt} = \left[\frac{dH_R(T_R)}{\partial x_W}\right]_{x_S, x_N} \cdot \frac{\partial x_W}{dt} + \left[\frac{dH_R(T_R)}{\partial x_S}\right]_{x_W, x_N} \cdot \frac{\partial x_S}{dt} + \left[\frac{dH_R(T_R)}{\partial x_N}\right]_{x_W, x_S} \cdot \frac{\partial x_N}{dt} \tag{7}$$

Notice that both, the total heat effect due to mixing (dilution) – $Q_{dilution}$ (Eq. (1)) as well as the heat flow generated due to a continuous dilution process – $\dot{Q}_{dilution}$ (Eq. (6)), depend on the compositions