



A novel approach for estimation of solvent activity in polymer solutions using genetic programming



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ABSTRACT

In this paper, genetic programming (GP) as a novel approach for the explicit modeling the phase equilibria of polymer solutions is presented. The objective of this study is to develop robust model based on experimental data for prediction of solvent activity in polymer/solvent mixtures. Molecular weight, density, chemical structures of polymer and solvent, and concentration of polymer solution were considered as input parameters of the model. Activity of solvent is considered as output parameter of the model. Some statistical parameters were calculated in order to investigate the reliability of model. The results showed very well agreement with the experimental data with an average error of less than 3%.

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1. Introduction

In the recent decades, wide-spread applications of polymers in many areas such as membrane formation, textile industry, etc. has increased the interest and therewith research in the field of polymers [1–4]. Generally, in most of applications of polymers we are often dealing with polymer solutions [5–7]. Phase equilibrium has a key role in the processing and application of polymer solutions [8–11]. Moreover, the proper design and control of polymer reactions usually require information about the phase equilibrium [12,13]. Usually, determination of solvent activities in polymer/solvent mixtures is required for investigation of a polymer solution's phase equilibria [14–16].

Researches on estimation of solvent activity in binary mixtures started in 1895 by Max Margules [17]. The researches in the area of determination of component activity in binary mixtures, in which both component considered as low molecular weight, continued by many researchers that results in presentation of different theories and models such as regular solution [18], NRTL [19], UNIQUAC [20], UNIFAC [21] models and Wilson [22], Van Laar [23], Scatchard-Hildebrand [24] theories, etc. [18]. Many other investigations were done particularly to estimate the activity of solvent in polymer solutions that the mixture comprised from components that have different molecular weights. Since Flory

[25] developed his equation of state for prediction of phase behavior of polymer solutions, many efforts have been done in order to develop models for accurate predictions of solvent activities in polymer solutions [11,26–28]. Oishi and Prausnitz [29] developed a molecular thermodynamic method to making estimation for solvent activity when any experimental equilibrium data for the mixture are not available. Their estimation method was based on the UNIFAC correlation which follows from the concept of group contributions. Their presented method suffers from not considering the molecular weight of polymer in the model. Elbro [30] derived an equation for prediction of activity coefficient which included combinatorial and free volume contributions from a Van der Waals free volume type of expression. Kontogeorgis and Fredenslund [31] developed an activity coefficient model that was a combination of the works that was carried out by Elbro et al. [30] and Oishi and Prausnitz [29]. A local composition model based on the lattice theory developed by Wu et al. [12]. This model is a modification of NRTL equation and represents an expression for the free energy of polymer solutions. Using the presented model by Wu et al. [12] the activity of solvent can be obtained by some relatively simple mathematical calculations on free energy expression. Another theory has been proposed by Keshmirizadeh et al. [32] based on hard-sphere limit of binary solutions with different molecular weight of components for calculating activity coefficient of solvent in polymer/solvent mixture. According to their theory the activity coefficient of solvent can be calculated from molecular weights and densities of the solvent and polymer

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as the input data, but as negative points, their model needed an adjustable parameter and chemical structure of polymer and solvent were not considered in the proposed model.

It has been reported [33] that applications of physical-mathematical models such as models that mentioned above are limited to some few polymer/solvent mixtures in each case and there has not been presented a general model with high accuracy to be applicable in all polymer systems. The solvent activity is a complex function of many variable, such as molecular weights and densities of polymer and solvent, temperature, the UNIFAC Structural Groups parameter of solvent and repeating unit of polymer, etc. [29,32]. Genetic programming (GP) as a branch of genetic algorithm (GA) has proved to be a powerful tool for modeling of highly complex and non-linear systems in a wide variety of applications [34–39]. GP is a progressive technique for commonly generating nonlinear input–output empirical models in any complex system.

As mentioned previously, because of high degree of complexity and high number of parameters that should be considered in prediction of activity in polymer solutions, it seems GP to be a potential tool for reliable and accurate prediction of solvent activity parameter in polymer solutions. In this paper, GP is used as a novel approach for reliable determination of solvent activity in wide range of commonly used polymer solutions.

2. Theory

2.1. Solvent activity modeling

Based on the UNIFAC model, solvent activity is a function of chemical structure of solvent and repeating unit of polymer [29]. On the other hand, from the hard sphere-limit theory solvent activity depends on molecular weights and densities of solvent and polymer [32]. In the other theories that mentioned above, activity was considered to be a function of some of these variables. Therefore, in the present study activity of solvent is assumed to be an unknown non-linear function dependence on the nine inputs Mw_1 , Mw_2 , ρ_1 , ρ_2 , R_1 , R_2 , Q_1 , Q_2 , wt_1 , where, Mw is the molecular weight, ρ the density, R and Q are the UNIFAC model parameters and wt represents the solvent weight fraction. Also subscript 1 and 2 refer to solvent and polymer, respectively. The GP is employed to determine this functionality.

2.2. Determination of solvent–polymer interaction parameter

The classical Flory–Huggins model [40] is used for the thermodynamic analysis of the phase behavior during processing polymer solutions. The model results in an expression for the Gibbs energy of mixing of the system (ΔG^{mix}) according to Eq. (1):

$$\frac{\Delta G^{\text{mix}}}{RT} = n_1 \ln \varphi_1 + n_2 \ln \varphi_2 + \chi_{12} n_1 \varphi_2 \quad (1)$$

where n_1 and n_2 are the number of moles of solvent and polymer, respectively; φ_1 and φ_2 are the volume fractions of solvent and polymer, respectively; R is the gas constant; T is the absolute temperature, and χ_{12} is the Flory–Huggins interaction function (concentration dependent), that must be obtained experimentally.

It was assumed that, the total volume (and thus also the volume fractions of the components in the liquid mixture) is linearly dependent on the molar volumes of the components. Therefore, volume fraction of each component can be calculated as follows:

$$\varphi_i = \frac{n_i v_i}{n_1 v_1 + n_2 v_2} \quad (2)$$

where v_1 and v_2 are the molar volume of solvent and polymer, respectively. It should be noted that, the molar volumes may

depends on pressure, temperature and composition, but these dependency was neglected in this work.

The relation for the solvent activity can be obtained by deriving $\Delta\mu_1$, the excess chemical potential of component 1 in the binary solvent (1)/polymer (2) mixture by calculating the first derivative of the Gibbs energy of mixing from Eq. (1) with respect to n_1 as follows [40]:

$$\ln a_1 = \frac{\Delta\mu_1}{RT} = \ln \varphi_1 + \left(1 - \frac{v_1}{v_2}\right) \varphi_2 + \chi_{12} \varphi_2^2 \quad (3)$$

where $v_1/v_2 \approx 0$ is the ratio of molar volumes of solvent and polymer. Solvent activity data can be used to calculate the solvent/polymer interaction parameter using Eq. (3), according to Eq. (4):

$$\chi_{12} = \frac{\ln\left(\frac{a_1}{1-\varphi_2}\right) - \left(1 - \frac{v_1}{v_2}\right) \varphi_2}{\varphi_2^2} \quad (4)$$

3. Genetic programming

Genetic programming (GP), offered by Koza [41,42] as a method to genetically develop populations of mathematical models for prediction of a system behavior with even high complexity. GP, which is based on the bio-inspired technique, is defined as automatically defined function; that is able to automatically discover a computer programming that is well predict a system or problem [35,43]. Each program in the GP is expressed as a tree. An example of a GP tree is shown in Fig. 1. The binary arithmetic functions, ‘-’, ‘+’ and ‘*’ each have two sub-trees. The sub-tree on the left containing ‘-’, 4 and ‘y’, represents the mathematical expression ‘4–y’. The tree as a whole represents $f(x, y, z) = 4 - y + z + 6 * x$. In Fig. 1, the connections are called nodes. Due to the location in the tree, these nodes are classified into two types: (1) internal nodes are called as function (nonterminal); these function nodes use one or more input values and generate a single output value (e.g. +, -, ×, sin, cos, exp, etc.) and provide the internal cells with expression trees; (2) nodes at the end of trees (leaf nodes) are called terminal and indicates input variables.

Fig. 2 is a flowchart of a GP modeling. The basic mechanism of GP for a specific problem that requires finding a mathematical model is based on a repetitive computational process. Based on

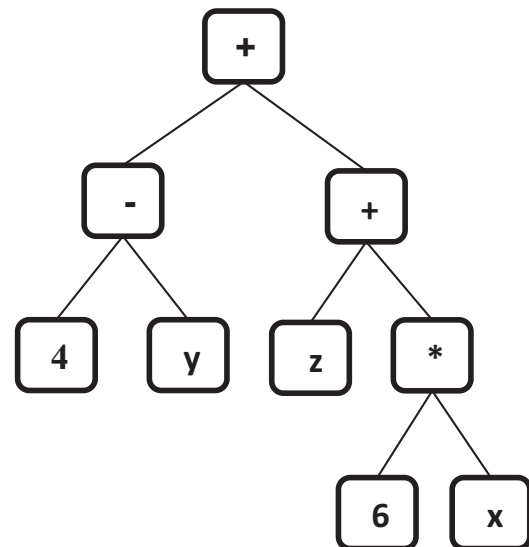


Fig. 1. Example of a GP function tree.

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