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A KNOWLEDGE-BASED EXPERT SYSTEM FOR THE PREDICTION OF TERNARY AZEOTROPE FORMATION IN ORGANIC MIXTURES

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Abstract – New functions of AZEOPERT [Kim and Simmrock, 1997] were investigated to predict the occurrence of ternary azeotropes and their azeotropic compositions in an organic mixture. This study describes its new problem-solving strategy. The knowledge base of AZEOPERT for ternary azeotropes is hierarchically structured with the several levels of domain-specific knowledge on ternary azeotropy. First, an azeotropic data bank including ternary azeotropic experimental data was implemented in AZEOPERT as the lowest level. It may be used to determine whether or not ternary azeotropic experimental data for the consulted organic mixture are already available. Moreover, compiled heuristic knowledge as the second level and class-oriented model-based knowledge as the highest level were implemented in the knowlege base. The problem-solving strategy through the integration of model-based reasoning into compiled reasoning gives a very efficient, general way for the prediction of ternary azeotrope formation in a wide varitey of organic mixtures, and especially, in unknown mixture systems.

Key words: Ternary Azeotrope, Expert System, Heuristics, Compiled Knowledge, Model-Based Knowledge

INTRODUCTION

Studies on artificial intelligence (AI) have had many important successes. The considerable development in artificial intelligence could afford the use of expert or knowledge-based systems [Stephanopoulos and Mavrovouniotis, 1988] as an auxiliary tool in the field of chemical engineering [Banares et al., 1988]. In the coming years the application areas of expert systems in chemical engineering will expand dramatically and expert systems will play an important role in solving chemical engineering problems, especially the problems that have no well-defined theories. At present, most expert systems in chemical engineering are concerned with application areas such as diagnosis, configuration, selection, prediction, interpretation, control, planning, intelligent support systems, and design in functional respects [Sangiovanni and Romans, 1987]. Although many of the tasks encountered in the chemical engineering practice cannot be completely articulated into a well-informed algorithmic procedure, they can be successfully solved with a variety of heuristic problem-solving methods [Song and Park, 1990; Lee et al., 1993] and expert systems that provide a novel means of tackling such ill-defined problems.

Many of the initial expert systems in chemical engineering treated simplified tasks, which allowed the use of an exclusive representation and problem-solving method to solve the problem. Unfortunately, these initial programs lacked intelligent facilities to reflect the rich variety of knowledge necessary to solve chemical engineering problems. This is likely to change rapidly, though, for expert systems dealing with real solutions to the problems in chemical engineering are beginning to appear due to the rapid development of artificial intelligence techniques.

In chemical engineering, process synthesis is one of the promising new fields of research of knowledge-based expert systems [Simmrock et al., 1990]. Most of the process synthesis studies have been concerned with the separation of multicomponent ideal mixtures in simple distillation columns dominant throughout the chemical industry, because there is no difficulty in predicting which components can be taken from the the top of the column and which can be taken from the bottom of the column. However, the synthesis of distillation sequences of simple columns may be complicated by the formation of azeotropes due to nonidealities in the mixture. The mixture is impossible to separate by conventional distillation. These components must be separated by using the special separation processes such as azeotropic distillation or extractive distillation, when azeotrope forming components are encountered. Therefore, information of the occurrence of azeotropes in the mixture is one of the basic and most important thermodynamic data for producing a judicious design for the separation step [Kim and Kang, 1995].

In a previous work AZEOPERT [Kim and Simmrock, 1997] was developed to predict the occurrence of binary azeotropes in organic mixtures, and it is examined to evaluate the feasibility of applying techniques from the area of artificial intelligence to conventional thermodynamic problems in the field of chemical engineering. The main objective of this study is to extend the functions of AZEOPERT in order to predict the formation of ternary azeotropes in an organic mixture, especially the ternary azeotrope formation that until now has been not reported. The other main objective of this work is to demonstrate how domain knowledge can be represented for the effective prediction of ternary azeotrope formation.

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TERNARY AZEOTROPY

Raoult's law is taken as the definition of an ideal mixture. The formation of the constant-boiling mixture may occur when the mixutre has deviations from Raoult's law, particularly for the mixture of close-boiling components of the different series of homologues. The constant-boiling mixtures are referred to as azeotropes. Azeotropes exhibit minimum or maximum boiling points that represent, respectively, positive or negative departures from Raoult's law. The vapor and liquid are of the same compositions. The occurrence of azeotropes depends essentially upon the degree of nonideality of the mixture and the difference in boiling points between the components. The closer the boiling points of the components are, the more likely they will be azeotropic; the more ideal the solution of the components is, the less likely they will form an azeotropic system [Horsley, 1973]. However, an azeotrope will be formed despite only slight departures from ideal mixtures when the two components boil close together, and a mixture of wide boiling components may not exhibit an azeotrope even though they form a very non-ideal fluid mixture.

Until now a great number of experimental azeotrope data have been accumulated espècially by Horsley [1973]. But, the number of experimental data on ternary azeotropes published until now in the world is not more than 1,000. Moreover, although a number of correlations for ternary azeotropes have been proposed, there is no accurate correlation which is able to generally apply to all kinds of mixtures. They are highly empirical and specific, due to the lack of enough knowledge of intermolecular forces and a satisfactory thermodynamic model.

The nonideality of the mixture is largely due to differences in intermolecular forces of attraction among the components present. Hydrogen bonding is the most important effect on the occurrence of azeotropes. Therefore, the degree of nonideality in mixtures can be predicted with reasonable accuracy with the classification of components on the basis of the tendency of hydrogen bonding of the certain groups and the series of homologues. Berg [1944] has classified liquids into five groups according to their hydrogen bonding capabilities and has satisfactorily predicted the degree of nonideality in the mixture. Swietoslawski [1959] and other workers have predicted the series of azeotropes on the basis of the series of homologues. However, the occurrence of azeotropes can be only qualitatively predicted with the prediction of the degree of nonideality in a mixture.

A more accurate prediction can be achieved by taking account of the difference in boiling points between the pure components. This boiling point difference effect on azeotropy can be well explained with the "azeotropic range" concept that was introduced by Swietoslawski [1950] and has been developed by Malesinki [1956] and Yoshimoto [1956] on the general assumption that the components form a regular solution.

1. The Classification of Ternary Azeotropes

Ternary azeotropic systems may be classified broadly in relation to the character of the azeotropes as follows: They can be classified into minimum- , maximum- or saddle azeotropes, according to the boiling point characteristics at the azeotropic point. A minimum azeotrope may occur if the deviation from Raoult's law is positive and it is characterized by a minimum-boiling temperature under constant pressure conditions. For a maximum azeotrope, the deviation from Raoult's law is negative and it has a maximum-boiling temperature at constant pressure and a minimum total vapor pressure at constant temperature. If the positive deviation is large enough, phase splitting can occur and a minimum heterogeneous azeotrope may be formed with one vapor phase in equilibrium with two liquid phases. All heterogeneous azeotropes found experimentally have been minimum; the existence of maximum heteroazeotropes is rather doubtful.

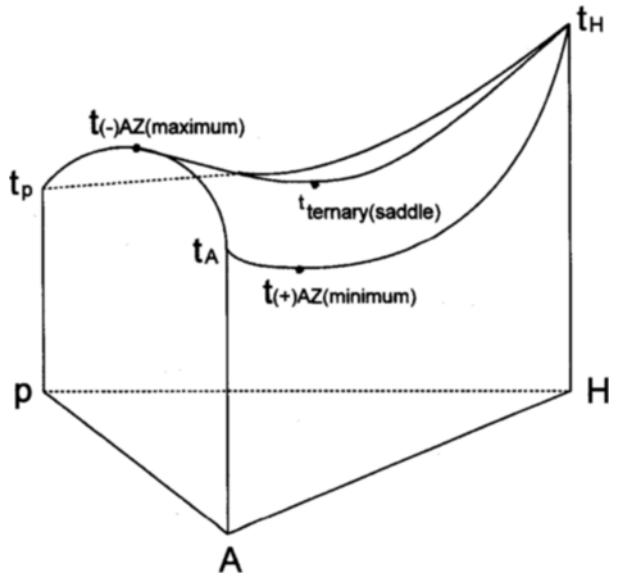

Fig. 1. The ternary saddle azeotrope. $t_{ternary}$ is the azeotrope point.

In ternary component systems saddle azeotropes, found by Ewell [1945] and later called positive-negative azeotropes by Swietoslawski [1963], may be formed. Fig. 1 shows a typical saddle-type azeotrope formed in ternary mixtures. Saddle azeotropes are characterized by a hyperbolic point that is neither a minimum nor a maximum in either boiling temperature or total vapor pressure, and exhibit the presence of "top-ridge" line.

2. Studies on Azeotropic Systems

In 1802 the existence of azeotropes was first discovered by Dalton [1802]. He noticed that aqueous hydrochloric acid boils at a higher temperature than water. He also discovered several other negative azeotropes formed by water and inorganic acids. In 1869 the first positive homoazeotrope, ethanol-water was examined by Yelin [1824].

Between 1881 and 1884, on the basis of Gibbs' work, Konovalov [1884] formulated a rule: an extremum on the vapor pressure curve appears if and only if the compositions of the coexisting phases are identical. In this respect the Gibbs-Konovalov law is of fundamental importance in the area of azeotropy.

In 1897 the Bancroft rule [1897], which has exerted a positive influence on the development of azeotropy, was published. It states that azeotropes are formed if the vapor pressure curves of the pure components intersect at a given temperature. The Bancroft rule was tested against many experimental data. Since many exceptions to this rule have been discovered, at the present stage of knowledge on azeotropy the Bancroft

rule no longer plays an important role.

In 1900 Zawidzki [1900] showed in his pioneering study on liquid solutions that non-ideal binary solutions could be classified into two types with positive and negative deviations from Raoult's law.

In 1918 Lecat [1918] collected about 1,000 azeotropes in his monograph. This monograph showed that the appearance of maximum or minimum vapor pressures of binary and ternary mixtures should not be regarded as a rare phenomenon. And Young discovered the first ternary heteroazeotrope, formed by ethanol, benzene, and water.

In 1945 the first ternary saddle (positive-negative) azeotrope was found by Ewell and Welch in the system acetone-chloroform-methanol. A tangent azeotrope was defined by Swietoslawski [1963] as one that has the composition and the boiling temperature of one of the pure components.

Since the early 1950s Polish scientists Swietoslawski and coworkers have carried out extensive and systematic studies, based on the idea that homologous series of compounds form series of azeotropes with particular azeotropic agents in the "azeotropic range." Due to these studies many kinds of new multicomponent azeotropes such as the quaternary heteroazeotropes and quinary azeotrope were discovered.

More recently, Horsley [1973] collected 15,823 binary, 725 ternary, 21 quaternary, and 2 quinary experimental data in his Azeotropic Data-III published in 1973. The number of the azeotropic systems in Azeotropic Data-III is as follows: binary 7,945 (52 % of total binary systems), ternary 371 (51 % of total ternary systems), quaternary 9 (43 % of total quarternary systems), and quinary 1. Ternary saddle azeotropes occur in 40 systems; 267 (72 % of total ternary azeotropic systems) ternary azeotropic systems contain water as one component. There are also 4 ternary negative azeotropes. Quaternary systems form 8 positive azeotropes and 1 saddle azeotrope [Kurtyka, 1988].

3. The Series of Azeotropes and Azeotropic Range

In general, it can be expected that the azeotropic parameters of a series of homologues will exhibit some regularities, because the physico-chemical properties of homologues of a given series vary in an ordered manner [Malesinski, 1965]. These characteristics of homologues can be used to predict the occurrence of azeotropes in organic mixtures. Lecat arranged experimental azeotropic data in his first works [Lecat, 1918] by relating a certain "azeotropic ability" to the chemical character of the components. Later, Swietoslawski [1950] defined the azeotropic range, the most useful characteristics of azeotropes, based on the regular solution theory and Yoshimoto [1956] and Malesinski [1956] developed the concept of the azeotropic range through a number of case studies. This azeotropic range concept has played an important role in the area of azeotropy and has been used by many workers in recent studies to predict azeotrope formation in organic mixtures. Without this azeotropic range concept, some general conditions for predicting azeotrope formation could not be formulated. Thus, the component classification based on the hydrogen bonding tendency and based on the series of homologues and the azeotropic range can be the underlying concepts to predict ternary azeotrope formation in organic mixtures with reasonable accuracy.

The ternary azeotropic range can be similarly defined by using the concept of the binary azeotropic range [Kim and Simmrock, 1997]. In the case of the ternary azeotropic range, we have two constant components and one homologous series. The series of ternary azeotropic systems then lie between two particular limiting binary azeotropes, but the best scheme for a series of ternary azeotropes is obtained by drawing the boiling temperature isobars formed by the binary azeotropes (1,2) within the series of binary azeotropes (2,3i), not with the series of pure homologues 3i. Fig. 2 shows the azeotropic range for series of ternary azeotropes. The ternary azeotropic range can be considered as a certain azeotrope temperature range ($T_{2,3l}$,$T_{2,3u}$) of the series of binary azeotropes (2,3i) below and above the binary azeotrope temperature $T_{1,2}$ of two constant components (1,2). That is, the range of formation of ternary azeotropes is limited by two binary azeotropes (2,3*l*) and (2,3u). The difference in the binary azeotrope temperatures of the homologues forming the limiting azeotropes is called the ternary azeotropic range Z:

$$Z = T_{2,3u} - T_{2,3l}.$$

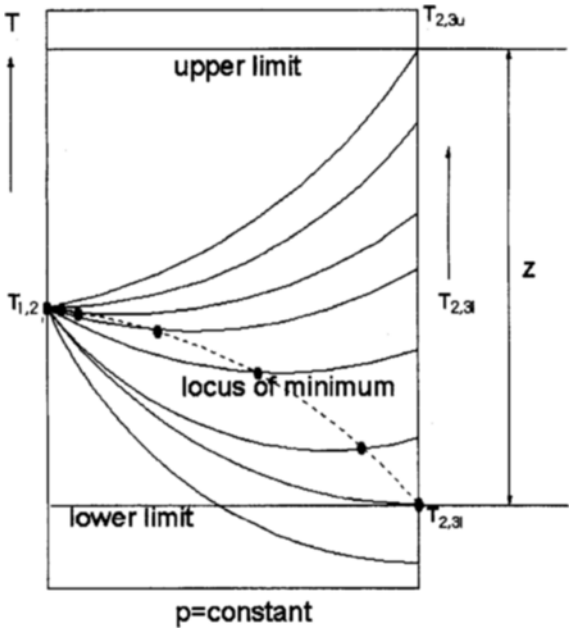

Fig. 2. The azeotropic range of the ternary azeotropes [Malesinski, 1965].

THE PREDICTION OF TERNARY AZEOTROPE FORMATION

1. Hierarchical Knowledge Base and Knowledge Representation Formalism

The knowledge base for ternary azeotropes is structured into a hierarchy with the top level associated with model-based knowledge and the second level associated with component-specific compiled heuristic knowledge. And the ternary azeotropic data bank is integrated into the knowledge base as the first level. Fig. 3 shows how the domain knowledge is organized into the knowledge base of AZEOPERT for ternary azeotrope prediction.

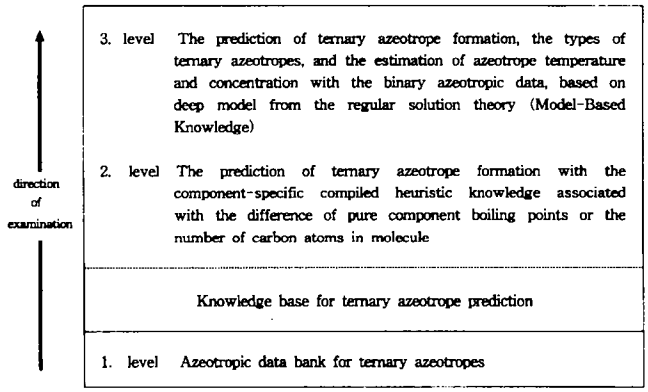

Fig. 3. Hierarchical knowledge structure for ternary azeotrope prediction.

AZEOPERT begins with an examination of the lowest level, the ternary azeotropic data bank, in order to confirm whether there are already ternary azeotropic data for the consulted ternary system in the ternary azeotropic data bank. If there are no ternary azeotropic data for the consulted ternary system, AZEOPERT proceeds on to the next higher level, the level of the component-specific compiled knowledge to make a predictive reasoning. Unless AZEOPERT makes a predictive reasoning with the compiled heuristic knowledge, it can finally draw a predictive reasoning at the level of the model-based knowledge.

The reasoning procedure for the prediction of ternary azeotrope formation proceeds through a hierarchy of knowledge levels like that for the prediction of binary azeotrope formation [Kim and Simmrock, 1996]. However, in the case of ternary prediction the model-based reasoning is considered as a major reasoning method rather than a default reasoning method, since the compiled heuristic knowledge involves only a very small number of ternary systems. In this manner, AZEOPERT can predict the occurrence of ternary azeotrope formation in a wide variety of organic mixtures regardless of known azeotropic systems or unknown azeotropic systems. The rules in each level are formulated by a combination of theoretical considerations, practical experience, and case studies through the ternary azeotropic data bank. Therefore, in this procedure, the user gets all the answers from the rules and the ternary azeotropic data bank which is part of the knowledge base.

One of the important decisions in implementing an expert system is how the domain-specific knowledge will be explicitly represented. This knowledge representation formalism plays a key role in the design of expert systems. Knowledge may be represented in several ways: frames, objected oriented, semantic networks, etc. Among them, in general, production rules and frames are more often used for a wide variety of applications in the engineering domain. Production rules have been used as the knowledge representation formalism in AZEOPERT.

Production rules or IF-THEN statements consist of a series of conditional parts and action parts. If the conditions of a rule are satisfied, the action part makes conclusions and executes a series of operations that will modify the state of the problem [Buchanan and Shortliffe, 1984]. The characteristics of uniformity and modularity of production rules make it possible to construct a flexible program with respect to the addition and expansion of the knowledge base and a uniform structure with all domain knowledge being implemented in the same constrained syntax. In AZEOPERT production rules are represented as in the following form.

```
Rule : Ternary_5

 Three components K1, K2 and K3 form a minimum ternary azeotrope
    if component K1 is water
       and if component K2 is trichloroethylene
       and if component K3 belongs to the n-alkanols
       and if the normal boiling point of component K3 is ≥ 77.0 ℃
       and if the normal boiling point of component K3 is ≤ 119.0 ℃.

Rule : Ternary_9

 Three components K1, K2 and K3 form a minimum ternary azeotrope
    if component K1 is water
       and if component K2 is ethylalcohol
       and if component K3 belongs to the hydrocarbons
       and if the normal boiling point of component K3 is ≥ 59.0 ℃
       and if the normal boiling point of component K3 is ≤ 122.0 ℃.

Rule : Ternary_29

 Three components K1, K2 and K3 form a minimum ternary azeotrope
    if component K1 is water
       and if component K2 belongs to the aliphatic alcohols
       and if component K3 belongs to the halogenated hydrocarbons.

Rule : Ternary_35

 Three components K1, K2 and K3 form no ternary azeotrope
    if component K1 is metahnol
       and if component K2 belongs to the hydrocarbons
       and if component K3 belongs to the hydrocarbons.

Rule : Ternary_37

 Three components K1, K2 and K3 form a minimum ternary azeotrope
    if component K1 is 1,4-butyleneglycol
       and if component K2 belongs to the hydrocarbons
       and if component K3 belongs to the alcohols
       and if the number of carbon atoms of component K2 is ≥ 8
       and if the number of carbon atoms of component K2 is ≤ 15
       and if the number of carbon atoms of component K3 is ≥ 5
       and if the number of carbon atoms of component K3 is ≤ 9.

Rule : Ternary_39

 Three components K1, K2 and K3 form a saddle ternary azeotrope
    if component K1 is phenol
       and if component K2 is aniline
       and if component K3 belongs to the n-alkanes
       and if the number of carbon atoms of component K3 is ≥ 9
       and if the number of carbon atoms of component K3 is ≤ 14.

Rule : Ternary_42

 Three components K1, K2 and K3 form a saddle ternary azeotrope
    if component K1 is acetic acid
       and if component K2 belongs to the lutidine isomers
       and if component K3 belongs to the hydrocarbons
       and if the normal boiling point of component K3 is ≥ 97.0 ℃
       and if the normal boiling point of component K3 is ≤ 196.0 ℃.
```

Fig. 4. Typical compiled heuristic rules implemented in AZEOPERT for the prediction of ternary azeotrope formation.

```
THEN <prediction>,
  IF (satisfy) 1) condition 1
               2) condition 2
               .
               .
               n) condition n
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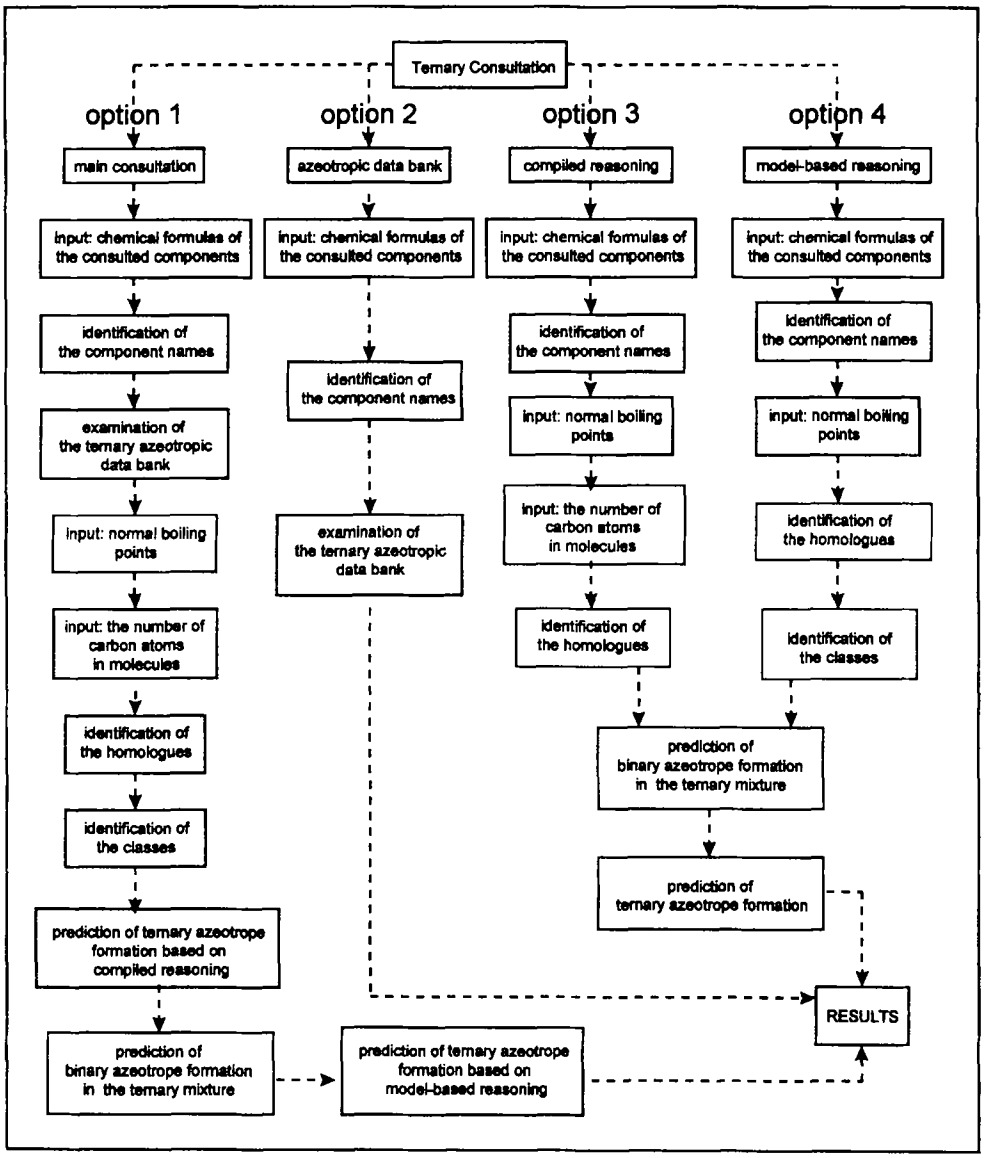

Fig. 5. Problem-solving strategy for ternary consultation.

A <condition> part of rules implemented in AZEOPERT comprises a number of components linked by logical "AND" connectives. In order to test whether an <prediction> is justified, AZEOPERT tests whether the components of the associated <condition> are satisfied. The true values of the components in <condition> part are determined directly from input data entered by the user during the consultation. Fig. 5 shows some of typical production rules in the knowledge base of AZEOPERT.

2. Model-Based Knowledge for the Prediction of Ternary Azeotrope Formation

In this approach a model is used for the prediction of ternary azeotrope formation in the organic mixture. This model was originated by Haase [1956] and developed by Malesinski [1965] based on the theory of regular solutions. Malesinski's method makes it possible to predict the occurrence of ternary azeotropes of various types and to calculate their compositions and boiling temperatures from the binary azeotropic data. In this work the binary azeotropic data are estimated with the interaction parameter between the various classes of liquids calculated by Eduljee and Tiwari [1976].

As mentioned earlier, the most important single cause of deviaton from ideal behaviour in the mixture is hydrogen bonding. The concept of hydrogen bonding is that hydrogen can coordinate between two molecules of oxygen, nitrogen, or fluorine. It can also coordinate between one of these donor atoms (oxygen, nitrogen, or fluorine) and a carbon atom, provided a sufficient number of negative atoms or groups are attached to the carbon atom. The strength of hydrogen bonding depends on the nature of the atoms between which the hydrogen is coordinating. It may be classified generally into strong hydrogen bonding and weak hydrogen bonding. Table 1 illustrates the strength of hydrogen bondings. On the basis of the strength of hydrogen bondings, organic components can be classified into five different classes [Ewell and Berg, 1944].

The binary azeotrope composition x_2 can be obtained by eliminating T_a between Eqs. (1) and (2) and expanding into

Table 1. The strength of hydrogen bondings

Strong bonding	Weak bonding
O-HO	H-HN
N-HO	O-HCCL2, HCCL-CCl, HCNO2, HCCN
O-HN	N-HCCL2, HCCL-CCl, HCNO2, HCCN

a convergent power series [Yoshimoto, 1957].

$$S_1(T_1 - T_a) = NWx_2^2 \quad (1)$$

$$S_2(T_1 - T_a) = NWx_1^2 \quad (2)$$

$$x_2 = \frac{(S_1S_2)^{1/2} - S_1}{S_2 - S_1} + \frac{(S_1S_2)^{1/2}}{2W}(T_1 - T_2) + \frac{(S_1S_2)^{1/2}(S_2 - S_1)}{8W^2}(T_1 - T_2^2) + \frac{3(S_1S_2)^{1/2}(S_2 - S_1)^2}{48W^3}(T_1 - T_2)^3 + \cdots\cdots \quad (3)$$

Neglecting the third and higher order terms,

$$x_2 = \frac{(S_1S_2)^{1/2} - S_1}{S_2 - S_1} + \frac{(S_1S_2)^{1/2}}{2W}(T_1 - T_2). \quad (4)$$

The binary azeotrope temperature T_a is obtained from Eqs. (1) and (4).

$$(T_1 - T_a)^{1/2} = (W/S_1)^{1/2}\frac{(S_1S_2)^{1/2} - S_1}{S_2 - S_1} + (W/S_1)^{1/2}\frac{(S_1S_2)^{1/2}}{2W}(T_1 - T_2). \quad (5)$$

Here, binary interaction parameters W for various class combinations listed in Table 2 are estimated from Eq. (4). A plot of $(T_1 - T_2)$ against x_2 for related classes should yield a straight line with slope $[(S_1S_2)^{1/2}/2W]$ and intercept $[\{(S_1S_2)^{1/2} - S_1\}/(S_2 - S_1)]$. Thus, values of W can be calculated from the slope of each line as explained in Eduljee and Tiwari's work [1976].

The azeotrope composition of a ternary azeotrope under isobaric conditions is related to the two pairs of binary azeotropes by the following equations [Eduljee and Tiwari, 1979].

$$x_j = x_j^{(j,i)} + \frac{(W_{jk} - W_{ik} - W_{ji})}{2W_{ji}}x_k = 0 \quad (6)$$

where

$i = 1, 2, 3 \quad j, k(\neq i) = 1, 2, 3.$

For a fixed i, Eq. (6) gives the following two equations from which the ternary azeotrope compositions may be evaluated. If the binary azeotrope compositions between components (1,2) and (2,3) are available, then setting i=2, the following equations may be solved for the ternary azeotrope compositions x_1 and x_3:

$$x_1 = \frac{x_1^{(1,2)} + ax_3^{(2,3)}}{1 - ab} \quad (7)$$

$$x_3 = \frac{x_3^{(2,3)} + bx_1^{(1,2)}}{1 - ab} \quad (8)$$

where

$$a = \frac{W_{13} - W_{23} - W_{12}}{2W_{12}} \text{ and } b = \frac{W_{13} - W_{23} - W_{12}}{2W_{23}}$$

$x_1^{(1,2)}$, $x_3^{(2,3)}$ = mole fractions of components 1 and 3 in the binary azeotropes (1,2) and (2,3)

x_1, x_3 = mole fractions of the above components in the ternary azeotrope

W_{ij} = the binary interaction parameters.

The ternary system is nonazeotropic if, for example, the composition of one component of the system is zero or takes a negative value.

The boiling temperature of a ternary azeotrope, $T_{ternary}$, with component 2 as the reference component, can be computed from the equation

$$T_{ternary} = T_1 - \frac{\delta_1^{(1,2)} + \delta_1^{(1,3)} + \frac{(\delta_1^{(1,2)}\delta_1^{(1,3)})^{1/2}}{W_{12}W_{13}}(W_{23} - W_{12} - W_{13})}{1 - \frac{(W_{23} - W_{12} - W_{13})^2}{4\,W_{12}\,W_{13}}} \quad (9)$$

where $\delta_2^{(1,2)} = T_2 - T^{(1,2)}$ and $\delta_2^{(2,3)} = T_2 - T^{(2,3)}$.

The ternary azeotropic system is a minimum azeotrope if the ternary azeotrope temperature $T_{ternary}$ is (or equal to) less than the pure component boiling points T_1, T_2 and T_3; it is a maximum azeotrope if the ternary azeotrope temperature $T_{ternary}$ is (or equal to) greater than the pure component boiling points T_1, T_2 and T_3; otherwise it is a saddle azeotrope.

Ternary azeotrope compositions and temperature can be satisfactorily predicted with the above equations using binary interaction parameters W_{ij} obtained from a general classification of liquids, when used in conjunction with binary azeotropic data. This approach gives the attractive possibility of effectively predicting ternary azeotropes from pure component properties and binary azeotropic data via Eqs. (6) and (9).

However, because in many cases the binary predictions based on Eduljee and Tiwari's work are insufficiently precise for this purpose, it is better to use as often as possible binary experimental azeotropic data instead. Therefore, AZEOPERT first

Table 2. Interaction parameter W for various class combinations [Eduljee and Tiwari, 1976]

Class	W, cals/mole
1-1	-
1-2	-
1-3	1565
1-4	1745
1-5	1915
2-2	760
2-3	670
2-4	925
2-5(a)	885
2-5(b)	1237
3-3	190
3-4	-460
3-5	585
4-4	144
4-5	545
5-5	288

(a): excluding formic acid azeotropes
(b): formic acid azeotropes

examines the binary azeotropic data bank in order to confirm whether there are already the required binary azeotropic data in the azeotropic data bank. And unless there are the required binary azeotropic data in the azeotropic data bank, AZEOPERT estimates binary azeotropic data based on Eduljee and Tiwari's work.

The resulting prediction of ternary azeotropic data is satisfactory considering the generality of the classification scheme. In many cases AZEOPERT makes a reasoning for the prediction of ternary azeotrope formation with this model-based knowledge. The ternary model-based reasoning is primarily carried out on the basis of experimental binary azeotropic data from the binary azeotropic data bank. If there are no experimental binary azeotropic data, AZEOPERT predicts binary azeotropic data for the ternary model-based reasoning. The result window for the model-based ternary azeotrope prediction contains binary azeotropic data as well as ternary azeotropic data including azeotrope temperature and concentration.

3. Ternary Azeotropic Data Bank and Compiled Heuristic Rules

The ternary azeotropic data bank mainly contains the experimental ternary azeotropic data taken from Horsley's Azeotropic Data Book [1973] and it has been complemented by own comprehensive collection of experimental ternary azeotropic data published in the literature since 1972. No systematic attempt has been made to evaluate the accuracy of the ternary azeotropic data. However, obviously incorrect data have been corrected with values in [Gmehling and Onken, 1977]. At present about 995 ternary azeotropic data sets are stored in the ternary azeotropic data bank. Most of the ternary azeotropic data are concerned with aqueous mixtures including water. Table 3 shows the structure of the ternary azeotropic data bank connected with AZEOPERT via network. The structure of the whole ternary azeotropic data bank can be seen from Table 3. Each data record contains formulas, component names, system pressure, the occurrence of a ternary azeotrope, reactivity, azeotrope temperature, normal boiling points, weight percent, and reference number.

The ternary azeotropic data bank has been implemented with the ORACLE relational data base management system (Verson 6.0) that runs under the Apple/UNIX operating system like the binary azeotropic data bank and can be accessed by AZEOPERT through a File-Transfer operation. The File-Transfer operation is carried out by Prolog predicates and the SQL data base language. A total of about 45 compiled heuristic rules for the prediction of ternary azeotrope formation have been implemented in the knowledge base of AZEOPERT. These heuristic rules are component-specific. The predictive reasoning with these heuristics is somewhat limited because of the small number of heuristic rules and the component-specific characteristics. Since the known azeotropic data for the ternary systems are inherently very few, competent compiled heuristic rules could not be formulated through case studies with the ternary azeotropic data bank.

Fig. 4 shows typical compiled heuristic rules implemented in AZEOPERT for the prediction of ternary azeotrope formation. These heuristics were formulated based on the tables like Table 4, which shows the structure of the data bank derived from the case study for the system water/ethyl alcohol/hydrocarbons. For example, the heuristic for the system water/ethyl alcohol/hydrocarbons is formulated as follows: As mentioned earlier, the azeotropic range contains two limits: the lower and the upper boundary in which a ternary azeotrope will be formed. The boundary values of each compiled heuristic rule for ternary azeotropes are adopted from these kinds of tables. Based on these tables, when each heuristic rule was formulated, the lower and the upper boundary values were strictly interpreted for accuracy of prediction.

For example, the rule Ternary_9 shown in Fig. 4 can be formulated from Table 4. Table 4 shows that the lower boundary of a ternary azeotropic range for the system water/ethyl alcohol/hydrocarbons is located below 60.2 and the upper boundary is located between 121.6 and 145.1. In this case a high certainty region with reasonable tolerance (between 59.0 and 122.0) was adopted as the temperature range forming ternary azeotropes for accuracy of prediction. In practice, it is reasonable to leave some tolerance for the difference of normal boiling points because there are very frequently different normal boiling point data for the same component in the literature [Kim and Simmrock, 1977]. The occurrence of ternary azeotropes in the uncertainty regions, below 59.0 for the lower region and above 122.0 for the upper region, may be qualitatively predicted with model-based reasoning.

4. Problem-Solving Strategy

The problem-solving strategy of AZEOPERT is quite different from that of conventional predictive expert systems. Many conventional expert systems use only compiled knowledge in order to draw a reasoning. AZEOPERT makes use of several different problem-solving methods such as the ternary azeotropic data bank, component-specific compiled, and model-based reasoning. Each problem-solving method can be invoked sequentially or separately until making a reasoning.

Fig. 5 illustrates the problem-solving strategy for the prediction of ternary azeotrope formation. In option 1, main consultation, AZEOPERT first examines the ternary azeotropic data bank, in order to confirm whether there are already the azeotropic data for the consulted ternary system. If there are no azeotropic data for the consulted ternary system, AZEOPERT automatically invokes its component-specific knowledge base to draw reasonings on the basis of the facts about the consulted ternary system. If there are no component-specific heuristic rules in the knowledge base that apply to the consulted ternary system, the reasoning will automatically proceed on to the next level, model-based knowledge. In this level, AZEOPERT simultaneously estimates the ternary azeotrope temperature, concentration, and the type of the ternary azeotrope.

As shown in Fig. 5 (Option 2, 3, and 4), each problem-solving method implemented in AZEOPERT can separately be called; thus, the result of each problem-solving method can be compared with each other in order to confirm the certainty of results. The separate invocation of each reasoning method is especially very useful for confirming the correctness of predictive results for the uncertain region. In this manner, AZEOPERT can effectively and reliably predict azeotrope formation in a wide variety of organic ternary mixtures regardless of known or unknown azeotropic systems.

In the case of the prediction of ternary azeotrope forma-

Table 3. Structure of the ternary azeotropic data bank [Horsley, 1973]

A-Comp.		B-Component		C-Component		Azeotropic data							
Form.	Name	Form.	Name	Form.	Name	Press. (MPa)	Rea.	B.P. [°C]	Concentration A	B	C		Ref.
H2O1	Water	C2H6O1	Ethyl alcohol	C6H14O1	Ethylisobutylether	0.1013	AZE nv	66	6.5	15.8	77.7	ge	981
H2O1	Water	C2H6O1	Ethyl alcohol	C6H14O1	Isopropylether	0.7904	AZE nv	128.5	9.1	14.2	76.7	ge	982
H2O1	Water	C2H6O1	Ethyl alcohol	C6H14O1	Isopropylether	0.3952	AZE nv	105.8	7.1	11.9	81	ge	982
H2O1	Water	C2H6O1	Ethyl alcohol	C6H14O1	Isopropylether	0.1013	AZE nv	66	7.0	14.7	78.3	ge	981
H2O1	Water	C2H6O1	Ethyl alcohol	C6H14O2	Acetal	0.1013	AZE nv	11.4	27.6	1.0	nv	ge	45
H2O1	Water	C2H6O1	Ethyl alcohol	C6H14O2	Ethoxypropoxymethane	0.1013	NON nv	nv	nv	nv	nv	nv	1035
H2O1	Water	C2H6O1	Ethyl alcohol	C6H15N1	Triethylamine	0.1013	AZE nv	74.7	9	13	78	ge	977
H2O1	Water	C2H6O1	Ethyl alcohol	C7H8	Toluene	0.1013	AZE nv	74.55	nv	nv	nv	nv	563
H2O1	Water	C2H6O1	Ethyl alcohol	C7H8	Toluene	0.1013	AZE nv	74.4	12	37	51	ge	982
H2O1	Water	C2H6O1	Ethyl alcohol	C7H12	1-Heptyne	0.1013	AZE nv	71.0	nv	nv	nv	nv	563
H2O1	Water	C2H6O1	Ethyl alcohol	C7H14	Methylcyclohexane	0.1013	AZE nv	70.5	nv	nv	nv	nv	563
H2O1	Water	C2H6O1	Ethyl alcohol	C7H14	Methylcyclohexane	0.1013	AZE nv	69.59	6.8	32.4	60.8	ge	949
H2O1	Water	C2H6O1	Ethyl alcohol	C7H14O2	Isoamylacetate	0.1013	AZE nv	69.0	nv	nv	nv	nv	377
H2O1	Water	C2H6O1	Ethyl alcohol	C7H18	Heptane	0.1013	AZE nv	69.5	nv	nv	nv	nv	563
H2O1	Water	C2H6O1	Ethyl alcohol	C7H18	Heptane	0.1013	AZE nv	68.8	6.1	33.0	60.9	ge	982
H2O1	Water	C2H6O1	Ethyl alcohol	C8H8	Styrene	0.1013	NON nv	nv	nv	nv	nv	nv	981
H2O1	Water	C2H6O1	Ethyl alcohol	C8H18O1	Butylether	0.1013	NON nv	nv	nv	nv	nv	nv	981
H2O1	Water	C2H6O1	Ethyl alcohol	C8H18O2	2-Ethyl-1,3-hexanediol	0.1013	NON nv	nv	nv	nv	nv	nv	981
H2O1	Water	C2H6O2	Glycol	C4H8O2	Dioxane	0.1013	NON nv	nv	nv	nv	nv	nv	201
H2O1	Water	C2H7N1	Dimethylamine	C4H11N1O1	2-(Dimethylamino)ethanol	0.1013	NON nv	nv	nv	nv	nv	nv	981
H2O1	Water	C2H8N2	Ethylenediamine	C6H6	Benzene	0.1013	NON nv	nv	nv	nv	nv	nv	981
H2O1	Water	C3H3N1	Acrylonitrile	C3H4O1	Acrolein	0.1013	NON nv	nv	nv	nv	nv	nv	905
H2O1	Water	C3H3N1	Acrylonitrile	C3H5N1	Propionitrile	0.1013	NON nv	nv	nv	nv	nv	nv	981
H2O1	Water	C3H3N1	2-Propyne-1-ol	C5H8O2	3,3-Dimethoxypropyne	0.1013	AZE nv	88.95	nv	nv	nv	nv	264

Press.: azeotropic pressure, Rea.: reactivity, B.P.: azeotrope temperature, Concentration: %, Ref.: reference number, AZE: azeotrope, NON: nonazeotrope, nv: non-existent, ge: weight %

Table 4. The structure of the data bank derived from the case study for system water/ethyl alcohol/hydrocarbons

Component A	Component B	Hydrocarbons	T_{nbp} [°C]	T_a [°C]	Type
Water	Ethyl alcohol	Biallyl	60.2	52	min. azeotrope
Water	Ethyl alcohol	1-Hexene	63.6	-	min. azeotrope
Water	Ethyl alcohol	Hexane	68.7	56.0	min. azeotrope
Water	Ethyl alcohol	1-Hexyne	70.2	59.9	min. azeotrope
Water	Ethyl alcohol	Benzene	80.2	64.86	min. azeotrope
Water	Ethyl alcohol	3-Hexyne	80.5	64.4	min. azeotrope
Water	Ethyl alcohol	Cyclohexane	80.75	62.6	min. azeotrope
Water	Ethyl alcohol	1,3-Cyclohexadiene	80.8	63.6	min. azeotrope
Water	Ethyl alcohol	Cyclohexene	82.75	64.05	min. azeotrope
Water	Ethyl alcohol	1,4-Cyclohexadiene	85.6	65.5	min. azeotrope
Water	Ethyl alcohol	1-Heptene	93.64	-	min. azeotrope
Water	Ethyl alcohol	Heptane	98.45	68.8	min. azeotrope
Water	Ethyl alcohol	1-Heptyne	99.5	71.0	min. azeotrope
Water	Ethyl alcohol	Methylcyclohexane	101.8	69.59	min. azeotrope
Water	Ethyl alcohol	Toluene	110.6	74.4	min. azeotrope
Water	Ethyl alcohol	1-Octene	121.6	-	min. azeotrope
Water	Ethyl alcohol	Styrene	145.1	-	non azeotrope

T_{nbp}: normal boiling point, T_a: ternary azeotrope temperature

tion, AZEOPERT makes a reasoning like the reasoning procedures for the prediction of binary azeotrope formation [Kim and Simmrock, 1997]. But the important difference of the problem-solving strategy for the ternary azeotropes is that in many cases the model-based reasoning method gives more promising results rather than compiled heuristic reasoning. In model-based reasoning, AZEOPERT uses the binary azeotropic data to make a reasoning for the prediction of ternary azeotrope formation. Thus, AZEOPERT first examines the binary azeotropic data bank to acquire the experimental binary azeotropic data. If in the binary azeotropic data bank there are no binary azeotropic data required for the prediction of ternary azeotrope formation, AZEOPERT would estimate the binary azeotropic data by itself.

Table 5 shows the predictive results of different kinds of

Table 5. Experimental data [Horsley, 1973 and others] and predicted results of different kinds of reasoning methods for ternary systems

Ternary systems	Experimental T_{az}: (°C) X: mole frac.	Compiled reasoning	Model-based reasoning
Water (1) 2-Butanone (2) Cyclohexane (3)	Minimum azeo. T_{az}=63.6 X(1)=0.1879 X(2)=0.3289	Minimum azeo.	Minimum azeo. T_{az}=65.45 X(1)=0.3113 X(2)=0.3394
Water (1) Acetone (2) Hexane (3)	Saddle azeo. T_{az}=61-71 X(1)=0.0532 X(2)=0.4970	Saddle azeo.	Minimum azeo. T_{az}=49.00 X(1)=0.0664 X(2)=0.7363
Water (1) Crotonaldehyde (2) 2-Methylheptane (3)	Minimum azeo. T_{az}=80-85 X(1)=no data X(2)=no data	Minimum azeo.	Minimum azeo. T_{az}=83.95 X(1)=0.6151 X(2)=0.2834
Water (1) Butanol (2) Butyl ether (3)	Minimum azeo. T_{az}=90.6 X(1)=0.6916 X(2)=0.1947	Non predictable	Non predictable
Acetic acid(1) Pyridine (2) o-Xylene (3)	Saddle azeo. T_{az}=132.2 X(1)=0.2522 X(2)=0.3300	Saddle azeo.	Nonazeotrope
Isopropanol (1) Ethyl acetate (2) Cyclohexane (3)	Minimum azeo. T_{az}=90.6 X(1)=0.3792 X(2)=0.2992	Non predictable	Minimum azeo. T_{az}=69.66 X(1)=0.2747 X(2)=0.3687
Water (1) Acetone (2) Isopropyl acetate (3)	Nonazeotrope	Nonazeotrope	Nonazeotrope
Water (1) Butyraldehyde (2) Butyl acetate (3)	Nonazeotrope	Nonazeotrope	Nonazeotrope
Water (1) Acetone (2) 2-Butanone (3)	Nonazeotrope	Nonazeotrope	Nonazeotrope
Water (1) Methanol (2) Isopropanol (3)	Nonazeotrope	Nonazeotrope	Non predictable
Methanol (1) Benzene (2) Cyclohexane (3)	Nonazeotrope	Nonazeotrope	Nonazeotrope

reasoning methods implemented in AZEOPERT for ternary systems, along with the experimental data. The occurrence of a ternary azeotrope can be also more accurately predicted with the compiled reasoning. But, as mentioned earlier, the application area of both compiled reasoning and model-based reasoning is limited. Especially, model-based reasoning for ternary system cannot predict ternary azeotrope formation in highly nonideal systems including water and alcohols. In predicting ternary azeotrope temperatures and concentrations with the model-based reasoning, the reasoning accuracy is not good as that for binary systems.

CONCLUSIONS

First, expert systems can be used in the domain having no exact theories for problem solving or in the domain in which existing algorithmic models are not adequate to solve the problem and are very limited. Therefore, the problem-solving method using an expert system provides an efficient means of tackling ill-defined problems such as the prediction of the occurrence of ternary azeotropes in the organic mixture. In this study new functions of a knowledge-based expert system, AZEOPERT, were developed in order to predict ternary azeotrope

formation between organic components in the mixture, the type of formed azeotrope, and the estimation of ternary azeotrope temperature and concentration, especially the ternary azeotrope formation that until now has been not reported. Moreover, it was demonstrated how the domain-specific knowledge on ternary azeotropy can be represented in the knowledge base of AZEOPERT for the effective prediction of ternary azeotrope formation.

The domain-specific knowledge has been implemented in the knowledge base of AZEOPERT using a hierarchically structured knowledge representation. AZEOPERT predicts the occurrence of ternary azeotropes with the hierarchical integration of the different types of knowledge such as the azeotropic data bank, compiled knowledge derived from the generalization of a large number of case studies with the ternary azeotropic data bank, and model-based knowledge derived from deep knowledge, regular solution model. The rules in each level are formulated by a combination of theoretical considerations, practical experience, and case studies through the ternary azeotropic data bank. Therefore, in this procedure, the user gets all the answers from compiled knowledge, model-based knowledge, and the azeotropic data bank which is part of the knowledge base. When the result is suspected, its correctness can be examined using several different kinds of reasoning methods implemented in AZEOPERT. The hierarchical knowledge representation of AZEOPERT makes it possible to predict the occurrence of ternary azeotropes in the organic mixture more efficiently and flexibly.

The knowledge-based expert system AZEOPERT in this work may be an intelligent means for the solution of complex ternary azeotropic problems, and the ternary azeotrope data from AZEOPERT may serve as a useful aid to perform process synthesis, to select auxiliary material for azeotropic distillation and extractive distillation, to select solvents for the extraction process, and to select environment-friendly alternative cleaning solvents to CFC solvents.

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NOMENCLATURE

N : Avogadro's number
P : system pressure [MPa]
S_i : molar entropy of vaporization [J/(mole K)]
T : temperature [K]
T_a : binary azeotrope temperature [K]
$T_{ternary}$: ternary azeotrope temperature [K]
T_i : normal boiling point of component i [K]
T_{2i} : normal boiling points of a series of homologues at binary systems [K]
$T_{2,3i}$: binary azeotrope temperatures between component 2 and a series of homologues at ternary systems [K]
$T^{(i,j)}$: azeotrope temperature of binary (i,j) [K]
W_{ij} : interaction parameter of binary (i,j) [J/mole]
x_i : mole fraction of component i in liquid phase
x_{2i} : mole fractions of a series of homologues at binary systems
$x_i^{(i,j)}$: azeotropic mole fraction of component i in binary (i,j)

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