



# Determination of boiling points of azeotropic mixtures using quantitative structure–property relationship (QSPR) strategy



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## ARTICLE INFO

### Article history:

Received 23 March 2013

Received in revised form 31 August 2013

Accepted 6 September 2013

Available online 24 October 2013

### Keywords:

Quantitative structure–property relationship

Normal boiling point

Ant colony optimization

Azeotrope

## ABSTRACT

Azeotropes, which are solutions that contain two or more chemicals, are very important in industry. Experimental techniques as well as theoretical approaches such as ab initio have been developed for estimating mixture properties and phase equilibrium data. Both approaches are accurate and effective, but are costly and time-consuming. The quantitative structure–property relationship (QSPR) method, which is efficient and extremely fast, could be a viable alternative approach. In this work, we developed QSPR models for prediction of boiling points ( $T_b$ ) of binary azeotropes. The  $T_b$  values of azeotropic mixtures were investigated by means of multiple linear regressions (MLRs). Two different data matrixes were calculated for characterizing azeotropic mixtures based upon the centroid approximation and the weighted-contribution-factor approximation. The ant colony optimization algorithm (ACO) was employed to select relevant descriptors. For both approximations, significant QSPR models were obtained by using the ACO–MLR algorithm. The descriptors that appeared in the best MLR models are related to those properties, including mass, ability to form H-binding, numbers of heteroatom, solvation entropy, and solvation energy, that control the boiling point.

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## 1. Introduction

An azeotrope is a mixture of two or more chemicals in solution that cannot be separated by basic distillation processes because the ratio of the chemicals in the vapor phase is the same as that in the liquid phase. In industry, azeotropes are very important due to the benefits of azeotropic behavior, perhaps the most important is the unexpected ability to mix flammable and nonflammable ingredients to produce a stable nonflammable mixture. The chemicals of an azeotrope can never be separated in a hot environment and thus dangerous flammable vapors cannot exist. This is applicable in the production of nonflammable solvents that are safer and more reliable to use especially in industrial facilities. In addition, azeotropes are useful across a broad range of applications and recovered by simple distillation [1]. Moreover azeotropic formation is very important in distillation processes [2]. Formation of an azeotrope in an industrial process alters product distribution and restricts the separation amount of a multicomponent mixture that can be achieved by distillation.

The thermodynamic behavior of phase equilibria and physical properties of mixtures are essential for design and optimization of numerous chemical processes. Thermodynamic models used for phase equilibria calculations can be broadly classified as equation-of-state (EOS) models, which are capable of handling the fluid behaviors and

excess Gibbs energy ( $G^E$ ) models, which are capable of handling highly non-ideal mixtures. Equations of state either using van der Waals equation or some of its modifications are used to predict properties of mixtures [3–12]. The more accurate equations of state, however, commonly make use of a number of compound-specific parameters that have to be either measured (critical parameters, etc.) or estimated using fitting constants. Moreover, some of the fitting parameters used for equations of state might be relevant only for homologous classes of compounds (for instance, hydrocarbons). In general, current EOS and  $G^E$  model generalizations are not uniformly accurate and there is a need for reliable thermodynamic models capable of giving a priori predictions of the phase behavior of diverse systems in the absence of experimental data [13].

Activity coefficient models including non-random two-liquid (NRTL) and universal quasi-chemical (UNIQUAC) models are widely used in the chemical and petrochemical industry today [14–19]. These are found to be especially useful for highly non-ideal vapor–liquid equilibrium (VLE) systems. However, the models fail to provide reliable generalizations for systems with limited or no data. Further, the model parameters tend to be highly correlated.

Applications of ab initio approaches to predict VLE behaviors have been reported in the literature. For example, Lee et al. showed that quantum mechanical calculations can be used to predict vapor–liquid equilibria of mixtures away from the critical point of any constituent component [20]. Athès et al. demonstrated the ability of the COSMO-SAC (conductor-like screening model-segment activity

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coefficient) approach to model vapor–liquid equilibria of water–ethanol solutions containing 13 aroma compounds [21]. The conductor like screening model for real solvents (COSMOS-RS) [22–24] provides reliable estimate of vapor–liquid and liquid–liquid equilibria based on quantum chemical calculations for the chemical species involved. It is a relatively new approach, which utilizes unimolecular quantum chemical calculations of the individual species and does not consider the mixture itself. The COSMOS-RS approach uses eight adjustable parameters and one additional parameter for each element. The theory of COSMOS-RS resolves the issue of isomers and gives accurate representations of LLE. However, it sometimes fails to describe the VLE of even simple organic systems [23,24]. Besides, considerable work has been done on developing models utilizing direct molecular dynamics/Monte Carlo simulation techniques [25,26]. However, these approaches are highly time consuming, require enormous computational burden, involve several approximations, and are yet to be applied to a wide range of systems.

Quantitative structure–property relationship (QSPR) modeling has the potential to provide reliable property estimates based solely on chemical structure information. Theoretical assessment of QSPR models could significantly reduce the costs of selection of proper agents for industrial process. Various studies for the correlation of pure–fluid properties using QSPR models exist in literature [27–30]. In many cases, QSPR approach has been used to predict properties of individual compounds. Although QSPR methodology could, in principle, be applied to estimate some desired properties of mixtures, very little work has been done on QSPR models for mixtures [31–33]. The main difficulty in the QSPR study of mixtures is the calculation of numerical descriptors to characterize a mixture. Two simple approaches were introduced to characterize a mixture [33]: (1) descriptors of a mixture are calculated as averages of the corresponding molecular descriptors for each component in the mixture (centroid approximation) and (2) scaled descriptors using weighting factors proportional to the molar fraction of each component in the mixtures were used as descriptors of a mixture (weighted–contribution–factor approximation). The latter is of limited practical interest because experimental measures of the mixture’s composition at the azeotropic point are needed. Katritzky et al. used both approaches to predict normal boiling point of binary mixtures [33]. The predictive power of linear models was rather poor: the standard deviation of about 23 K has been obtained at the fitting stage and has not even been reported for the external test set. Recently, Solov’ev et al. described QSPR modeling for both normal boiling point and the composition of binary azeotropes using ensemble multiple

### Procedure of the memorized ACS algorithm

```

Set parameters
Create pheromone vector with unity entries for all descriptors
Define a matrix (M) with m rows as external memory
i ← 1;
while (i ≠ L') do
    j ← 1;
    while (j ≠ m) do
        Take pheromone trails
        Run the ACS algorithm with predefined pheromone trails
        Take the resulted the best-so-far ant
        M(j,:) ← the best-so-far ant
    End-while
    Updating pheromone vector by all ants in M
    Do pheromone evaporation
end-while
end-procedure

```

Fig. 2. High-level view of the Memorized\_ACS algorithm for descriptor selection.

linear regression (eMLR) and sub-structural molecular fragment (SMF) descriptors [34]. Descriptors for a mixture were generated by concatenation of fragment descriptors of its individual molecular components. Each developed MLR model contained, on average, 36 SMF descriptors for modeling of  $T_b$ . Considering the number of mixtures in the training set which was 176, indicates that the ratio of the number of mixtures in the training set to the number of descriptors in the model (Topliss ratio [35]) is low, thus individual models may be unstable. The final statistical features of their approach were good because the ensemble MLR models (contained at least 82

### Procedure of ACS algorithm

```

Set parameters
Create pheromone vector with unity entries for all descriptors
while (not terminate) do
    Calculate probability vector (P) based on the pheromone trails.
    Build ant colony based on P.
    Construct ants' solutions; building MLR model with the selected descriptors by each ant.
    Consider the best solution, Find iteration-best ant.
    Updating pheromone vector by the iteration-best ant.
    Do pheromone evaporation
end-while
end-procedure

```

Fig. 1. High-level view of the ACS algorithm for descriptor selection.

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