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Modeling and predicting the Henry's law constants of methyl ketones in aqueous sodium sulfate solutions with artificial neural network

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Abstract

Henry's law constant is an important property for predicting the solubility and vapor–liquid equilibrium. Usually, Henry's law constants increase as temperature and salt concentration increase and polynomial correlations are commonly used to model these effects.

In this article, the artificial neural network (ANN) method is used for modeling the Henry's law constant dependence on temperature and salt concentration, with methyl ketones in aqueous sodium sulfate solutions chosen for the study.

In the first part, one network is used for each system. The network topology is optimized and the 2-2-1 architecture is found to be the best. The network satisfactorily estimates the Henry's law constants of all systems in the study with an average relative deviation (ARD) of less than 1% for all systems, which is comparable to available correlations.

In second part, which is based on the results of the first part, an ANN is designed for all systems. The new network has a 3-2-1 topology, giving an ARD of correlation of less than 1% and ARD of prediction, depending on systems and data availability, of less than 3.5%. The predictive ability is the most important advantage of the 3-2-1 ANN compared to 2-2-1 ANN and other correlations.

Keywords: Artificial neural network (ANN); Henry's law constant; Back propagation (BP); Methyl ketones; Sodium sulfate; Solution

1. Introduction

Experimental and theoretical studies of gas solubility are useful in design and operation of different industrial processes, as well as, indirectly, in providing the necessary information about molecular interactions in solutions. To develop a reliable molecular theory, an accurate intermolecular potential is necessary. The Henry's law constant is directly related to the residual chemical potential of solute at infinite dilution, which is evaluated from the intermolecular potential between a solute molecule and a solvent molecule. Therefore, the Henry's law constant is a suitable macroscopic property for testing the intermolecular potential between different kinds of molecules. Since Henry's law constants (H) are affected by temperature and solutes present in the solutions, accurate measurement of these constants is not easy. Experimental data are usually not available and therefore should be predicted using various thermodynamic models. Many investigations are performed to model the dependence of Henry's law constant on several parameters that temperature and salt concentration are the most important ones.

Temperature is known as the most important variable affecting the solubility and Henry's law constant. Jou et al. [1,2] studied the solubility of ethane in diethylene glycol (DEG) and *N*-formyl molpholine (NFM) and calculated the Henry's law constants by Krichevsky–Ilinskaya equation. They observed that Henry's law constants increase as temperature increases. Same studies were performed for solubility of H_2S and CO_2 in DEG by Jou et al. [3]. Bonifacio et al. [4] investigated the solubility of xenone in *n*-hexane and obtained same results. They used the equation introduced by Clarke and Glew, to model the dependence of Henry's law constant on temperature. Henry's law constants of propane, propene, *trans*-2-butene and 1,3-butadiene in methanol were studied by Miyano and Fukuchi [5] and observed same results. Some related investigations [6,7] confirm the usual effect of temperature on Henry's law constant but there are some exceptions. Angelo and Francesconi [8] stud-

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ied the solubility of hydrogen in *n*-alcohols and demonstrate that the Henry's law constants decrease while the temperature increases. Schnabel et al. [9] predicted the Henry's law constants of oxygen and nitrogen in ethanol by molecular simulation and indicated that Henry's law constants decrease as a consequence of increasing temperature. They also studied the methane–ethanol and CO_2–ethanol systems. For these systems, when temperature increases Henry's law constants increase and then decrease.

Salt concentration affects the Henry's law constant too. Solubility of methane and carbon dioxide in water solutions containing KCl, KBr, LiCl, LiBr, NaCl, $NaNO_3$ and KNO_3 were studied by Kiepe et al. [10–12] and these researches and like approved that the Henry's law constants increase as salt concentration increases. They also observed the usual effect of temperature on solubility and Henry's law constant.

Modeling the Henry's law constant and its dependence on temperature and salt concentration requires appropriate equations estimating the effects of temperature and salt concentration. Teja et al. [13] studied Henry's law constant of methanol in aqueous systems and introduced the following equation for estimation of Henry's law constant:

$$\ln H = \ln P_1^{\text{sat}} + \frac{A}{T_r} + \frac{B(1-T_r)^{0.355}}{T_r} + \frac{C\exp(1-T_r)}{T_r^{0.41}} + Dz \qquad (1)$$

where P_1^{sat} is the vapor pressure of solvent (water), A, B and C are parameters depending on solvent and solute, D the salt parameter and z is the mole fraction of salt. Chai et al. [14] used Eq. (1) for predicting the Henry's law constant (H) of methyl ketones in water containing Na_2SO_4. A modified form of Eq. (1) was applied for several systems by Falabella et al. [15] and the calculated parameters were reported. The results of using Eq. (1) for aqueous solutions are very good and confirm the superiority of this correlation over other ones. Even equations as precise as Eq. (1) and like, have lots of disadvantages, for instance, they cannot produce reliable estimations for new systems.

Artificial neural network (ANN) is a powerful method for modeling any kind of systems. Recently ANN is widely used for modeling of different thermodynamics properties such as vapor pressure, density, compressibility factor and vapor–liquid equilibrium (VLE). Mohanty [16,17] and Urata et al. [18] used the neural network for VLE calculations. ANN was also used to design a mixing rule for VLE calculations [19], model the protein solubility [20], predict solubility of anthracene in binary and ternary solvents [21] and estimate solubility of some other systems [22–24]. Niall et al. [25] used ANN with quantitative structure–property relationship (QSPR) to predict Henry's law constants. Liu et al. [26] employed the ANN with QSPR models based on quantum chemical descriptors for estimating various properties of polymethacrylates. Puzyn et al. [27] modeled the Henry's law constants of chloronaphtalene congeners by using QSPR models.

Considering the ability of ANN method for correlating of different thermodynamics properties, in this work, ANN method is used to model the Henry's law constants of methyl ketones in aqueous sodium sulfate solutions.

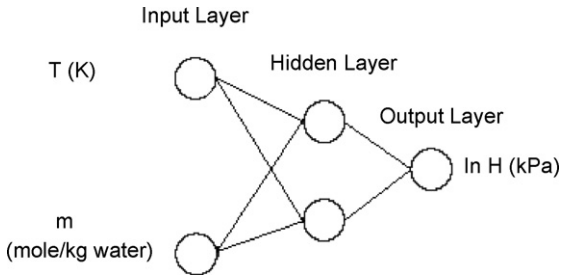

Fig. 1. Architecture of the 2-2-1 network (biases are not shown).

2. Method

2.1. Artificial neural network

Artificial neural network is a mathematical and numerical method based on biological neural network. An ANN consists of some connected neurons and process information. A network is made of one input layer, one output layer and may also consist of some hidden layers. Each layer is made of some neurons connected to other neurons in previous and next layers. A neuron has an input, an output and a transfer function. The Sigmoidal transfer function is one of the performed functions, expressed as the following equation:

$$a_j = \frac{1}{1+e^{-S_i}} \qquad (2)$$

where a_j is the output of jth neuron and S_j is the input of jth neuron, produced by outputs of previous layer. S_j is given as

$$S_j = \sum_{i=1}^{n}(w_{ij}a_i) + b_j \qquad (3)$$

where a_i s are the outputs of ith neuron from previous layer, w_{ij} presents the weights applied to the connection of neuron ith and jth, and b_j is a bias number. Fig. 1 indicates the architecture of used ANN for all systems. Temperature (K) and salt concentration (mol/kg water) are inputs and $\ln H$ (kPa) is the output of network.

ANN is an adaptive network that changes its structure based on external or internal information that flows through the network during the learning (training) phase. Estimation of optimum weights and biases of network needs an algorithm called propagation method. Several kinds of propagation methods are available and back propagation (BP) is the easiest and simplest one with enough reliability. BP and other usual propagation methods are explained completely in mathematical literatures [28,29].

Before using the appropriate propagation method to calculate optimum parameters of ANN, it is necessary to scale outputs and inputs between 0 and 1. Eq. (4) is used as a linear function for scaling.

$$(\text{Scaled})_{\text{value}} = (\text{Actual})_{\text{value}} \times m + c \qquad (4)$$

Adjustable parameters of this equation (m and c) are tabulated in Table 1, produced by two data points: (lowest actual value, 0) and (highest actual value, 1).