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Role of azeotropy in characterization of complex hydrocarbon mixtures by true-boiling-point distillation

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Abstract

True-boiling-point distillation is an efficient batch distillation being one of the most commonly applied techniques to study the polydispersity of complex hydrocarbon mixtures. True-boiling-point curves are obtained by plotting the temperature at the top of the column versus the fraction of mass distilled. The name expresses the assumption that the complex mixture is separated into its components according to their boiling points. However, in the case of azeotropy (e.g. between aliphatics and aromatics) this assumption is not correct.

Therefore, based on continuous thermodynamics, a method is developed for describing quantitatively the azeotropic effect. The method presumes distillation of pure compounds or of azeotropic mixtures (if the efficiency of the column is sufficiently large). It is demonstrated for mixtures consisting of a petroleum fraction (low in aromatics) and of alcohols. © 1997 Elsevier Science B.V.

Keywords: Vapour–liquid equilibria; True-boiling-point distillation; Influence of azeotropy; Complex hydrocarbon mixtures; Method of calculation; Continuous thermodynamics

1. Introduction

Most industrial separation operations for petroleum fractions require quantitative predictions of vapour–liquid equilibria of such complex hydrocarbon mixtures. Once a suitable thermodynamic model has been chosen the most important problem is an adequate description of the composition of the complex mixture

To get information about the polydispersity of petroleum and its fractions the classical way is the true-boiling-point analysis (TBP analysis). In spite of the existence of other modern methods TBP analysis is still one of the most commonly applied techniques since this method has two important

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advantages. On the one hand, the measurement is direct and simple, and on the other hand, the volumes of fractions obtained are large enough for further analysis.

TBP distillation is a batch distillation with a very efficient column, i.e. the number of plates and the reflux ratio have to be very large. The plot of the temperature at the top of the column versus the fraction of mass distilled is called TBP curve [1,2]. This curve is considered to be an integral distribution function tacitly presuming the separation of the components according to their boiling temperatures.

If azeotropy occurs the TBP curve is not equivalent to the integral distribution of the complex mixture. Since the 1940s this defect of the TBP curves has been known [3–5]. Nevertheless, until now the role of azeotropy in TBP distillation is underestimated. Often azeotropic effects are neglected since in the past a procedure to describe them adequately did not exist.

In this paper, a method is developed allowing to describe quantitatively these effects of azeotropy. The method is based on the presumption that always the lowest boiling pure species or the lowest boiling azeotrope leave the column. Especially complex mixtures of aliphatics with some alcohols as additional discrete components are considered. Here, binary minimum azeotropes (in boiling temperature) between the aliphatics and the alcohols are formed. Calculated results are compared with experimental ones.

2. Distribution functions for describing of composition

Since 1980 continuous thermodynamics was developed to overcome the discrepancy between continuous distribution functions obtained by characterization experiments of petroleum fractions or similar mixtures and the discontinuous treatment by traditional thermodynamics [6–9]). To describe the composition of a complex mixture distribution (density) functions $W(\tau)$ are applied. These are defined by the statement that the integral

$$\int_{\tau_a}^{\tau_b} W(\tau)\,\mathrm{d}\tau \tag{1}$$

gives the mole fraction of all species with boiling temperatures τ within the interval $\tau_a \leq \tau < \tau_b$. In analogy to the mole fractions in traditional thermodynamics, the distribution (density) function has to fulfil the normalization condition

$$\int_{\tau_0}^{\tau^0} W(\tau)\,\mathrm{d}\tau = 1 \tag{2}$$

Here, τ_0 and τ^0 denote the beginning and the end of the boiling point range of the complex mixture.

The corresponding integral distribution function is denoted by $I(\tau)$:

$$I(\tau) = \int_{\tau_0}^{\tau} W(\tau')\,\mathrm{d}\tau' \quad I(\tau^0) = 1 \tag{3}$$

$$\frac{\mathrm{d}I(\tau)}{\mathrm{d}\tau} = W(\tau) \tag{4}$$

$I(\tau)$ is the mole fraction of all species with boiling temperatures lower than τ.

3. Distillation without formation of azeotropes

In the theoretical case of a column with an infinite number of plates and with an infinite reflux ratio the TBP curve is equivalent to the integral distribution function if azeotropy does not occur. If the mixture contains not only the species described by the continuous distribution function but if there are also c discrete components differing in their properties considerably from the other ones, the total distribution (density) function reads

$$W(\tau) = x_A W_A(\tau) + \sum_{i=1}^{c} x_i \delta(\tau - \tau_i) \tag{5}$$

Here, x_A is the overall mole fraction of all species of the ensemble treated continuously, e.g. aliphatics, x_i is the mole fraction of the discrete component i and τ_i is the boiling point temperature of the pure substance i. Furthermore, $\delta(Z)$ is Dirac's function defined by $\delta(Z) \to \infty$ for $Z \to 0$ and $\delta(Z) = 0$ otherwise, where additionally the condition $\int \delta(Z)\,\mathrm{d}Z = 1$ holds (integrating for the total domain of definition of Z). A discrete component i gives an infinitely narrow peak in $W(\tau)$ at the τ value τ_i, the area of which equals the mole fraction x_i.

The integral distribution function writes in this case

$$I(\tau) = \int_{\tau_0}^{\tau} W(\tau')\,\mathrm{d}\tau' = x_A I_A(\tau) + \sum_{i=1}^{n(\tau)} x_i \tag{6}$$

where

$$\mathrm{I}_A(\tau) = \int_{\tau_0}^{\tau} \mathrm{W}_A(\tau')\,\mathrm{d}\tau'$$

Here $n(\tau)$ is the number of discrete components with $\tau_i < \tau$. The relationship between $W(\tau)$ and $I(\tau)$ for two discrete components is shown in Fig. 1.

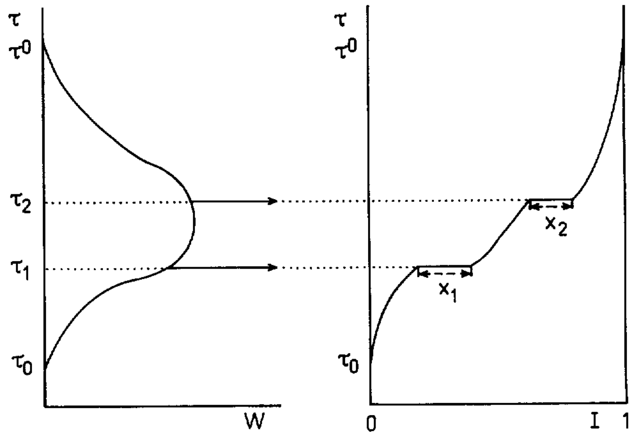

Fig. 1. Distribution (density) function $W(\tau)$ and integral distribution function $I(\tau)$ of a mixture consisting of an aliphatic ensemble and two discrete components in the case without azeotropy. $I(\tau)$ is the TBP curve which would be obtained by a column of perfect efficiency.

4. Distillation with one discrete component able to form azeotropes

If some components of the complex mixture form binary azeotropes not only pure compounds but also azeotropic mixtures leave the column. Paraffins and naphthenes show the same behaviour considering the formation of azeotropes with such compounds as aromatics, alcohols, aromatic amines and others. Therefore, all the aliphatic species may be assumed to belong to the same continuous ensemble.

In the azeotropic point the vapour phase and the liquid phase possess the same composition. This condition and generalized Raoult's law as applied to any components j and k result in

$$\frac{p_j^*}{p_k^*} = \frac{\gamma_k}{\gamma_j} \tag{7}$$

In this, p_j^* and p_k^* are the vapour pressures of the pure components j and k; γ_j and γ_k are the activity coefficients of these components in the liquid phase. If all occurring species belong to the same class of compounds, e.g. aliphatics, the ratio of their activity coefficients has nearly the value of unity because of the chemical similarity of the species. In contrary to that the ratio of vapour pressures will be different from this value. Therefore, two different classes of compounds (aliphatics and aromatics or aliphatics and alcohols) are necessary to get azeotropic effects. In the case considered here binary azeotropes between aliphatic species and discrete components are important.

Most of binary azeotropes show a minimum with respect to boiling temperature corresponding to a maximum with respect to vapour pressure (positive deviations from Raoult's law). The following treatment will be restricted to this case. The corresponding phase diagram shown in Fig. 2(a) is well known. Considering the distillation of a mixture consisting of a continuous ensemble of aliphatics and of a discrete component i it is necessary to know how the azeotropic temperature ϑ_i and the

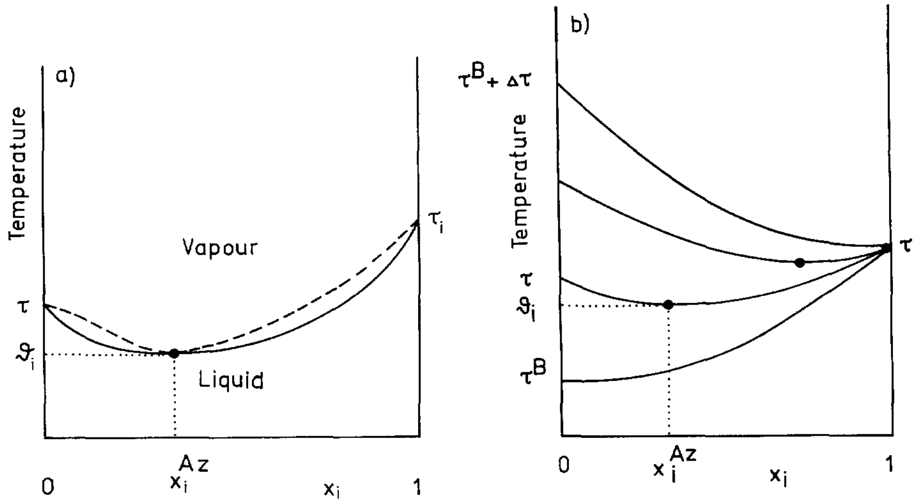

Fig. 2. Azeotropy with minimum in boiling temperature: Temperature–mole fraction (x_i) diagrams at constant pressure. (a) A binary system consisting of an aliphatic species (boiling temperature τ) and a discrete component i (boiling temperature τ_i): ●, azeotropic point. (b) Binary systems with different aliphatic species and the same discrete component i. The dew lines are neglected The diagram shows the variation of the azeotropic temperature ϑ_i and of azeotropic composition x_i^{Az} with the boiling temperature τ of the aliphatic species.

corresponding mole fraction x_i^{Az} vary with the kind of the aliphatic species, i.e. to know the functions $\vartheta_i = \vartheta_i(\tau)$ and $x_i^{\mathrm{Az}} = x_i^{\mathrm{Az}}(\tau)$ (Fig. 2(b): approximation relations are presented in Appendix B). The limits of the τ range of aliphatics forming azeotropes (with a given discrete component i) are as follows:

low temperature limit: $\tau = \tau^{\mathrm{B}}$; $\vartheta = \tau^{\mathrm{B}}$; $x_i^{\mathrm{Az}} = 0$; the azeotropic point lies on the axis of the pure aliphatics,

high temperature limit: $\tau = \tau^{\mathrm{B}} + \Delta\tau$; $\vartheta_{\mathrm{i}} = \tau\mathrm{i}$; $x_i^{\mathrm{Az}} = 1$; the azeotropic point lies on the axis of the pure discrete component i.

Between these limits the function $\vartheta_i = \vartheta_i(\tau)$ increases continuously where in the limiting cases the slopes are given by

$$\lim_{\tau \to \tau^{\mathrm{B}}} \left(\frac{\partial \vartheta_i}{\partial \tau} \right) = 1 \tag{8a}$$

$$\lim_{\tau \to \tau^{\mathrm{B}} + \Delta\tau} \left(\frac{\partial \vartheta_i}{\partial \tau} \right) = 0 \tag{8b}$$

τ^{B} and $\tau^{\mathrm{B}} + \Delta\tau$ identify the lowest boiling and the highest boiling species of the continuous ensemble of aliphatics which are able to form azeotropes with the discrete component i. Eqs. (8a) and (8b) are universal (see Appendix A), i.e. their validity is not influenced by the choice of the expressions for the excess Gibbs energy and for the vapour pressure. Using specific relations for these quantities in Appendix B approximation relations for $\vartheta_i(\tau)$ and $x_i^{\mathrm{Az}}(\tau)$ are derived fulfilling Eqs. (8a) and (8b).

In Fig. 3 the functions $\vartheta_i = \vartheta_i(\tau)$ and $x_i^{\mathrm{Az}} = x_i^{\mathrm{Az}}(\tau)$ are presented with ethanol as discrete component i using data of several well-known binary azeotropes [10]. The following considerations on TBP distillation assume the column to be sufficiently efficient and $\tau_i > \tau_0$, $\tau^{\mathrm{B}} > \tau_0$. At first the lowest boiling aliphatics leave the column. Then the distillation of azeotropes follows. Due to the continuous increase of the function $\vartheta_i = \vartheta_i(\tau)$, in this azeotropic distillation the sequence of aliphatic species is the same as the sequence of τ values. During the distillation of azeotropes the difference between the boiling temperature τ of the pure aliphatics and the distillation temperature (i.e. ϑ_i)

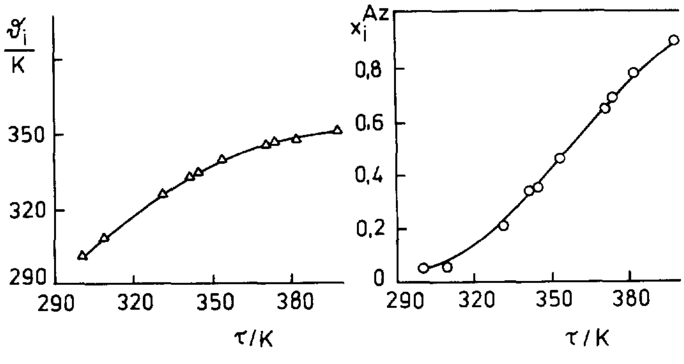

Fig. 3. (a) The boiling temperatures ϑ_{i} and (b) the mole fractions x_i^{Az} of ethanol for binary azeotropes aliphatic/ethanol ($= i$) vs. the boiling temperature τ of the aliphatic.

always increases. The upper limit of the azeotropic distillation depends on the amount of discrete component initially present in the feed mixture. The following three cases are possible:

(a) If there is only a small initial amount of the discrete component azeotropes are formed only with aliphatic species possessing boiling temperatures τ lower than that of the discrete component (τ_i).

(b) If the initial amount of the discrete component i is larger the formation of azeotropes is extended to aliphatic species with boiling temperatures τ larger than that of the discrete component (τ_i).

(c) If there is an excess amount of the discrete component i, then it distils purely after all azeotropes.

In Fig. 4, the boiling point curve $I_{\mathrm{Head}}(T)$ as obtained experimentally and the corresponding distribution (density) function $W_{\mathrm{Head}}(T)$ are presented schematically for these three cases. T means the head temperature of the column. W_{Head}, I_{Head} and T correspond to the quantities W, I and τ in Eqs. (1)–(6) and obey the corresponding equations, i.e.

$$\int_{T_a}^{T_b} W_{\mathrm{Head}}(T)\,\mathrm{d}T \tag{9}$$

gives the mole fraction (with respect to the total feed) of all species—aliphatics and discrete component—leaving the column within the head temperature interval $T_a \leq T < T_b$. In the case without azeotropy the quantities W_{Head}, I_{Head} and T are identical with W, I and τ. τ^{E} denotes the boiling temperature of the highest boiling aliphatic species which, in the considered case, forms an azeotrope with the discrete component. T^{E} is the head temperature at which this azeotrope leaves the column. According to Fig. 4 the following ranges have to be distinguished: distillation of aliphatics 1, distillation of azeotropes, distillation of the pure discrete component i, gap/jump, distillation of aliphatics 2.

4.1. Distillation of aliphatics 1: $\tau_0 \leq T < \tau^B$

As long as the head temperature T is lower than τ^{B} pure aliphatic species leave the column. Similarly to the case without azeotropy it may be written:

$$T = \tau; \quad W_{\mathrm{Head}}(T) = x_{\mathrm{A}} W_{\mathrm{A}}(\tau); \quad I_{\mathrm{Head}}(T) = x_{\mathrm{A}} I_{\mathrm{A}}(\tau) \tag{10}$$

4.2. Distillation of azeotropes: $\tau^B \leq T < T^E$

As soon as T becomes larger than the boiling temperature of the lowest boiling aliphatic being able to form azeotropes the product distilling is not an aliphatic but rather an azeotrope of an aliphatic and the discrete component i. Therefore, the head temperature T now is unequal to the boiling temperature τ of the corresponding aliphatic. T now equals the boiling temperature of the azeotrope $\vartheta_i(\leq \tau)$.

$$T = \vartheta_i = \vartheta_i(\tau); \quad \mathrm{d}T/\mathrm{d}\tau = \vartheta_i'(\tau) \tag{11}$$

The mole fraction of the discrete component within the azeotropes distilled is given by $x_i^{\mathrm{Az}} = x_i^{\mathrm{Az}}(\tau)$; $0 < x_i^{\mathrm{Az}}(\tau) < 1$. The distribution (density) function $W_{\mathrm{Head}}(T)$ reads

$$W_{\mathrm{Head}}(T) = \frac{\mathrm{d}\tau}{\mathrm{d}T} \frac{1}{1 - x_i^{\mathrm{Az}}(\tau)} x_{\mathrm{A}} W_{\mathrm{A}}(\tau) \tag{12}$$

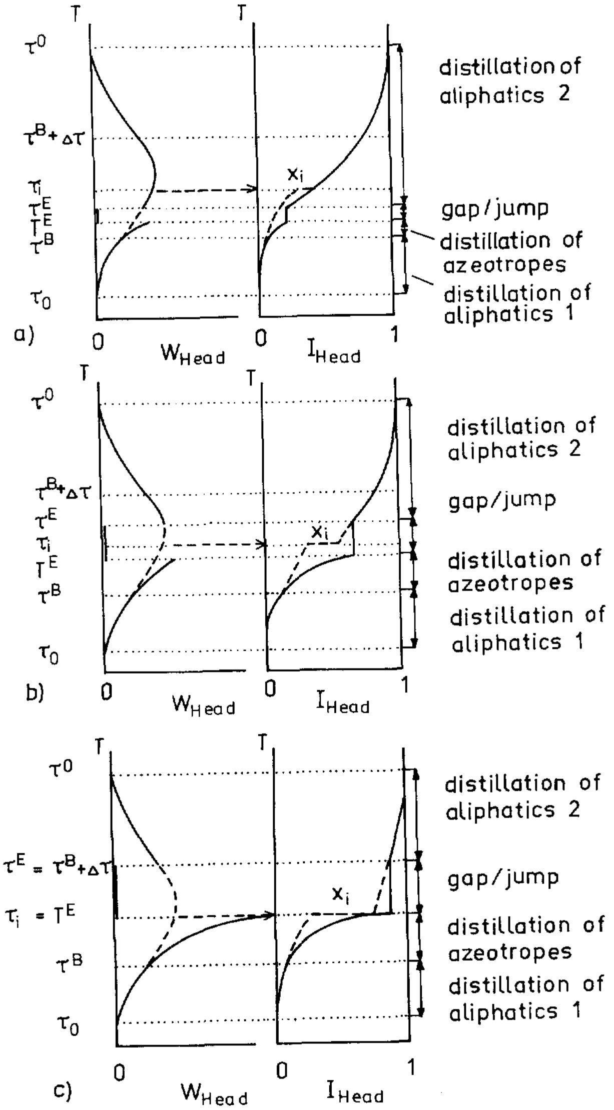

Fig. 4. The functions $W_{\mathrm{Head}}(T)$ and $I_{\mathrm{Head}}(T)$ for the cases (a), (b) and (c) discussed in the text: ———, in the case of azeotropy; ---, in the fictitious case without azeotropy.

where T and τ are interrelated by Eq. (11). The factor $\mathrm{d}\tau/\mathrm{d}T$ in Eq. (12) takes into account that the aliphatic species belonging to the boiling range $\mathrm{d}\tau$ now distil in the smaller head temperature range $\mathrm{d}T$, i.e. $\mathrm{d}\tau/\mathrm{d}T > 1$. The factor $1/[1 - x_i^{\mathrm{Az}}(\tau)]$ accounts for the amount of discrete component distilling together with the aliphatics. Eq. (12) may also be applied to the range of distillation of aliphatics 1. Applying $\tau = T$, $\mathrm{d}\tau/\mathrm{d}T = 1$ and $x_i^{\mathrm{Az}}(\tau) = 0$, Eq. (12) reduces to the relation given by Eq. (10).

Using Eq. (12) the integral distribution function may be calculated

$$I_{\mathrm{Head}}(T) = \int_{\tau_0}^{T} W_{\mathrm{Head}}(T')\,\mathrm{d}T' = \int_{\tau_0}^{T} \frac{\mathrm{d}\tau'}{\mathrm{d}T'} \frac{x_A W_A(\tau')}{1 - x_i^{\mathrm{Az}}(\tau')}\,\mathrm{d}T' \qquad (13)$$

or

$$I_{\mathrm{Head}}(T) = \int_{\tau_0}^{\tau} \frac{x_A W_A(\tau')}{1 - x_i^{\mathrm{Az}}(\tau')}\,\mathrm{d}\tau' \qquad (14)$$

Here, the upper limit τ of the integral is the τ value related to the head temperature T according to the function $T = \vartheta_i(\tau)$, i.e. $t = \theta_i(T)$ where ϑ_i indicates the function inverse to $T = \vartheta_i(\tau)$.

The mole fraction of the discrete component i which, because of azeotropic effects, distils with the aliphatics is x_i^{Az}. Thus, the mole fraction (with respect to the total feed) of the component i distilling up to the head temperature T is given by

$$I_{i,\mathrm{Head}}(T) = \int_{\tau_0}^{\tau} \frac{x_i^{\mathrm{Az}}(\tau')}{1 - x_i^{\mathrm{Az}}(\tau')} x_A W_A(\tau')\,\mathrm{d}\tau' \qquad (15)$$

The head temperature of the upper limit of the distillation of azeotropes is designated as T^{E}. It is related to the boiling temperature τ^{E} of the corresponding aliphatic by $\tau^{\mathrm{E}} = \theta_i(T^{\mathrm{E}})$. in dependence on the mole fraction x_i of the discrete component i in the feed there are two possibilities for reaching this limit:

- total consumption of the discrete component (cases (a), (b)); T_{E} results from

$$x_i - I_{i,\mathrm{Head}}(T^{\mathrm{E}}) = 0;\ \text{i.e.}\ x_i - \int_{\tau_0}^{\tau^{\mathrm{E}}} \frac{x_i^{\mathrm{Az}}(\tau')}{1 - x_i^{\mathrm{Az}}(\tau')} x_A W_A(\tau')\,\mathrm{d}\tau' = 0 \qquad (16)$$

- total consumption of the aliphatics able to form azeotropes (case (c)) resulting in

$$T^{\mathrm{E}} = \tau_i; \quad \tau^{\mathrm{E}} = \theta_i(T^{\mathrm{E}}) = \theta_i(\tau_i) = \tau^{\mathrm{B}} + \Delta\tau \qquad (17)$$

4.3. Distillation of the pure discrete component i: $T = T_E = \tau_i$

This range occurs only if there is an excess amount of the discrete component i in the feed (case (c)), i.e. all aliphatics able to form azeotropes are consumed (Eq. (17)) and an amount of the discrete component remains. Then this residue distils as pure substance at its boiling temperature $T = \tau_i$. Its mole fraction (with respect to the feed) is given by

$$x_i^{\mathrm{res}} = x_i - I_{i,\mathrm{Head}}(\tau_i) > 0 \qquad (18)$$

The integral distribution function I increases by this amount at $T = \tau_i$.

4.4. Gap / jump

After the distillation of the azeotropes (and perhaps of the excess of the discrete component) there are in the mixture no components present able to distil, because the aliphatics usually boiling in this range were already removed at lower temperatures $T = \vartheta_i < \tau$. Therefore, a gap in $W_{\text{Head}}(T)$ occurs, where no substance leaves the column:

$$W_{\text{Head}}(T) = 0 \tag{19}$$

Eq. (19) may be considered as a special case of Eq. (12), since an increase of the head temperature T does not correspond to an increase of the boiling temperature τ of the pure aliphatic species, i.e. $\mathrm{d}\tau/\mathrm{d}T = 0$. According to Eq. (13) there is a jump of I_{Head} in this range

$$I_{\text{Head}}(T) = \text{const.} = I_{\text{Head}}(T^{\text{E}}) = I_{\text{Head}}(\tau^{\text{E}}) \tag{20}$$

The head temperature increases abruptly from T_{E} to τ^{E}. The constant value of Eq. (20) is given by

$$I_{\text{Head}}(T^{\text{E}}) = x_{\text{A}} I_{\text{A}}(\tau^{\text{E}}) + x_i; \quad \tau^{\text{E}} = \theta_i(T^{\text{E}}) \tag{21}$$

This relation is valid in all three cases (a), (b) and (c), expressing that at $T = T_{\text{E}}$ all aliphatics boiling up to τ^{E} and the total amount of the discrete component have left the column.

4.5. Distillation of aliphatics 2: $\tau^E \leq T \leq \tau^0$

After the temperature jump an azeotropic influence on the distillation behaviour does no longer exist. Hence, the aliphatic species distil as usually, resulting in

$$T = \tau;\ x_i^{\text{Az}}(\tau) = 0;\ W_{\text{Head}}(T) = x_{\text{A}} W_{\text{A}}(\tau);\ I_{\text{Head}}(T) = x_{\text{A}} I_{\text{A}}(\tau) + x_i \tag{22}$$

The treatment given here is based on the quantities x, W and I related to the amounts of substances. Quantities applied in practice (e.g. TBP curve) usually are related to mass or volume. Nevertheless, the equations previously derived do not loose their validity. The quantities x, W and I then mean the corresponding quantities related to mass or volume.

5. Distillation with several discrete components able to form azeotropes

In the following the method previously described is applied to the formation of azeotropes with several discrete components which

- form binary minimum azeotropes with the aliphatic species,
- but to do not form azeotropes between themselves.

This case occurs if all discrete components have a similar chemical structure, e.g. if all of them are aromatics or alcohols. In Fig. 5(a)–(e) possible $T(\tau)$ diagrams are presented for systems consisting of an aliphatic ensemble and of two discrete components 1,2. The aliphatic species either distil as pure substances (diagonal $T = \tau$) or they can distil as azeotropes with the discrete component 1 ($T = \vartheta_1(T)$) or with the discrete component 2 ($T = \vartheta_2(\tau)$). Generally, the lowest curve (i.e. that with the lowest T values) will be realized. The relative amounts of the species have also to be accounted for.

- Fig. 5(a): The two intervals $\Delta\tau_1$ and $\Delta\tau_2$ of possible formation of azeotropes are separated from each other. The distillation behaviour as described in Section 4 will happen twice where all three cases (a)–(c) are possible for each of the discrete components 1 and 2 depending on their relative amounts.

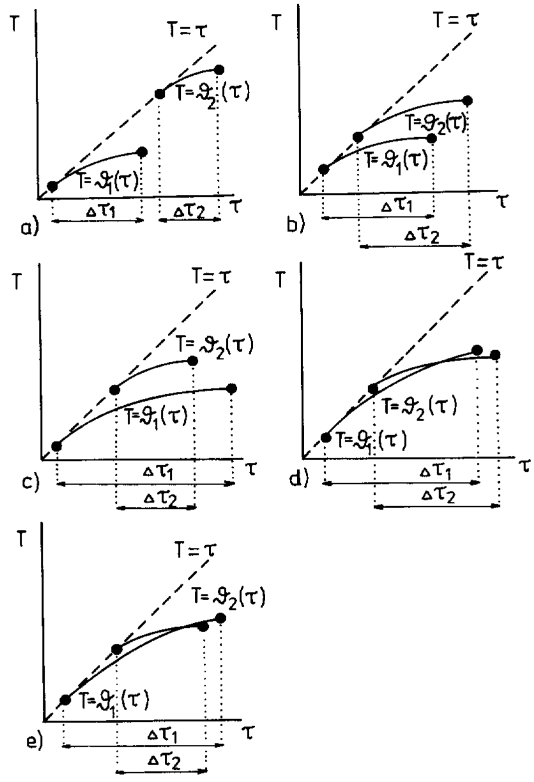

Fig. 5. Head temperature T vs. boiling temperature τ of the aliphatic species in the case of two discrete components without (a)–(c) or with (d), (e) intersection of the curves $\vartheta_1(\tau)$ and $\vartheta_2(\tau)$.

- Fig. 5(b): The distillation of the pure aliphatics is followed by the interval $\Delta\tau_1$ corresponding to the azeotropic distillation with the discrete component 1. The further distillation behaviour depends on the relative amount of this component:
  - If there is only a very small amount of the discrete component 1 its consumption is perfect before τ reaches the interval $\Delta\tau_2$. Then after the end of the azeotropic distillation with component 1 again pure aliphatic species will distil followed by the azeotropic distillation with discrete component 2.
  - If there is a medium amount of the discrete component 1 then after the end of the azeotropic distillation with this component directly follows the azeotropic distillation with discrete component 2.
  - If the amount of the discrete component 1 is so large that it is not completely consumed by azeotropic distillation then after this azeotropic distillation the rest of component 1 distils as pure substance (case (c) in Section 4). Then the azeotropic distillation with the discrete component 2 follows.

Regarding the end of the azeotropic distillation with the discrete component 2 the considerations of Section 4 apply.

- Fig. 5(c): Here the curve $T = \vartheta_i(\tau)$ extends to larger τ values than the curve $T = \vartheta_2(\tau)$. Thus, for sufficiently large amounts of the discrete component 1, it will happen that this component is not consumed till all aliphatics belonging to the interval $\Delta\tau_2$ left the column. In this case there is no azeotropic distillation with the discrete component 2 and this component will distil as pure substance after the azeotropic distillation with the discrete component 1 (and possibly after the distillation of the rest of component 1 as pure substance).

- Fig. 5(d), (e): The curves $T = \vartheta_1(\tau)$ and $T = \vartheta_2(\tau)$ may also intersect. Two examples are shown here. Again the distillation behaviour may easily be predicted according to the principle of lowest curve accounting also for the relative amounts. Thus, also if the feed mixture contains an amount of component 1 sufficient for the azeotropic distillation with it up to the end of the curve $T = \vartheta_1(\tau)$, at the intersection point the azeotropic distillation with the discrete component 2 will begin according to the curve $T = \vartheta_2(\tau)$.

Intersection of the curves and $\vartheta_1(\tau)$ and $\vartheta_2(\tau)$ presumes a considerably different curvature of these curves being not very probable. Hence, usually only the cases of Fig. 5(a)–(c) will occur.

6. Experimental proof and discussion

6.1. *Mixtures with one discrete component able to form azeotropes*

For an experimental proof mixtures consisting of a heavy petroleum fraction being poor of aromatics (aromatic contents < 5 wt.%) and of an alcohol (ethanol, 1-propanol, 2-propanol) as discrete component were studied by TBP analysis. With aliphatics such alcohols form azeotropes possessing a minimum in boiling point temperature. Applying capillary gas chromatography the quantitative determination of the alcohols is no problem.

The TBP analysis (batch distillation) was performed using a Fischer-Spaltrohr column with 30 theoretical plates at a reflux ratio of 25:1 (controlling the efficiency by using the test mixture *n*-heptane/methyl cyclohexane). To characterize the mixture of aliphatics gas-chromatographically simulated distillation was applied [11].

To perform the calculations the functions needed, $\vartheta_i(\tau)$ and $x_i^{\mathrm{Az}}(\tau)$, are obtained by smoothing the known experimental data [10] of binary mixtures of an aliphatic component and an alcohol.

Fig. 6 shows the influence of the azeotropy for the mixtures above mentioned. The diagonal corresponds to the distillation of pure aliphatics. The non-linear part of the curve corresponds to the distillation of azeotropes. In the case presented the end of the distillation of azeotropes is caused by a complete consumption of the discrete component (case (b) of Fig. 4). Therefore, not all of the possible azeotropes appear in the curve.

In Fig. 7 the experimental TBP curve $I_{\mathrm{Head,m}}(T)$ is compared with the calculated one. The subscript m indicates that this quantity is related to mass fraction instead of mole fraction. On the whole the coincidence of calculated and experimental values is satisfactory. Only the temperature jump is calculated at larger values of $I_{\mathrm{Head,m}}$ than measured.

The comparison of the calculated and the experimental distribution (density) function $W_{\mathrm{Head,m}}(T)$ may be seen in Fig. 8(a)–(c). Fig. 8(a) shows the distribution (density) function if there would be no azeotropic effects. In this case $T = \tau$ would be valid. Fig. 8(b) presents the calculated function $W_{\mathrm{Head,m}}(T)$. The contribution of 1-propanol to the total distribution (density) function (black area) was calculated with the aid of the function $x_i^{\mathrm{Az}} = x_i^{\mathrm{Az}}(\tau)$. Finally, Fig. 8(c) shows the experimental distribution (density) function obtained by numerical differentiation of the experimental TBP curve

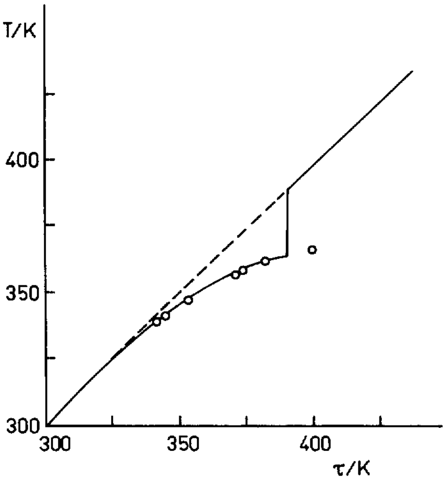

Fig. 6. Head temperature T vs. boiling temperature τ of the aliphatic species for a mixture consisting of a heavy petroleum fraction (88.5 wt.%) and 1-propanol (11–5 wt.%): ————, calculated on the basis of the method of this paper; - - -, fictitious curve disregarding azeotropic effects; ○, boiling temperatures of binary azeotropes of an aliphatic species and 1-propanol.

$I_{\mathrm{Head,m}}(T)$. To determine the contents of 1-propanol gas chromatography was applied. Both in the calculated curve and in the experimental one, the gap caused by azeotropy may be seen clearly. As in Fig. 7 the quantitative calculation of this gap in Fig. 8(b) and (c) is not perfect. Furthermore, one can see the absence of the small amount of the lowest boiling hydrocarbons in the experimental curve. This lack is caused by the limited efficiency of the column used.

Considering the formation of azeotropes with one discrete component the investigations result in the following conclusions:

1. Azeotropes cause considerable deviations of the TBP curve from the integral distribution function $I(\tau)$.
2. The method outlined above is suitable to estimate the influence of azeotropy.

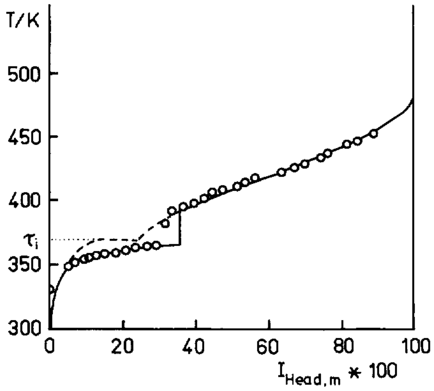

Fig. 7. TBP curve for a mixture consisting of a heavy petroleum fraction (88.5 wt.%) and 1-propanol (11.5 wt.%); ○, experimental points; ————, calculated curve; - - -, fictitious curve disregarding azeotropic effects.

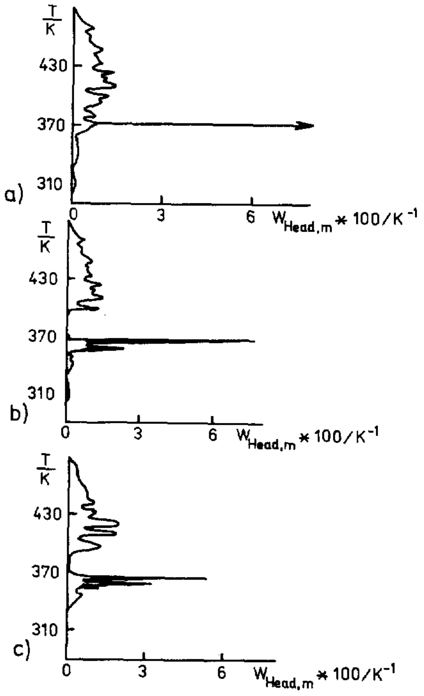

Fig. 8. Distribution (density) function $W_{\mathrm{Head,m}}(T)$ for a mixture consisting of 88.5 wt.% heavy petroleum fraction and 11.5 wt.% 1-propanol; the black area gives the fraction of the discrete component; the white area corresponds to the aliphatic ensemble. (a) Fictitious case disregarding azeotropy; (b) calculated according to the method of this paper, (c) experimental results.

3. Comparing calculation and experiment differences occur only in describing the gap/jump. However, model calculations show that these differences are caused by the unavoidable limitations of the efficiency of the column [12].

6.2. Mixtures with several discrete components able to form azeotropes

For the calculation again the formation of binary azeotropes with minimum boiling temperatures between the discrete components and the aliphatics is presumed.

Fig. 9 illustrates the azeotropic influence in a T–τ diagram for a mixture consisting of a heavy petroleum fraction and ethanol, 2-propanol and 1-propanol. For the composition chosen the distillation of azeotropes is finished in all three cases by the total consumption of the alcohols (corresponding to the case (b) of Fig. 4). At first, azeotropes with ethanol distil followed by those with 2-propanol and finally, azeotropes with 1-propanol distil. At the beginning and at the end distillation of pure aliphatic species occurs.

In Fig. 10 the experimental TBP curve $I_{\mathrm{Head,m}}(T)$ for this mixture is compared with the curve calculated as outlined above. There is a good coincidence of the calculated curve and the experimental one. Only, the temperature jumps are calculated at $I_{\mathrm{Head,m}}$ values somewhat too large.

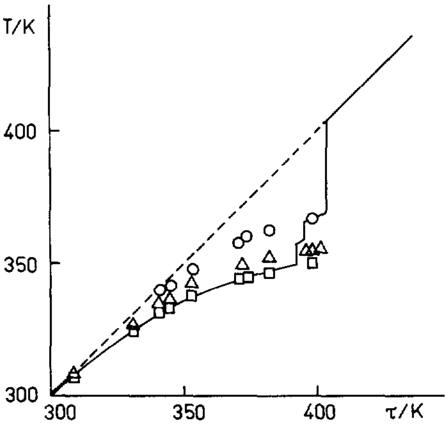

Fig. 9. Head temperature T vs. boiling temperature τ of the aliphatic species for a mixture consisting of a heavy petroleum fraction (70 wt.%) and of ethanol, 2-propanol, 1-propanol (in each case 10 wt.%): ———, calculated on the basis of the method of this paper; - - -, fictitious curve disregarding azeotropic effects; boiling temperatures of binary azeotropes of systems aliphatic/ethanol (□), aliphatic/2-propanol (△), aliphatic/1-propanol (○).

Fig. 11 compares the calculated and the experimental values of the contents of the alcohols in the fractions of the TBP distillation. In accordance to the considerations outlined above the sequence of the head products is: pure aliphatics, azeotropes with ethanol, azeotropes with 2-propanol, azeotropes with 1-propanol, and again pure aliphatics. The calculated curves presume correspondence of the alcohol contents in the fractions of the head product to the composition of the relevant binary azeotropes. Essentially, the coincidence of calculated and experimental results is satisfactory. Deviations occur near the temperature jump caused again by the limited efficiency of the column used. Due

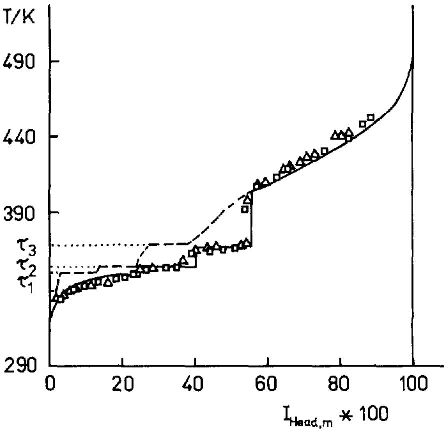

Fig. 10. TBP curve for a mixture consisting of a heavy petroleum fraction (70 wt.%) and ethanol ($i = 1$), 2-propanol ($i = 2$), 1-propanol ($i = 3$), (in each case 10 wt.%): □, △, experimental points of two independent measurements; ———, calculated curve based on the method of this paper; - - -, fictitious curve disregarding azeotropic effects.

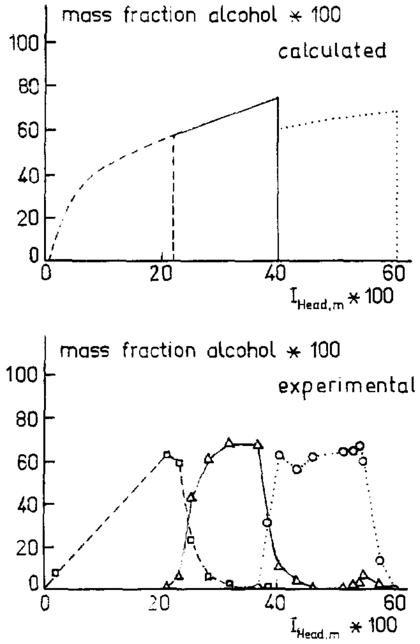

Fig. 11. Mass fractions of ethanol (□), 2-propanol (△) and 1-propanol (○) in the fractions of the TBP distillation for the mixture consisting of a heavy petroleum fraction (70 wt.%) and ethanol, 2-propanol, 1-propanol (in each case 10 wt.%).

to this limitation the regions of pure aliphatics and of the different azeotropes are not separated clearly from each other.

7. Conclusions

In petrol chemistry TBP distillation is one of the most commonly applied techniques to study the polydispersity of complex hydrocarbon mixtures. Since the forties, it is known that TBP analysis is influenced by azeotropic effects. Nevertheless until now either effects have been either neglected or insufficiently taken into account.

In this paper a method is developed permitting a quantitative treatment of the azeotropic influence. The method is based on continuous thermodynamics and is restricted to minimum azeotropes (with respect to the boiling temperature). The mixtures studied experimentally consist of an ensemble of many aliphatics and of some alcohols as discrete components.

In the regions corresponding to the formation of azeotropes all components distil below the boiling temperatures they possess as pure substances. The ends of these regions are marked by temperature jumps because the substances usually boiling in these ranges already left the column as azeotropes

8. List of symbols

A	$\Delta_{\mathrm{Vap}}S/R \approx \mathrm{const} = 10.3$
G^{E}	molar excess Gibbs energy
$I(\tau)$	integral distribution function

$I_{\mathrm{Head}}(T)$	TBP curve
$n(\tau)$	number of discrete components i obeying $\tau_i < \tau$
p	pressure
p^+	reference pressure, $p^+ = 101.325\,\mathrm{kPa}$
R	gas constant
$\Delta_{\mathrm{Vap}}S$	molar entropy of vaporization
T	head temperature of the column
$W(\tau)$	distribution (density) function
$W_{\mathrm{Head}}(T)$	distribution (density) function, related to $I_{\mathrm{Head}}(T)$
x	mole fraction

8.1. Greek letters

γ	activity coefficient in the liquid phase
$\Delta\tau_i$	interval of possible formation of azeotropes with the discrete component i
δ	Dirac's function
ϑ	azeotropic temperature
θ	inverse function to $\vartheta(\tau)$
τ	boiling temperature of a pure species
τ_0, τ^0	beginning and end of the boiling temperature interval of the continuously described species

8.2. Subscripts

A	aliphatics
i, j, k	discrete components
m	related to mass
0.5	related to $x_i = 0.5$

8.3. Superscripts

Az	azeotrope
B	beginning of the range of distillation of azeotropes
E	end of the range of distillation of azeotropes
*	pure substance

Acknowledgements

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Appendix A. Proof of Eqs. (8a) and (8b)

In the azeotropic point the following relations hold

$$p = \gamma_A(\tau, \vartheta_i, x_i^{Az}) p_A^*(\tau, \vartheta_i) \tag{A1}$$

$$p = \gamma_i(\tau, \vartheta_i, x_i^{Az}) p_i^*(\vartheta_i) \tag{A2}$$

leading to

$$\mathrm{d}\ln p = \mathrm{d}\ln \gamma_A(\tau, \vartheta_i, x_i^{Az}) + \mathrm{d}\ln p_A^*(\tau, \vartheta_i) \tag{A3}$$

$$\mathrm{d}\ln p = \mathrm{d}\ln \gamma_i(\tau, \vartheta_i, x_i^{Az}) + \mathrm{d}\ln p_i^*(\vartheta_i) \tag{A4}$$

The Gibbs–Duhem equation reads

$$(1 - x_i^{Az})\mathrm{d}\ln \gamma_A(\tau, \vartheta_i, x_i^{Az}) + x_i^{Az}\mathrm{d}\ln \gamma_i(\tau, \vartheta_i, x_i^{Az}) = 0 \tag{A5}$$

Hence (for physically sensible activity coefficient functions) Eq. (A3) reduces in the low temperature limit $\tau \to \tau^B$, $x_i^{Az} = 0$ at constant pressure to

$$0 = \mathrm{d}\ln p_A^*(\tau, \vartheta_i) = \frac{\partial \ln p_A^*}{\partial \tau}\mathrm{d}\tau + \frac{\partial \ln p_A^*}{\partial \vartheta_i}\mathrm{d}\vartheta_i; \quad \tau \to \tau_B \tag{A6}$$

resulting in

$$\lim_{\tau \to \tau B}\left(\frac{\partial \vartheta_i}{\partial \tau}\right) = -\frac{\lim_{\tau \to \tau^B} \partial \ln p_A^*/\partial \tau}{\lim_{\tau \to \tau^B} \partial \ln p_A^*/\partial \vartheta_i} \tag{A7}$$

To obtain the r.h.s. quantities $\ln p_A^*(\tau,\vartheta_i)$ is expanded into a Taylor series with respect to ϑ_i at $\vartheta_i = \tau$ reading (for physically sensible vapour pressure functions)

$$\ln(p_A^*/p^+) = (\vartheta_i - \tau)f(\tau) + \ldots \tag{A8}$$

since $p_A^*(\tau, \tau) = \mathrm{p}^+$. The function f is not needed in detail. For $\tau \to \tau_B$ one finds $\vartheta_i \to \tau$. Thus, Eq. (A8) leads to

$$\lim_{\tau \to \tau^B}\left(\frac{\partial \ln p_A^*}{\partial \vartheta_i}\right) = -\lim_{\tau \to \tau^B}\left(\frac{\ln p_A^*}{\partial \tau}\right) = f(\tau) \tag{A9}$$

Introducing Eq. (A9) into Eq. (A7), Eq. (8a)

$$\lim_{\tau \to \tau^B}\left(\frac{\partial \vartheta_i}{\partial \tau}\right) = 1 \tag{A10}$$

is verified.

To prove Eq. (8b) one can start with Eq. (A4) reducing with the help of Eq. (A5) in the high temperature limit $\tau \to \tau^B + \Delta\tau$; $x_i^{Az} \to 1$ at constant pressure to

$$\mathrm{d}\ln p_i^*(\vartheta_i) = 0; \quad \tau \to \tau^B + \Delta\tau \tag{A11}$$

Thus, in this case one may write

$$0 = \frac{\partial \ln p_i^*}{\partial \tau} = \frac{\partial \ln p_i^*}{\partial \vartheta_i}\frac{\partial \vartheta_i}{\partial \tau}; \quad \tau \to \tau^B + \Delta\tau \tag{A12}$$

Since the first of the two factors on the r.h.s. generally differs from zero, Eq. (A12) results in Eq. (8b)

$$\lim_{\tau\to\tau^{\mathrm{B}}+\Delta\tau}\left(\frac{\partial\vartheta_i}{\partial\tau}\right)=0 \tag{A13}$$

Appendix B. Approximation relations for the functions $\vartheta_i(\tau)$ and $x_i^{\mathrm{Az}}(\tau)$

The following derivations serve to give an idea of the functions $\vartheta_i(\tau)$ and $x_i^{\mathrm{Az}}(\tau)$. Binary azeotropes are considered, where one component is a species of a practically continuous ensemble A (e.g. aliphatics) and the other is a discrete component i. Then the boiling temperatures ϑ_i as well as the mole fractions x_i^{Az} of the azeotropic mixtures with this component i show a typical dependence on the boiling temperatures τ of the pure A species. The relations describing the azeotropic point are Eqs. (A1) and (A2).

Combining the integrated Clausius–Clapeyron equation and Trouton's rule the vapour pressures of the pure components may be expressed by

$$p_{\mathrm{A}}^{*}(\tau,\vartheta_i)=p^{+}\exp[A(1-\tau/\vartheta_i)] \tag{B1}$$

$$p_i^{*}(\vartheta_i)=p^{+}\exp[A(1-\tau_i/\vartheta_i)] \tag{B2}$$

Here, p^{+} denotes the reference pressure ($p^{+}=101.325\,\mathrm{kPa}$) and $A=\Delta_{\mathrm{Vap}}S/R\approx\mathrm{const}=10.3$. Introduction of Eqs. (B1) and (B2) into Eqs. (A1) and (A2) leads with $p=p^{+}$ to

$$0=\ln\gamma_{\mathrm{A}}(\tau,\vartheta_i,x_i^{\mathrm{Az}})+A(1-\tau/\vartheta_i) \tag{B3}$$

$$0=\ln\gamma_i(\tau,\vartheta_i,x_i^{\mathrm{Az}})+A(1-\tau_i/\vartheta_i) \tag{B4}$$

The difference of the two equations results in

$$A(\tau-\tau_i)/\vartheta_i=-\ln\gamma_i(\tau,\vartheta_i,x_i^{\mathrm{Az}})+\ln\gamma_{\mathrm{A}}(\tau,\vartheta_i,x_i^{\mathrm{Az}}) \tag{B5}$$

The activity coefficients are related to the molar excess Gibbs energy G^{E} by

$$R\vartheta_i\ln\gamma_{\mathrm{A}}(\tau,\vartheta_i,x_i^{\mathrm{Az}})=\left[G^{\mathrm{E}}-x_i\frac{\partial G^{\mathrm{E}}}{\partial x_i}\right]^{\mathrm{Az}} \tag{B6}$$

$$R\vartheta_i\ln\gamma_i(\tau,\vartheta_i,x_i^{\mathrm{Az}})=\left[G^{\mathrm{E}}+(1-x_i)\frac{\partial G^{\mathrm{E}}}{\partial x_i}\right]^{\mathrm{Az}} \tag{B7}$$

The superscript Az indicates that all quantities within the brackets refer to the azeotropic point.

Using a simple relation for G^{E} the functions $\vartheta_i(\tau)$ and $x_i^{\mathrm{Az}}(\tau)$ are given by closed expressions, e.g. with Porter's assumption

$$G^{\mathrm{E}}=4G_{0.5}^{\mathrm{E}}(\tau)x_i(1-x_i) \tag{B8}$$

and using Eqs. (B5), (B6) and (B7) the function $x_i^{\mathrm{Az}}(\tau)$ reads

$$x_i^{\mathrm{Az}}=\frac{1}{2}\left[1+\frac{RA}{4G_{0.5}^{\mathrm{E}}(\tau)}(\tau-\tau_i)\right] \tag{B9}$$

With the aid of Eqs. (B3), (B6) and (B8) one obtains

$$\vartheta_i = \tau - \frac{4G^{\mathrm{E}}_{0.5}(\tau)}{RA}\left(x_i^{\mathrm{Az}}\right)^2 \tag{B10}$$

Combining the last both equations the function $\vartheta_i(\tau)$ reads

$$\vartheta_i = \tau - \frac{G^{\mathrm{E}}_{0.5}(\tau)}{RA}\left[1 + \frac{RA}{4G^{\mathrm{E}}_{0.5}(\tau)}(\tau - \tau_i)\right]^2 \tag{B11}$$

An improved treatment is possible using refined expressions for the excess Gibbs energy.

Considering the low temperature limit: $\tau \rightarrow \tau^{\mathrm{B}}$, $\vartheta \rightarrow \tau^{\mathrm{B}}$, $x_i^{\mathrm{Az}} \rightarrow 0$ and the high temperature limit: $\tau \rightarrow \tau^{\mathrm{B}} + \Delta\tau$, $\vartheta \rightarrow \tau_{\mathrm{i}}$, $x_i^{\mathrm{Az}} \rightarrow 1$ with the aid of Eqs. (B9) and (B10) one sees the validity of Eqs. (8a) and (8b).

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