APPLICATION OF THE MAXIMUM LIKELIHOOD METHOD TO THE PARAMETER EVALUATION IN HETEROGENEOUS SYSTEMS

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Received January 10, 1989
Accepted March 13, 1989

Dedicated to late Academician Eduard Hála

The maximum likelihood method was applied to the calculation of parameters of a thermodynamic model in a heterogeneous binary system. The calculation program was tested on using the tetrahydrofuran–water system.

When correlating the mutual solubility of liquids, three procedures are in principle used. In the first case, the values of composition x_1 and z_1 are directly correlated as a function of temperature – see, e.g., Tsonopoulos and co-workers[1,2]. In the second case, the relations are applied which stem from the new knowledge of the behaviour at the critical point and in its vicinity – see, e.g., Vnuk[3]. Most often is used, however, the third (thermodynamic) procedure in which one starts from the equation for the excess Gibbs energy $G^E(T, x_1)$ or from equations of state.

In this work we apply the thermodynamic procedure and parameters $\{b_j\}$ in the relation for the excess Gibbs energy are determined above all on the basis of data on mutual solubility (thereinafter LLE data). The advantage of this approach is above all the fact that the correlation obtained is not being an end in itself or it has not only the interpolation purpose but is utilizable also for the prediction of behaviour of multicomponent systems. This procedure has been used by a number of authors[4–10].

When determining the parameters, the classical least-squares method has recently been replaced by the maximum likelihood method[11–13] (thereinafter ML method) which takes fully into account all the experimental facts and is applied also in this work.

THEORETICAL

Correlation Relation Used

To describe the phase equilibrium, the superposition of the Wilson[14] and Redlich–Kister[15] (thereinafter RK) equations which has, for a binary system, the form[16]

$$G^E/(RT) = Q_{\text{Wilson}} + Q_{\text{RK}}\,, \tag{1}$$

$$Q_{\text{Wilson}} = -x_1 \ln(x_1 + A_{12}x_2) - x_2 \ln(x_2 + A_{21}x_1)\,, \tag{2}$$

$$A_{ij} = (V_j^L/V_i^L) \exp[-C_{ij}(T)]\,, \tag{3}$$

$$C_{12} = b_1/T^* + b_2 + b_3T^*\,, \tag{4a}$$

$$C_{21} = b_4/T^* + b_5 + b_6T^*\,, \tag{4b}$$

$$Q_{\text{RK}} = x_1x_2 \sum_j B_j(x_1 - x_2)^{j-1}\,, \tag{5}$$

$$B_j = b_{4+3j} + b_{5+3j}/T^* + b_{6+3j}/T^{*2}\,, \quad j = 1, 2, \ldots \tag{6}$$

was used in this work. For the numerical reasons it is suitable lest the orders of calculated parameters $\{b_{ij}\}$ should differ significantly. For this reason the transformation of temperature $T^* = T/300$ is chosen. In the calculation program it is possible to choose the set of parameters $\{b_j\}$ considered. If, e.g., the set of indices (1, 2, 4, 5, 7, 8, 10) is considered, then parameters b_1, b_2, b_4, b_5 in the Wilson equation, parameters b_7 and b_8 at the first term of the RK equation, and the only parameter b_{10} at the second term of the RK equation were chosen for the description of phase equilibrium of the system. The values of all the other parameters are in this case zero (in a general case they are equal to the constants given in advance).

The superposition of the Wilson and RK equations was chosen because this combination had proved formerly to be useful when correlating the LLE data of binary systems where other correlations had often failed[10]. The modified Wilson equation (the Wilson equation with the first term of the RK equation) used formerly, however, had predicted frequently higher activity coefficients in the homogeneous liquid phase. To restrain this effect, a greater number of concentration terms was considered in the RK equation.

Calculation Procedure

To calculate parameters $\{b_j\}$ in correlation equation (*1*), the objective function was used

$$F_{\text{ML}} = F_{\text{LLE}} + F_{\text{VLE}}\,, \tag{7}$$

where

$$F_{\mathrm{LLE}} = \sum_{n(\mathrm{LLE})} \left\{ \left(\frac{x_{1\mathrm{L}}^{\mathrm{e}} - \hat{x}_{1\mathrm{L}}}{\sigma_{x_{1\mathrm{L}}}} \right)^2 + \left(\frac{z_1^{\mathrm{e}} - \hat{z}_1}{\sigma_{z_1}} \right)^2 + \left(\frac{T_{\mathrm{L}}^{\mathrm{e}} - \hat{T}_{\mathrm{L}}}{\sigma_{T_{\mathrm{L}}}} \right)^2 \right\} + \\ + \left(\frac{x_{1\mathrm{c}}^{\mathrm{e}} - \hat{x}_{1\mathrm{c}}}{\sigma_{x_{1\mathrm{c}}}} \right)^2 + \left(\frac{T_{\mathrm{c}}^{\mathrm{e}} - \hat{T}_{\mathrm{c}}}{\sigma_{T_{\mathrm{c}}}} \right)^2, \tag{8a}$$

$$F_{\mathrm{VLE}} = \sum_{n(\mathrm{VLE})} \left\{ \left(\frac{x_{1\mathrm{V}}^{\mathrm{e}} - \hat{x}_{1\mathrm{V}}}{\sigma_{x_{1\mathrm{V}}}} \right)^2 + \left(\frac{y_1^{\mathrm{e}} - \hat{y}_1}{\sigma_{y_1}} \right)^2 + \left(\frac{T_{\mathrm{V}}^{\mathrm{e}} - \hat{T}_{\mathrm{V}}}{\sigma_{T_{\mathrm{V}}}} \right)^2 + \left(\frac{p^{\mathrm{e}} - \hat{p}}{\sigma_{\mathrm{p}}} \right)^2 \right\}. \tag{8b}$$

F_{LLE} is the part of the objective function which is related to the LLE data and which requires as good as possible agreement in the measured data on composition of coexisting phases, temperature T_{L}, and critical point determined by parameters $x_{1\mathrm{c}}$, T_{c} (of course, as far as it was specified in the system considered). F_{VLE} is the part of the objective function which is related to the VLE data and which is identical with the objective function used by other authors[11–13]. It is evident that the F_{VLE} part can be included into the calculations just in the case that the data on vapour–liquid equilibrium are known.

By utilizing the choice of suitable values of standard deviations $\sigma_{x_{1\mathrm{L}}}$, σ_{z_1} and $\sigma_{T_{\mathrm{L}}}$ (different for each phase and dependent on temperature), it is possible to apply, without complications, even the data determined by the turbidity method (i.e., indirect data). In such a case we proceeded so that for a given composition, e.g., $x_{1\mathrm{L}}^{\mathrm{e}}$ and temperature $T_{\mathrm{L}}^{\mathrm{e}}$ (which the values of $\sigma_{x_{1\mathrm{L}}}$, $\sigma_{T_{\mathrm{L}}}$ correspond to), the equilibrium composition z_1^{e} was determined from an auxiliary diagram in which the results of all measurements were drawn. Considering that composition z_1^{e} was not determined by direct experiment but read from the diagram, the corresponding value of σ_{z_1} is proportionately higher (unless this point were to be included into the calculation at all, then we would choose $\sigma_{z_1} \gg 1$). In case of the indirect VLE data (usually the p–x_1 data at constant temperature), it is possible to use the data on vapour phase compositions given by Gmehling and co-workers[17] and a proportionately higher value of σ_{y_1}.

The set of parameters $\{b_j\}$, which minimizes the objective function F_{ML}, was determined in the following way: *1*) Let us choose the initial approximation $\{b_j^0\}$; the choice of this first approximation will be discussed below. *2*) For the given set of parameters, the nearest calculated point (e.g. $(\hat{x}_{1\mathrm{L}}, \hat{z}_1, \hat{T}_{\mathrm{L}})$ or $(\hat{x}_{1\mathrm{V}}, \hat{y}_1, \hat{T}_{\mathrm{V}}, \hat{p})$) is determined for each experimental point (e.g. $(x_{1\mathrm{L}}^{\mathrm{e}}, z_1^{\mathrm{e}}, T_{\mathrm{L}}^{\mathrm{e}})$ or $(x_{1\mathrm{V}}^{\mathrm{e}}, y_1^{\mathrm{e}}, T_{\mathrm{V}}^{\mathrm{e}}, p^{\mathrm{e}})$), and the critical point is calculated (if it is included into the calculation). *3*) The increments of parameters $\{\Delta b_j\}$ are determined so that the relations

$$\hat{x}_{1\mathrm{L}}^{\mathrm{new}} = \hat{x}_{1\mathrm{L}}^{\mathrm{old}} + \sum_j (\partial \hat{x}_{1\mathrm{L}} / \partial b_j)\, \Delta b_i\,,$$

$$\hat{z}_1^{\text{new}} = \hat{z}_1^{\text{old}} + \sum_j (\partial \hat{z}_1 / \partial b_j)\, \Delta b_j\,, \tag{9}$$

$$\vdots$$

are inserted into relations (*7*) and (*8*), and, on using the classical least-squares method, the optimum values of increments $\{\Delta b_j\}$ are assessed (see relations (*27*)). The value of relaxation (reduction) parameter η, where $\eta \in (0, 1\rangle$,

$$b_j^{\text{new}} = b_j^{\text{old}} + \eta\, \Delta b_j\,, \quad j = 1, 2, \ldots, M \tag{10}$$

is determined to hold $F_{\text{ML}}(\boldsymbol{b}^{\text{new}}) < F_{\text{ML}}(\boldsymbol{b}^{\text{old}})$. The validity of the inequality is tested first for $\eta = 1$. If it does not hold, then $\eta = 1/2$, or if need be, $1/4$, $1/8$, etc. *4*) If $\eta = 1$ and simultaneously

$$(F_{\text{ML}}^{\text{old}} - F_{\text{ML}}^{\text{new}})/F_{\text{ML}}^{\text{old}} < \varepsilon\,, \tag{11}$$

where ε, $0 < \varepsilon \ll 1$, is a "sufficiently" small number chosen in advance ($\varepsilon = 0{\cdot}001$ was chosen), then the calculation is finished. In the opposite case we return to point *2*), and the calculation cycle is repeated.

As it is evident from the above-mentioned, the main points of the calculation are the determination of the nearest points and the calculation of derivatives of single variables with respect to the parameters. To these problems, two following subchapters are devoted.

The Nearest Point Calculation

LLE. Let us denote, by symbol Φ, the function

$$\Phi = (x_1^{\text{e}} - \hat{x}_1)^2/\sigma_{\text{x}}^2 + (z_1^{\text{e}} - \hat{z}_1)^2/\sigma_{\text{z}}^2 + (T^{\text{e}} - \hat{T})^2/\sigma_{\text{T}}^2\,, \tag{12}$$

where, for the sake of simplicity of record, the unsubstantial subscripts are omitted. The minimum of function Φ was determined for the given set of parameters $\{b_j\}$ by the following way: Function Φ is considered to be a function of temperature T only, i.e., $\Phi = \Phi(\hat{T}, \hat{x}_1(\hat{T}), \hat{z}(\hat{T}))$. For each temperature chosen, the values of composition of coexisting phases $\hat{x}_1$ and $\hat{z}_1$ were determined from the equilibrium conditions

$$\ln \hat{x}_1 + \ln \bar{\gamma}_1 = \ln \hat{z}_1 + \ln \tilde{\gamma}_1\,, \tag{13a}$$

$$\ln \hat{x}_2 + \ln \bar{\gamma}_2 = \ln \hat{z}_2 + \ln \tilde{\gamma}_2\,, \tag{13b}$$

where $\bar{\gamma}_i$ and $\tilde{\gamma}_i$ is the value of activity coefficient of the i-th component at point (T, x_1) and (T, z_1), respectively. The minimum of function Φ is determined from the

equation $\Phi' = \mathrm{d}\Phi/\mathrm{d}T = 0$, i.e.

$$\frac{\hat{x}_1 - x_1^e}{\sigma_x^2}\frac{\mathrm{d}\hat{x}_1}{\mathrm{d}T} + \frac{\hat{z}_1 - z_1^e}{\sigma_z^2}\frac{\mathrm{d}\hat{z}_1}{\mathrm{d}T} + \frac{\hat{T} - T^e}{\sigma_T^2} = 0\,, \tag{14}$$

the values of derivatives occurring in Eq. (*14*) being determined by differentiating the left- and right-hand sides of Eqs (*13*) with respect to temperature

$$\left(\frac{1}{\hat{x}_1} + \frac{\partial \ln \bar{\gamma}_1}{\partial x_1}\right)\frac{\mathrm{d}\hat{x}_1}{\mathrm{d}T} - \left(\frac{1}{\hat{z}_1} + \frac{\partial \ln \bar{\gamma}_1}{\partial x_1}\right)\frac{\mathrm{d}\hat{z}_1}{\mathrm{d}T} = \frac{\partial \ln \bar{\gamma}_1}{\partial T} - \frac{\partial \ln \bar{\gamma}_1}{\partial T}\,, \tag{15a}$$

$$\left(-\frac{1}{\hat{x}_2} + \frac{\partial \ln \bar{\gamma}_2}{\partial x_1}\right)\frac{\mathrm{d}\hat{x}_1}{\mathrm{d}T} + \left(-\frac{1}{\hat{z}_2} + \frac{\partial \ln \bar{\gamma}_2}{\partial x_1}\right)\frac{\mathrm{d}\hat{z}_1}{\mathrm{d}T} = \frac{\partial \ln \bar{\gamma}_2}{\partial T} - \frac{\partial \ln \bar{\gamma}_2}{\partial T}\,. \tag{15b}$$

As an initial approximation of temperature when solving Eq. (*14*), the experimental value of temperature was chosen in the first calculation cycle (i.e., for $\boldsymbol{b} = \boldsymbol{b}^0$), in each next calculation cycle then the value of the nearest point determined in the preceding calculation cycle. When solving Eq. (*14*), the Newton method was largely applied whose iteration prescription can be expressed in terms of function Φ in the form

$$T^{\mathrm{new}} = T^{\mathrm{old}} - \eta\Phi'(T^{\mathrm{old}})/\Phi''(T^{\mathrm{old}})\,, \tag{16}$$

where the relaxation (reduction) parameter η, $0 < \eta \leqq 1$, was chosen in the initial steps of the iteration process so that the absolute value of increment of temperature should not exceed the value of 0·2 K. Only in case of $\Phi'' < 0$ (unsuitable first approximation of temperature; very rare case), the gradient method $\Delta T = -\eta\Phi'(T^{\mathrm{old}})$ was applied, where parameter η, $\eta > 0$, was chosen so that $|\Delta T| = 0{\cdot}1$ K. To calculate the second derivative $\Phi''(T)$, it is necessary to know the values of second derivatives $\mathrm{d}^2\hat{x}_1/\mathrm{d}T^2$ and $\mathrm{d}^2\hat{z}_1/\mathrm{d}T^2$. These values can be easily obtained by the repeated differentiation of the left- and right-hand sides of system of equations (*15*) with respect to temperature. It is advisable to take notice that the coefficient of matrix of the Newton method for the solution of system of equation (*13*), the coefficients of matrix of system of equations (*15*) as well as the coefficients of matrix of system of equations for calculating the above-mentioned second derivatives are identical, i.e., the said systems of equations differ only in the right-hand sides. This fact accelerates very much the calculation procedure.

The basic assumption of success of the proposed procedure is a safe and sufficiently rapid calculation of the composition of coexisting phases $\hat{x}_1$ and $\hat{z}_1$ (i.e., the solution of system of equations (*13*)) for the given value of temperature. The Newton

method with two independent values of relaxation (reduction) parameters[18], η and μ, $0 < \eta, \mu \leqq 1$ was used

$$\hat{x}_1^{\text{new}} = \hat{x}_1^{\text{old}} + \eta\, \Delta x\,, \tag{17a}$$

$$\hat{z}_1^{\text{new}} = \hat{z}_1^{\text{old}} + \mu\, \Delta z\,, \tag{17b}$$

where Δx and Δz are the increments determined by the Newton method. The values of η and μ are chosen so that the new approximations of compositions of coexisting phases should not lie in the labile region and the absolute values of increments should not ecseed the value of 0·01. As the first approximation of the solution of system of equations (*13*), the resulting values of preceding calculations or the experimental values in the first calculation cycle are used. The calculated values of the LLE composition depend very sensibly on the values of parameters $\{b_j\}$ chosen. Therefore, it may happen in the initial calculation cycles that the experimental temperatures of some points (x_1^e, z_1^e, T^e) are higher or lower than the calculated upper or lower critical temperature, respectively. In such a case, system of equations (*13*) has no solution at $\hat{x}_1 \neq \hat{z}_1$ for $T = T^e$ (the iteration process converges to the trivial solution $\hat{x}_1 = \hat{z}_1$), and the experimental points said are not considered in the given calculation cycle. In next calculation cycles when still better and better agreement occurs between the experimental and calculated coordinates of the critical point, these experimental points are gradually included into the calculation process.

VLE. Let us denote by symbol Ψ the function

$$\Psi = (x_1^e - \hat{x}_1)^2/\sigma_x^2 + (y_1^e - \hat{y}_1)^2/\sigma_y^2 + (T^e - \hat{T})^2/\sigma_T^2 + \\ + (p^e - \hat{p})^2/\sigma_p^2\,. \tag{18}$$

Function Ψ is a function of variables $\hat{x}_1$ and $\hat{T}$, i.e., $\Psi = \Psi(\hat{x}_1, \hat{T}, \hat{y}_1(\hat{x}_1, \hat{T}), \hat{p}(\hat{x}_1, \hat{T}))$ where for values $\hat{y}_1$ and $\hat{p}$ hold the equilibrium conditions

$$\hat{p} = \varphi_1 \hat{x}_1 \gamma_1 p_1^o + \varphi_2 \hat{x}_2 \gamma_2 p_2^o\,, \tag{19a}$$

$$\hat{y}_1 = \varphi_1 \hat{x}_1 \gamma_1 p_1^o / p\,. \tag{19b}$$

When determining the corrections for the nonideal behaviour of the vapour phase, it was assumed that the *P–V–T* behaviour of the gas mixture could be described by the virial expansion with two first terms. The minimum of function Ψ fulfils the system of two nonlinear equations

$$\frac{\hat{x}_1 - x_1^e}{\sigma_x^2} + \frac{\hat{y}_1 - y_1^e}{\sigma_y^2}\frac{\partial \hat{y}_1}{\partial x_1} + \frac{\hat{p} - p^e}{\sigma_p^2}\frac{\partial \hat{p}}{\partial x_1} = 0\,, \tag{20a}$$

$$\frac{\hat{y}_1 - y_1^e}{\sigma_y^2} \frac{\partial \hat{y}_1}{\partial T} + \frac{\hat{p} - p^e}{\sigma_p^2} \frac{\partial \hat{p}}{\partial T} + \frac{\hat{T} - T^e}{\sigma_T^2} = 0 . \tag{20b}$$

The system of equations (*20*) was solved by the Newton method analogously to the LLE case. The value of first derivatives $\partial y_1/\partial x_1$, $\partial y_1/\partial T$ as well as of second derivatives $\partial^2 y_1/\partial x_1^2$, $\partial^2 y/\partial x_1 \partial T$, $\partial^2 y_1/\partial T^2$ (and similarly for pressure p) were determined from Eqs (19) where it is suitable to consider the second equilibrium condition in logarithmic form. The values of derivatives of corrections φ_1 and φ_2 are considered to be zero, i.e., corrections φ_1 and φ_2 are considered in each calculation cycle constant determined from the values $(\hat{y}_1, \hat{T}, \hat{p})$ from the preceding calculation cycle (or from experimental values y_1^e, T^e, p^e in the first calculation cycle).

Calculation of Derivatives of Variables with Respect to Parameters

As the first possibility of calculating the values of derivatives given in Eqs (*9*), the method of numerical differentiation offers, i.e., e.g.

$$\partial \hat{x}_1/\partial b_k = [x_1(\mathbf{b} + h\mathbf{e}_k) - x_1(\mathbf{b} - h\mathbf{e}_k)]/2h , \quad k = 1, 2, \ldots, M , \tag{21}$$

where $\mathbf{e}_k$ is the vector whose k-th component equals unity and the other components are zero and symbol h denotes the step length of numerical differentiation. On the basis of the calculations carried out we assume that this method of determining the derivatives required is not numerically stable for the LLE data. The calculated LLE data are in some temperature and concentration regions very sensible to a change of the vector of parameters $\mathbf{b}$. Therefore it is necessary to choose the step length h very circumspectly, and with some systems it is not possible to choose a constant value of h in the whole temperature and concentration range. For the reasons said it is therefore more suitable to prefer the analytical method of the determination of the derivatives required which is more laborious but it is not only numerically stable but also less demanding from the point of view of time of computation.

LLE. The nearest point $(\hat{x}_1, \hat{z}_1, \hat{T})$ is determined by five equations involved in relations (*13*)–(*15*) in which variables $\hat{x}_1$, $\hat{z}_1$, $\hat{T}$, $\mathrm{d}\hat{x}_1/\mathrm{d}T$ and $\mathrm{d}\hat{z}_1/\mathrm{d}T$ occur as unknown quantities. Values of the variables are functions of single components of vector $\mathbf{b}$. If we differentiate the left- and right-hand sides of the equations mentioned above with respect to parameter b_k, we obtain a system of five linear equations for five unknowns $\partial \hat{x}_1/\partial b_k$, $\partial \hat{z}_1/\partial b_k$, $\partial \hat{T}/\partial b_k$, $\partial^2 \hat{x}_1/\partial T \partial b_k$, and $\partial^2 \hat{z}_1/\partial T \partial b_k$. Let us take a notice again that, e.g., the matrix of the system of equations resulting from the differentiation of the left- and right-hand sides of system of equations (*13*) with respect to parameter b_k has the same form as the matrix of system of equations (*15*). These facts dispatch very much the construction of the matrix of the above-mentioned

system of the five linear equations. When calculating the coefficients of this system of equations, it is suitable to use also the method of numerical differentiation. On differentiating the right-hand side of system of equations (*15*) with respect to parameter b_k, we meet with the expression

$$\left(\frac{\partial}{\partial b_k}\left(\frac{\partial \ln \bar{\gamma}_1}{\partial T}\right)\right)_{b_j \neq k} = \frac{\partial^2 \ln \bar{\gamma}_1}{\partial x_1 \partial T}\frac{\partial \hat{x}_1}{\partial b_k} + \frac{\partial^2 \ln \bar{\gamma}_1}{\partial T^2}\frac{\partial \hat{T}}{\partial b_k} + \left(\frac{\partial}{\partial b_k}\left(\frac{\partial \ln \bar{\gamma}_1}{\partial T}\right)\right)_{b_j \neq k, T, x_1}, \quad (22)$$

where it is emphasized under what conditions is to be differentiated. The last derivative on the right-hand side, whose non-nullity follows from the explicit dependence of activity coefficient on vector $\boldsymbol{b}$, is determined numerically according to a relation analogous to Eq. (*21*).

The necessity of calculating the unnecessary values of $\partial^2 \hat{x}_1/\partial T \partial b_k$ and $\partial^2 \hat{z}_1/\partial T \partial b_k$ follows from the fact that we did not used the Lagrange multipliers for the problem of finding the minimum of function (*12*) with boundary conditions (*13*). Both the above-mentioned derivatives replace these multipliers.

VLE. By differentiating the left- and right-hand sides of system of equations (*20*) with respect to parameter b_k, we obtain the system of two linear equations for two unknowns $\partial \hat{x}_1/\partial b_k$ and $\partial \hat{T}/\partial b_k$. In this rearrangement of system of equations (*20*) we use the relations

$$\hat{y}_1 = \hat{y}_1(\hat{x}_1(\boldsymbol{b}), \hat{T}(\boldsymbol{b}), \boldsymbol{b}), \quad (23a)$$

$$\hat{p} = \hat{p}(\hat{x}_1(\boldsymbol{b}), \hat{T}(\boldsymbol{b}), \boldsymbol{b}). \quad (23b)$$

The explicit dependence of variables $\hat{y}_1$ and $\hat{p}$ on vector $\boldsymbol{b}$ is involved in prescriptions for activity coefficients. From relation (*23*) then follows

$$\left(\frac{\partial \hat{y}_1}{\partial b_k}\right)_{b_j \neq k} = \frac{\partial \hat{y}_1}{\partial x_1}\frac{\partial \hat{x}_1}{\partial b_k} + \frac{\partial \hat{y}_1}{\partial T}\frac{\partial \hat{T}}{\partial b_k} + \left(\frac{\partial \hat{y}_1}{\partial b_k}\right)_{b_j \neq k, x_1, T}, \quad (24a)$$

$$\frac{\partial^2 \hat{y}_1}{\partial b_k \partial T} = \frac{\partial^2 \hat{y}_1}{\partial x_1 \partial T}\frac{\partial \hat{x}_1}{\partial b_k} + \frac{\partial^2 \hat{y}_1}{\partial T^2}\frac{\partial \hat{T}}{\partial b_k} + \left(\frac{\partial}{b_k}\left(\frac{\partial \hat{y}_1}{\partial T}\right)\right)_{x_1, T}, \quad (24b)$$

$$\frac{\partial^2 \hat{y}_1}{\partial b_k \partial x_1} = \frac{\partial^2 \hat{y}_1}{\partial x_1^2}\frac{\partial \hat{x}_1}{\partial b_k} + \frac{\partial^2 \hat{y}_1}{\partial T \partial x_1}\frac{\partial \hat{T}}{\partial b_k} + \left(\frac{\partial}{\partial b_k}\left(\frac{\partial \hat{y}_1}{\partial x_1}\right)\right)_{x_1, T}, \quad (24c)$$

and analogously for pressure p.

At the first and partly at the second and third relations it is emphasized under what conditions the differentiation is carried out. The derivatives which are given as the third term on the right-hand side of relations (*24*) were determined numerically according to the relation which is analogous to Eq. (*21*). After inserting the relations

(*24*) and the analogous relations for pressure into the system of equations (*20*), we obtain the above-mentioned system of two linear equations for two unknowns $\partial\hat{x}_1/\partial b_k$ and $\partial\hat{T}/\partial b_k$. Let us take a notice again that the matrix of this system is identical with the matrix of the system of the Newton method when solving the system of equations (*20*). The remaining two derivatives $\partial\hat{y}_1/\partial b_k$ and $\partial\hat{p}/\partial b_k$ are then determined from Eqs (*24*) and from the relations analogous to them.

Critical point. The critical point is determined, for a fixed set of parameters $\{b_j\}$, by solving the system of two equations for two unknowns $\hat{x}_{1c}$ and $\hat{T}_c$

$$G_{11}(\hat{x}_{1c}, \hat{T}_c, \mathbf{b}) = 0\,, \tag{25a}$$

$$G_{111}(\hat{x}_{1c}, \hat{T}_c, \mathbf{b}) = 0\,, \tag{25b}$$

where G_{11} and G_{111} is the second and third derivative of the Gibbs energy of mixing with respect to composition. The system of equations (*25*) was solved by the Newton method. The derivatives of critical values with respect to parameters were determined from the system of linear equations

$$G_{111}(\partial\hat{x}_{1c}/\partial b_k) + G_{11T}(\partial\hat{T}_c/\partial b_k) = -(\partial G_{11}/\partial b_k)_{x_1,T}\,, \tag{26a}$$

$$G_{1111}(\partial\hat{x}_{1c}/\partial b_k) + G_{111T}(\partial\hat{T}_c/\partial b_k) = -(\partial G_{111}/\partial b_k)_{x_1,T}\,, \tag{26b}$$

where G_{11T} and G_{111T} is the derivative of G_{11} and G_{111}, respectively, with respect to temperature. The values of derivatives on the right-hand side of system of equations (*26*) were assessed numerically. The matrix of system (*26*) and the matrix of the Newton method of solution of system (*25*) are identical.

Calculation of Increments $\{\Delta b_j\}$ and First Approximation of Parameters $\{b_j^0\}$

If we introduce, for the sake of simplification of the record, the new symbols in terms of the relations

$$\dot{x}_L^{(k)} = (\partial x_{1L}/\partial b_k)/\sigma_{x_{1L}}\,, \quad \Delta x_L = (x_{1L}^e - \hat{x}_{1L})/\sigma_{x_{1L}}\,, \tag{27a}$$

and analogously for the other variables, then from relations (*7*)–(*9*) follows that for the vector of increments $\Delta\mathbf{b}$ holds the system of linear equations $\mathbf{W}\Delta\mathbf{b} = \mathbf{d}$, where the coefficients of matrix $\mathbf{W}$ and of the vector on the right-hand side $\mathbf{d}$ can be determined from the relations

$$w_{jk} = \sum_{n(\mathrm{LLE})} [\dot{x}_L^{(k)}\dot{x}_L^{(j)} + \dot{z}^{(k)}\dot{z}^{(j)} + \dot{T}_L^{(k)}\dot{T}_L^{(j)}] + \dot{x}_c^{(k)}\dot{x}_c^{(j)} + \dot{T}_c^{(k)}\dot{T}_c^{(j)} + \\ + \sum_{n(\mathrm{VLE})} [\dot{x}_V^{(k)}\dot{x}_V^{(j)} + \dot{y}^{(k)}\dot{y}^{(j)} + \dot{T}_V^{(k)}\dot{T}_V^{(j)} + \dot{p}^{(k)}\dot{p}^{(j)}]\,, \tag{27b}$$

$$d_k = \sum_{n(\mathrm{LLE})} \left[\dot{x}_L^{(k)} \Delta x_L + \dot{z}^{(k)} \Delta z + \dot{T}_L^{(k)} \Delta T_L\right] + \dot{x}_c^{(k)} \Delta x_c + \dot{T}_c^{(k)} \Delta T_c + \\ + \sum_{n(\mathrm{VLE})} \left[\dot{x}_V^{(k)} \Delta x_V + \dot{y}^{(k)} \Delta y + \dot{T}_V^{(k)} \Delta T_V + \dot{p}^{(k)} \Delta p\right], \\ j, k = 1, 2, \ldots, M. \qquad (27c)$$

When determining new approximations $\{b_j^{\mathrm{new}}\}$, the values of increments can be reduced according to Eq. (*10*).

The use of the ML method, especially in case of the LLE data with critical region, is very sensible to the first approximation of parameters. To determine the first approximation, it is possible to employ the parameters calculated from the mutual solubility at two temperatures, or at one temperature and from the critical point, or from the parameters determined by the minimization of the activity differences at the compositions of coexisting phases found experimentally. For more detail see[19].

Application to the Tetrahydrofuran(1)–Water(2) System

This binary system (thereinafter we will use abbreviations THF and W) exhibits great deviations from the Raoult law[20–23] which along with an S-shaped H^E dependence on composition[22,24,25] at normal temperatures lead to the fact that the system at higher temperatures, as it has been predicted by Franks and Reid[26], separates into two liquid phases and forms a closed-loop curve of limited miscibility (Matouš and co-workers[23]) – see Fig. 1.

The employment of common correlation equations without special treatment (fixing up the G_{11} minimum or the critical point) for this system fails (Tassios[27], Matouš and co-workers[23], Novák and co-workers[19]). The very parameters of the

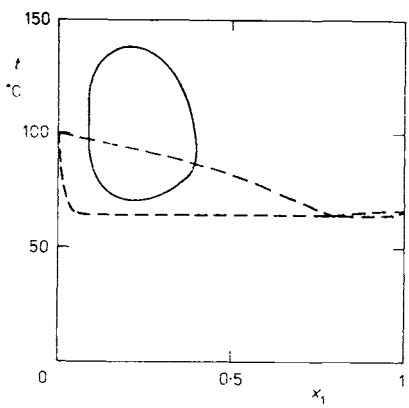

FIG. 1

Liquid–liquid equilibrium at $p > 100$ kPa (— · — · —) and vapour–liquid equilibrium at 101·32 kPa (— — —) in the THF(1)–W(2) system

RK equation obtained by Cigna and Sebastiani[20] from the VLE data at normal pressure corresponded to a heterogeneous system and led the authors[30] to the false conclusion that the system separated into two liquid phases already at the temperature corresponding to the normal presure even though this separation was not observed. The application of the modified Wilson equation[19] whose parameters were determined on the basis of LLE data was comparatively successful. A disadvantage of this equation was a less accurate description of VLE at low temperatures. For these reasons the modified Wilson equation was also extended by further terms of the RK equation.

When calculating the parameters of Eq. (*3*), the smoothed LLE data were used. In addition to the LLE data, the VLE were used, viz. by Shnitko and Kogan at normal pressure[21], Matouš and co-workers[23] at 70 and 50°C, and Signer and co-workers[22] at 25°C. To assess the corrections for the nonideal behaviour of the vapour phase, the virial equation with the second virial coefficient was employed. The second virial coefficient of the pure substances was calculated from the relation[13,28]

$$B_{ii} = \alpha_B + \beta_B/T \tag{28}$$

and the cross virial coefficient from the relation[29]

$$B_{ij} = \text{sign}\,(B_{ii})\,(B_{ii}B_{jj})^{1/2}\,. \tag{29}$$

Constants α_B, β_B as well as further quantities are summarized in Table I.

TABLE I

The pure substance constants used

Quantity	Tetrahydrofuran	Water
A^a	14·09365[b]	16·32931[c]
B	2 769·32	3 841·72
C	226·3	228·0
V_m^L, cm^3/mol[d]	81·75	18·07
α_B, cm^3/mol[e]	879	1 510
β_B, K . cm^3/mol[e]	$-6{\cdot}01 \,.\, 10^5$	$-7{\cdot}583 \,.\, 10^5$

[a] The Antoine equation was used in the form $\ln p^0/\text{kPa} = A - B/(t/°\text{C} + C)$; [b] see ref.[23]; [c] see ref.[30]; [d] see ref.[17]; [e] in case of water, constants α_B and β_B were determined from the data reported by Dymond and Smith[31] for the temperature interval 320–420 K, for THF only one experimental data point is available, and therefore the values estimated according to Pitzer and Curl[32] were used as well.

The estimate of the first approximation of parameters is with this system especially important because the system forms relatively small heterogeneous region (Fig. 1) which need not be cought at all with bad estimate of parameters. In this case we started from parameters C_{12}, C_{21} which were determined for the chosen value of B_1 on the basis of both critical points by solving conditions (*25*). In preceding calculations, good experience was obtained with these parameters:

LCST: $x_{1c} = 0{\cdot}220$, $T_c = 349{\cdot}95$ K, $C_{12} = 673{\cdot}1$ K, $C_{21} = 768{\cdot}9$ K, $B_1 = 0{\cdot}23$ (chosen);
UCST: $x_{1c} = 0{\cdot}1875$, $T_c = 410{\cdot}25$ K, $C_{12} = 834{\cdot}4$ K, $C_{21} = 567{\cdot}8$ K, $B_1 = 0{\cdot}80$ (chosen).

From these values, we easily determine the first approximation

$$C_{12} = 2{\cdot}675 - 263/T,$$
$$C_{21} = -3{\cdot}325 + 1\,936/T,$$
$$B_1 = 4{\cdot}108 - 1\,357/T.$$

The first approximations of further parameters were zero.

On using this initial approximation, a number of calculations were carried out in which different terms of the RK equation were considered and if need be even the use of quadratic terms in temperature dependence. After performing a good many calculations, the following set of parameters was chosen as the best

$$\begin{aligned} C_{12} &= 6{\cdot}7085 - 1\,687{\cdot}0/T, \\ C_{21} &= -0{\cdot}83984 + 1\,185{\cdot}5/T, \\ B_1 &= 1{\cdot}1675 - 348{\cdot}91/T, \\ B_3 &= -0{\cdot}28188 + 93{\cdot}133/T, \\ B_4 &= -0{\cdot}03497\,. \end{aligned} \tag{30}$$

This set yields the following deviations (exp − calc) in the critical point coordinates ($\sigma_{x_{1c}} = 0{\cdot}005$, $\sigma_{T_c} = 0{\cdot}2$ K were used in the calculations):

LCST: $\Delta x_{1c} = -0{\cdot}0037$, $\Delta T_c = 0{\cdot}63$ K; UCST: $\Delta x_{1c} = 0{\cdot}0077$, $\Delta T_c = -0{\cdot}36$ K.

The deviations in compositions of coexisting phases, temperature, and if need be in pressure are summarized in Table II. The used values of σ_{x_i}, σ_{y_i}, σ_{z_i}, and σ_T are as well given in this table. In case of pressure it was assumed that it was determined with a relative accuracy of 0·15%.

In Table III, the values of activity coefficients at 25°C are given calculated in terms of parameters (*30*) and those given by Shnitko and Kogan[20] and Signer and co-

-workers[21]. It can be seen that in most cases the calculated values lie between the experimental values of both the authors. The advantage of the set of parameters (*30*) compared to the modified Wilson equation consists among others in the fact that we succeded in decreasing the high value of the calculated limiting activity

TABLE II

The total deviations (exp — calc) in compositions of coexisting phases, temperature, and pressure in the single data sets used for calculating in the THF–W system

Type of data	No. of points	$\sigma_x \cdot 100$	$\sigma_y \cdot 100^a$	σ_T	$S_{x_1} \cdot 100$	$S_{y_1} \cdot 100^a$	S_T, K	S_p, kPa
LLE[b]	15	0·20	0·20	0·10	0·737	0·583	0·15	—
VLE[c] (p = 101·32 kPa)	17	0·05	0·10	0·05	0·14	0·31	0·09	0·23
VLE[b] (t = 70°C)	14	0·20	0·20	0·05	0·36	0·55	0·06	0·21
VLE[b] (t = 50°C)	20	0·20	0·20	0·05	0·35	0·34	0·04	0·05
VLE[d] (t = 25°C)	10	0·10	0·20	0·05	0·28	0·65	0·20	0·08
VLE (overall)	61				0·30	0·45	0·10	0·16

[a] In case of LLE data, the respective value corresponds to the second liquid phase; [b] see ref.[23]; [c] see ref.[21]; [d] see ref.[22].

TABLE III

The values of activity coefficients in the THF(1)–W(2) system at 25°C

x_1	This work		Signer et al.[22]		Shnitko and Kogan[21]	
	$\ln \gamma_1$	$\ln \gamma_2$	$\ln \gamma_1$	$\ln \gamma_2$	$\ln \gamma_1$	$\ln \gamma_2$
0·0	3·424	0	2·970	0	(3·5)[a]	0
0·1	2·002	0·062	2·024	0·039	1·922	0·069
0·2	1·380	0·168	1·416	0·148	1·296	0·185
0·3	1·000	0·294	1·030	0·270	0·933	0·311
0·4	0·732	0·437	0·751	0·419	0·692	0·449
0·5	0·526	0·606	0·542	0·593	0·515	0·586
0·6	0·359	0·809	0·372	0·802	0·376	0·765
0·7	0·223	1·064	0·231	1·065	0·262	0·997
0·8	0·113	1·395	0·113	1·425	0·170	1·319
0·9	0·034	1·849	0·030	1·949	0·088	1·866
1·0	0	2·545	0	2·913	0	(2·8)[a]

[a] The values read from a diagram by the authors of this work.

coefficient of tetrahydrofuran in water which was higher than 54 (i.e., $\ln \gamma_1^\infty \approx 4{\cdot}0$). This substantial improvement was successful not until taking higher terms of the RK equation.

The comparison of the calculated heats of mixing with experimental ones at 25°C is presented in Fig. 2. A relatively good agreement is evident from the figure.

CONCLUSION

The maximum likelihood method was applied to the correlation of the excess Gibbs energy of heterogeneous systems. As input data it is possible to use the data on mutual solubility (indirect ones obtained by the turbidity method as well), on critical point, and the vapour–liquid equilibrium data (indirect ones as well) from the homogeneous region if any. The data on $H^E(x_1, T)$ have not been included into the calculation for the time being and serve as a check of reliability of the set of parameters obtained.

The superposition of the Wilson and Redlich–Kister equations, which may be considered to be an extended modified Wilson equation (the Wilson equation with the first concentration term of the RK equation), was applied to the calculation. The calculation program can be used, however, also for other equations on replacing the respective procedure which assesses the values of activity coefficients, their derivatives with respect to composition, temperature, etc.

The calculation program was applied in this work to the very complicated system tetrahydrofuran–water which exhibits a closed region of limited miscibility. It is possible to say that nine parameters determined describe the behaviour of this system in the whole concentration range and in the temperature interval of 25 – 137·1°C (UCST) nearly in the limits of experimental errors. At first sight it could seem that the data presented in Table II are at variance with this conclusion. However, it is

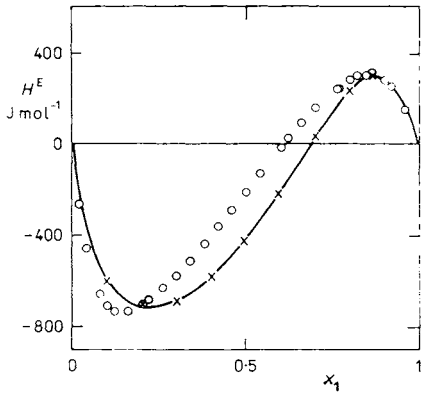

FIG. 2

Experimental (○, ref.[24]) and calculated (—×—×—×) dependence $H^E(x_1)$ in the THF(1)–W(2) system at 25°C

necessary to account of the fact that the errors reported by the authors of experimental works refer mostly to the reproducibility of the data and do not involve the error in method or apparatus. This can be documented when comparing the data, e.g., by Signer and co-workers[22] and Shnitko and co-workers[21] at 25°C. Even though both the authors report $\sigma_p = 0{\cdot}026$ kPa (ref.[22]) and $\sigma_p = 0{\cdot}066$ kPa (ref.[21]), their data differ on the average by 1 kPa, i.e., more than 20 times the declared error. The used (estimated) values of σ_x, σ_y, σ_T, and σ_p are therefore subject to a considerable uncertainty, and therefore the agreement between the calculated and estimated standard deviations of the measured quantities may be considered good.

In case of the THF–W system it is possible to say that the obtained thermodynamic description corresponds to the given system and that it is possible to apply it also to multicomponent systems. In case of such systems as, e.g., benzene-water, where the range of miscibility is very small, the present model need not yield the best results on applying to multicomponent systems. The reason is that the parameters of the model used are obtained from narrow concentration ends, and the model is extrapolated in case of a multicomponent mixture nearly to the whole concentration range and this extrapolation may be very inaccurate. If we wish to apply the description of such a system also to a multicomponent system, we recommend then to account of the data of multicomponent systems (whether qualitatively or quantitatively).

The detail description of the computation program including the used relations will be given elsewhere[33].

LIST OF SYMBOLS

A	constant of Antoine equation
A_{ij}	parameter of Wilson equation (*3*)
B	constant of Antoine equation
B_j	temperature dependent parameter in RK equations (*5*), (*6*)
B_{ij}	second virial coefficient
b_j	temperature independent constant in Eqs (*4*)–(*6*)
C	constant of Antoine equation
C_{12}, C_{21}	temperature dependent parameters in Eq. (*4*)
d_j	component of vector on right-hand side of Eq. (*27*)
F_{ML}, F_{LLE}, F_{VLE}	objective functions determined by Eqs (*7*) and (*8*)
G^E	excess Gibbs energy
G_{11}, G_{111}, G_{11T}	second (with respect to composition), third (with respect to composition), and third (twice with respect to composition and once with respect to temperature) derivative of Gibbs energy of mixing
H^E	enthalpy of mixing
M	number of adjustable parameters considered
n	number of experimental points
p	pressure
p_i^0	saturated vapour pressure of i-th component

$Q = G^E/RT$ dimensionless excess Gibbs energy
Q_{Wilson}, Q_{KR} parts of Q corresponding to Wilson and RK equations
R gas constant
$S_v = [\sum_{i=1}^{n} (v_i^e - \hat{v}_i)^2/n]^{1/2}$ mean quadratic deviation of general variable v
T thermodynamic temperature
t Celsius temperature
V_i^L molar volume of i-th component in liquid phase
W matrix defined by Eq. (*27*)
x mole fraction in liquid phase
y mole fraction in vapour phase
z mole fraction of second liquid phase
α_B, β_B parameters of Eq. (*28*)
γ activity coefficient
φ correction term for real behaviour of vapour phase
ε accuracy required
η, μ relaxation (reduction) parameters
σ standard deviation
Φ, Ψ functions defined by Eqs (*12*) and (*18*)

Subscripts

i, j, k component; summation index
L LLE data
V VLE data

Superscripts

e experimental value
— first liquid phase
≈ second liquid phase
∧ calculated value
· derivative with respect to parameter

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Translated by J. Linek.