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Sensitivity of azeotropic states to activity coefficient model parameters and system variables

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Abstract

The activity coefficient models, when based on parameters obtained through binary phase equilibrium information result in multiple sets that may either not be able to predict ternary and higher order azeotropes, or computed values are significantly different from experimental data, particularly at thermodynamic landmarks. Sensitivity of azeotropic states to model parameters and operating conditions is imbedded into a homotopy continuation formulation, providing a functionally sound basis for prediction of such states and their corresponding sensitivity. Furthermore, the validity of parameter set depends on the range of operating variables. The methodology allows systematic variation of model parameters and selection of a parameter set that allows computation of thermodynamic landmarks, such as azeotropy. The systematic analysis of the effects of parametric perturbation on the prediction of azeotropes and heteroazeotropes also provide useful insights into capabilities and limitations of phase equilibrium models. The technique is also useful in developing the effect of system variables on azeotropy conditions. We demonstrated the utility of our approach through modeling benzene–cyclohexane–*n*-propanol, ethyl acetate–ethanol–water and water–formic acid–acetic acid system.

Keywords: Azeotropy; Homotopy continuation; Heteroazeotropes; Activity coefficient model

1. Introduction

Recently, conceptual process design has become an important area of activity both for industry and academia. The basic purpose of conceptual process design is to conceive generate, compare and evaluate the different process alternatives at a very early stage of design with minimum information available. Conceptual process design allows systematic elimination of large number of available process alternatives and allows subsequent detailed analysis of substantially reduced set of alternatives. An effective conceptual design step requires efficient and reliable tools that require minimum information. One of the most widely used conceptual tools is Residue Curve Maps (RCMs) that are used for conceptual design of non-ideal distillation separation sequences. Residue curves is the most mature conceptual process design tool and is a part of almost all the available design packages. The methodology is well covered in a recent text Malone and Doherty [9].

Reliability of residue curves, as a conceptual design tool, depends on the accuracy of the model representing the phase equilibrium and algorithm used for prediction of thermodynamic landmarks, such as azeotropes. Tolsma and Barton [14,15] described a homotopy continuation based approach to compute all the possible azeotropes in multicomponent mixtures with mathematical guarantees. The mathematical treatment of Tolsma and Barton's [14,15] approach is independent of the representation of system non-idealities. However, numerical tracking of homotopy branches and in turn computation of azeotropes is highly dependent on phase equilibrium model and associated parameters. Aslam and Sunol [2] further enhanced their approach by incorporating both vapor and liquid phase non-idealities through equations of state, and thus computing azeotropes for entire pressure range. Tolsma and Barton [14,15] used activity coefficient models to describe the liquid phase non-idealities with binary interaction parameters regressed from binary phase equilibrium data. The activity coefficients, which are based on parameters obtained from binary information, when used in modeling the mixtures, with three or more components may not provide a realistic description of phase non-idealities for such mixtures mainly due to error associated with extrapolating

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the binary information to describe the phase non-idealities in ternary or higher order mixtures. Furthermore, they may not adequately represent thermodynamic landmarks, such as azeotropy.

Through homotopy continuation approach, all the azeotropes in multicomponent mixtures can be computed by solving for necessary condition of azeotropy. When liquid phase activity coefficients for multicomponent mixtures are obtained through parameters based upon binary information, their use can lead to errors in prediction of azeotropy (Englezos and Kalogerakis [3]). For such a case, the predicted values can be significantly different from experimental values, or provide the azeotropic values, which are lying outside the physical composition space where they are of little practical significance, or may not be able to predict the azeotropy. A systematic method is therefore needed to establish the effect of parametric perturbation on the prediction of azeotropes. Since activity coefficient model parameters can have multiple solutions (Rabinovich [10] and Walas [16]), a global solver such as homotopy continuation is needed to establish the sensitivity of model parameters on azeotropy. We are using a homotopy continuation based approach to develop the sensitivity of model parameters and system variables on azeotropic states. Our approach is based on exploiting the necessary and sufficiency condition of azeotropy and imbedding the sensitivity analysis with respect to model parameters or system variables. The resulting over determined system of equations is solved by pseudo arc length continuation algorithm as detailed by Allgower and Georg [1] and Speight [11]. We analyzed benzene–cyclohexane–*n*-propanol, ethylacetete–ethanol–water and water–formic acid–acetic acid system. We also demonstrated that if azeotropy is not predicted under the given set of activity model parameters, it could be obtained through selecting another set of parameters.

2. Theory

Fidkowski et al. [4] solved the necessary conditions of azeotropy ($x_i = y_i$) using homotopy continuation. The homotopy map is given as follows:

$$h_i(x, \lambda) = \lambda(x_i - y_i^{\text{Real}}) + (1 - \lambda)(x_i - y_i^{\text{Ideal}}) \tag{2.1}$$

where λ is the homotopy parameter, which varies from 0 to 1 and x_i is the liquid composition. The y_i^{Ideal} is the vapor composition for an ideal gas and ideal solution and y_i^{Real} is for a real gas and non-ideal solution. For $\lambda = 0$, the $x_i = y_i^{\text{Ideal}}$ and for $\lambda = 1$, the $x_i = y_i{}^{\text{Real}}$.

$$y_i^{\text{Ideal}} = K_i^{\text{Ideal}} x_i \tag{2.2}$$

$$y_i^{\text{Real}} = K_i^{\text{Real}} x_i \tag{2.3}$$

The K_i^{Ideal} is the ideal solution equilibrium constant and is derived from Raoult's law while K_i^{Real} is a non-ideal equilibrium constant which maps the liquid phase non-idealities with activity coefficients. The vapor phase is assumed ideal.

$$K_i^{\text{Ideal}} = \frac{P_i^{\text{sat}}}{P} \tag{2.4}$$

and

$$K_i^{\text{Real}} = \frac{\gamma_i P_i^{\text{sat}}}{P} \tag{2.5}$$

Tolsma and Barton [14,15] further enhanced the Fidkowski et al. [4] approach to isobaric conditions. They developed the following formulation shown in system of Eq. (2.6) using activity coefficients to map the liquid phase non-idealities and assuming ideal vapor phase.

$$F(x, T, \lambda) = \begin{pmatrix} x_1 - K_1^0 x_1 \\ \cdot \\ \cdot \\ \cdot \\ x_n - K_n^0 x_n \\ \sum_{i=1}^{n} x_i - 1 \end{pmatrix} \tag{2.6}$$

where K_i^0 is the pseudo equilibrium constant and is given as follows:

$$K_i^0 = \left[\lambda K_i^{\text{Real}} + (1 - \lambda) K_i^{\text{Ideal}}\right] \tag{2.7}$$

As we set $F(x, T, \lambda) = 0$, we have defined a solution space in x, T, λ for a fixed pressure. The mapped solution of above function is called the homogeneous homotopy path and is usually represented on a temperature and composition bifurcation diagram. Fig. 1 depicts a bifurcation diagram for a hypothetical system (ABC). As can be seen in Fig. 1, that two main characteristic points on this bifurcation diagram are bifurcation point appearing on pure component branches, bifurcation points appearing on binary and higher order branches and solution points at $\lambda = 1.0$. Importance of these characteristic points on a systematic sensitivity analysis of model parameters is described in following section.

3. Sensitivity analysis of azeotropic states

The homogeneous bifurcation diagram has two types of characteristic points as shown in Fig. 1.

- Bifurcation points (appearing) on *n*th order homotopy branches ($n = 1$, pure component; $n = 2$, binary branches and $n = 3$, ternary branches, etc.).
- Solution points.

Homogeneous homotopy path can be obtained by setting Eq. (2.6) equal to zero. However, if the model parameters are incorporated in Eq. (2.6), the homogeneous homotopy map will become

$$F(x, T, P, \lambda, \{A_{\text{p}i}\}_{i=1,\ldots,N_\text{p}}) = 0 \tag{3.1}$$

In Eq. (3.1), $A_{\text{p}i}$ are the model parameters used in activity coefficient expression to describe the liquid phase nonidealtes. For a homogeneous system, we get $n + 1$ equations