EXCESS ENTHALPY IN THE SYSTEMS NITROMETHANE–WATER AND METHYL *tert*-BUTYL ETHER–WATER. EMPLOYING DATA ON EXCESS ENTHALPY FOR THERMODYNAMIC DESCRIPTION OF HETEROGENEOUS SYSTEMS

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The excess enthalpies measured in nitromethane–water and methyl *tert*-butyl ether–water systems at several temperatures are given. The values of the excess enthalpy were determined in both the homogeneous and heterogeneous regions. It is shown how the data for the heterogeneous region can be included in the calculation of parameters of empirical relations for the excess Gibbs energy. It follows from these calculations that the relations for the excess Gibbs energy can be obtained on the basis of the excess enthalpy data measured at several temperatures if the data also cover the heterogeneous region.

Key words: Excess enthalpy; Heterogeneous systems; Parameter calculations; Maximum likelihood method; Calorimetry; Chemical thermodynamics.

Various empirical (*e.g.*, Redlich–Kister equation[1]) and semi-empirical relations (van Laar, Wilson, NRTL, UNIQUAC, *etc.*)[2–4] are used to describe the thermodynamic behaviour of liquid mixtures in terms of the excess Gibbs energy $G^E(T,x_1,\boldsymbol{b})$. These relations contain a number of adjustable parameters $\boldsymbol{b}$ that should be determined for a given system using experimental data. For homogeneous binary systems two or three parameters for each isotherm will usually suffice for a good description. Recent progressive developments in computer technology have stimulated efforts to describe binary systems in the whole range of concentrations and a broad temperature interval. In this connection, it appears that even the relations based on the concept of local composition do not allow description of the excess Gibbs energy and the excess enthalpy simultaneously with sufficient accuracy if a low number (from two to four) of parameters is employed. Therefore, more complex forms of appropriate parameter–temperature relationships should be generally used[2,5–7].

Still more complicated situations can be found in systems that separate into two liquid phases. In this case, the description of the equilibrium curve will be completely dependent on the characteristics of the excess Gibbs energy. To determine parameters $\boldsymbol{b}$ in $G^E(T,x_1,\boldsymbol{b})$ relations in heterogeneous systems, data measured in the homogeneous region, data pertaining to the liquid–liquid equilibrium curve and data obtained from the heterogeneous region can be employed. A number of procedures based on the classical method of least-squares, method of weighted least-squares or method of maximum likelihood can be found in the literature[2–4,8,9] for use of the first data group (*i.e.*, data determined in the homogeneous region). In the description of a system that separates into two liquid phases, however, the greatest priority should be assigned to adequate description of its equilibrium curve and, particularly, of its critical point. These data can be included in the objective function using two formal approaches:

a) By adding a term requiring the minimum value of the sum of the least-squares of the activity deviations in the coexisting phases.

b) By adding a term requiring the minimum value of the sum of squares of differences between the calculated and experimental compositions of the coexisting phases.

It has been shown that the former method has low effectiveness particularly in the vicinity of the critical point and usually fails if a weight is not used[4]. That was the reason why Voňka *et al.*[9] chose method *b*) using the minimum sum of the least squares of the differences between experimental and calculated compositions and also applying a similar condition to the critical point.

To calculate set of parameters $\boldsymbol{b}$ in the $G^E(T,x_1,\boldsymbol{b})$ relation, we employed the maximum likelihood method or the method of weighted least-squares which minimise the objective function F:

$$F = \sum_j \sum_i \left(\frac{v_i^{\mathrm{exp}} - v_i^{\mathrm{calc}}}{\sigma_{v_i}} \right)_j^2 , \qquad (1)$$

where v_i^{exp} and v_i^{calc} are the experimental and calculated values of variable v_i, respectively, and σ_{v_i} is the estimated error of the variable v_i. The summations in Eq. (*1*) are performed using all the available variables (the sum of j) in the binary system and all the corresponding experimental data points (the sum of *i*). The variables included in function *F* are given in Table I. The goal of this calculation is to obtain parameters describing the system under investigation as closely to reality (experiments) as possible. A good description of liquid–liquid equilibria (thereinafter LLE) together with the excess enthalpies (thereinafter H^E) is usually the most important task. If data on LLE are treated separately, the parameters obtained usually do not fit the excess enthalpies with sufficient accuracy and *vice versa*.

In this contribution we propose a procedure for employing data on H^E for improving the thermodynamic description of heterogeneous systems. It should be pointed out that the new calculation procedure employs all the experimental data on H^E in a heterogeneous mixture *i.e.*, data from both the homogeneous and heterogeneous regions. It can be found in the literature that, for thermodynamic description, the data obtained in the homogeneous region can be included without difficulty[10], but the data from the heterogeneous region are often rejected even though they have been measured.

TABLE I
Variables used in the objective function *F*, Eq. (*1*)

variable ν_i	Symbol	Data source	Method of calculation
Mole fraction in the first liquid phase	$\hat{x}_1$	LLE	MML
Mole fraction in the second liquid phase	$\hat{z}_1$	LLE	MML
Temperature	T_{LLE}	LLE	MML
Composition of the critical point	x_{1c}	LLE	MML
Temperature of the critical point	T_c	LLE	MML
Mole fraction in the liquid phase	x_1	VLE	MML
Mole fraction in the vapour phase	y_1	VLE	MML
Temperature	T_{VLE}	VLE	MML
Pressure	p	VLE	MML
Excess enthalpy	H^E	H^E	MLS
Limiting activity coefficients	γ^∞	γ^∞	MLS
Second derivative of excess Gibbs energy with respect of composition	$G11$	light scattering	MLS

The procedure for calculating parameters ***b*** in an empirical relation of the excess Gibbs energy has been employed for the nitromethane–water and methyl *tert*-butyl ether–water (thereinafter MTBE–water) systems. New experimental data were used for this purpose.

THEORETICAL

Inclusion of Data on H^E from the Heterogeneous Region in Parameter Calculation

We will distinguish between H^E values for the homogeneous region and those for the heterogeneous region. The values of the excess enthalpy in the homogeneous region $H^E(x_1)$ pertain to the given mole fraction x_1, but the values in the heterogeneous region $H^E(x_1^F)$ are formally related to mole fraction x_1^F (feed composition), *i.e.*, to the hypothetical composition of the system consisting of two coexisting phases with compositions $\hat{x}_1$ and $\hat{z}_1$. Their relationship can be described by the following equation:

$$x_1^F = \Phi \hat{x}_1 + (1 - \Phi) \hat{z}_1 \ , \qquad (2)$$

where $\Phi = n^{(1)}/[n^{(1)} + n^{(2)}]$ gives the relative amount of the first liquid phase and, $n^{(1)}$ and $n^{(2)}$ correspond to the mole amounts of the first and second liquid phases, respectively.

The isothermal dependence of H^E on composition x_1 in a heterogeneous system is depicted schematically in Fig. 1. The points measured in the het-

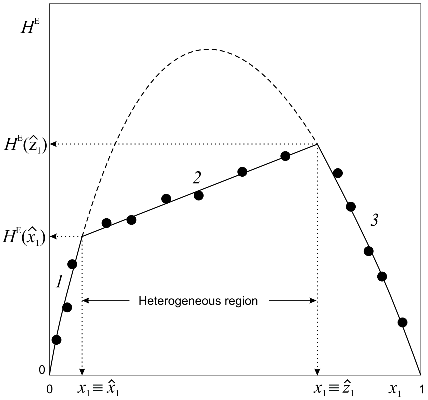

FIG. 1

Schematic isothermal dependence of the excess enthalpy H^E on composition x_1 in a heterogeneous binary system. ● Experimental data; ——— calculated values: in the homogeneous region (curves *1* and *3*), in the heterogeneous region (straight line *2*); --------- hypothetical curve erogeneous region can be included in the calculation by either of the following methods:

a) The direct experimental data from the homogeneous region are supplemented by the excess enthalpies $H^E(\hat{x}_1)$, $H^E(\hat{z}_1)$, *i.e.*, the values corresponding to the compositions of the coexisting phases $\hat{x}_1$, $\hat{z}_1$. These values can be determined from the intersections of the lateral homogeneous branches *1* and *3* with the straight line *2* which describes the course of $H^E(x_1)$ in the heterogeneous region (see Fig. 1). In this way it is possible to obtain values of $\hat{x}_1$, $\hat{z}_1$ and the corresponding values of $H^E(\hat{x}_1)$, $H^E(\hat{z}_1)$. Correlation of the data can then result in quite precise calculated values $H^E(\hat{x}_1)$, $H^E(\hat{z}_1)$ but the determined parameters may correspond to the heterogeneous system as well as to the homogeneous system.

b) The following method appears more exact and effective:

First, the $\hat{x}_1$ and $\hat{z}_1$ values for a given temperature T should be calculated using a suitably chosen set of parameters (see the next chapter) for the correlation relation employed. The values of $H^E(T,\hat{x}_1)$ and $H^E(T,\hat{z}_1)$ should be calculated by inserting the values of $\hat{x}_1$ and $\hat{z}_1$ obtained by numerical calculation into the appropriate thermodynamic relations (see Eqs (*9*)). Then the excess enthalpy of the system with composition x_1^F in its heterogeneous region can be obtained using the following equation:

$$H^E\left(T,x_1^F\right) = H^E\left(T,\hat{x}_1\right) + \frac{x_1^F - \hat{x}_1}{\hat{z}_1 - \hat{x}_1}\left[H^E\left(T,\hat{z}_1\right) - H^E\left(T,\hat{x}_1\right)\right]. \qquad (3)$$

The following contribution should then be included in the objective function Eq. (*1*):

$$F_{H,\mathrm{het}} = \sum\left[\frac{H^E\left(T,x_1^F\right)^{\mathrm{exp}} - H^E\left(T,x_1^F\right)^{\mathrm{calc}}}{\sigma_{H_{\mathrm{het}}}}\right]^2 , \qquad (4)$$

where $\sigma_{H_{\mathrm{het}}}$ is the estimated experimental error for H^E. The summation in Eq. (*4*) is performed for all the experimental data in the heterogeneous region.

New Calculation Procedure

The calculation consists of the following steps:

1. Initial parameter approximation.

2. Calculation of the coexisting phase compositions.

3. Calculation of dH^E/db_k factors for the heterogeneous region.
4. Application of the method of least-squares itself.

1. Initial Parameter Approximation

In the treatment of correlation equations containing parameters $\boldsymbol{b}$ which are not in a linear relationship to the variable to be minimised, the determination of a suitable first approximation of parameters $\boldsymbol{b}^{(o)}$ is one of the most serious problems. This issue is of special importance for the inclusion of H^E data in the heterogeneous region. Taking this into account, $\boldsymbol{b}^{(o)}$ parameters were determined first, using the data for liquid–vapour and liquid–liquid equilibria and the data for the excess enthalpy in the homogeneous region. It is pointed out that, for the liquid–liquid and liquid–vapour equilibrium data, the method of maximum likelihood was employed. The other data were then correlated by means of the method of weighted least-squares. The parameters obtained in this way more or less successfully describe the data included and used for the calculation. The parameters were then used as good first approximation for the second calculation step, in which the data on H^E in the heterogeneous region were included and arranged according to the individual isotherms.

2. Calculation of the Coexisting Phase Compositions at a Specified Temperature

Before the data on H^E in the heterogeneous region can be included in the calculation, the compositions of the coexisting phases should be calculated for each isotherm, based on the available parameters. The Newton's method with two independent values of the relaxation parameters[4,11], η and μ ($\eta,\mu \in \langle 0,1\rangle$), was used for determining the values of $\hat{x}_1$ and $\hat{z}_1$ at a fixed temperature.

$$\hat{x}_1^{\text{new}} = \hat{x}_1^{\text{old}} + \eta\Delta x_1 \;, \quad \hat{z}_1^{\text{new}} = \hat{z}_1^{\text{old}} + \mu\Delta z_1 \;, \tag{5}$$

where Δx_1 and Δz_1 are increments determined from the set of Eqs (*6*) and (*7*) following from the condition of equality of the activities of the components in the individual phases[11].

$$\left(\frac{\partial \ln \bar{a}_1}{\partial x_1}\right)\Delta x_1 - \left(\frac{\partial \ln \tilde{a}_1}{\partial z_1}\right)\Delta z_1 = \ln \frac{\tilde{a}_1}{\bar{a}_1} \tag{6}$$

$$\left(\frac{\partial \ln \bar{a}_2}{\partial x_1}\right)\Delta x_1 - \left(\frac{\partial \ln \tilde{a}_2}{\partial z_1}\right)\Delta z_1 = \ln \frac{\tilde{a}_2}{\bar{a}_2} \qquad (7)$$

The values of η and μ in Eqs (*5*) should be chosen to ensure that the new approximations for the coexisting phase compositions $\hat{x}_1^{\text{new}}$, $\hat{z}_1^{\text{new}}$ will not lie in an unstable region (where it holds that $(\partial a_1 / \partial x_1) < 0$), and the absolute values of Δx_1, Δz_1 will not exceed a value of 0.01. The compositions of the coexisting phases obtained successfully in previous calculations (*i.e.*, with the previous parameter set) were employed as a first approximation for the solution of set of Eqs (*6*) and (*7*), while the values of $x_1 = 0.01$ and $z_1 = 0.99$ were used for the first-round of calculations. The calculation of $\hat{x}_1$ and $\hat{z}_1$ is finished as soon as the following condition is met:

$$(\Delta x_1)^2 + (\Delta z_1)^2 < 10^{-10} \ . \qquad (8)$$

Then $\hat{x}_1 = \hat{x}_1^{\text{new}}$ and $\hat{z}_1 = \hat{z}_1^{\text{new}}$.

3. Calculation of $\mathrm{d}H^{\mathrm{E}}/\mathrm{d}b_k$ Factors for the Heterogeneous Region

For the calculated compositions of the coexisting phases $\hat{x}_1$ and $\hat{z}_1$, the values of the excess enthalpy $H^{\mathrm{E}}(\hat{x}_1, \boldsymbol{b})$, $H^{\mathrm{E}}(\hat{z}_1, \boldsymbol{b})$ were determined using the relations:

$$H^{\mathrm{E}}(\hat{x}_1, b) = -RT^2 \left(\frac{\partial Q}{\partial T}\right)_{x_1 = \hat{x}_1} \ , \quad H^{\mathrm{E}}(\hat{z}_1, b) = -RT^2 \left(\frac{\partial Q}{\partial T}\right)_{z_1 = \hat{z}_1} \ , \qquad (9)$$

where the variable Q is the dimensionless excess Gibbs energy (see Eq. (20)). The derivatives of H^{E} for the heterogeneous region with respect to parameters $\boldsymbol{b}$ (*i.e.*, the $\mathrm{d}H^{\mathrm{E}}/\mathrm{d}b_k$ factors) were evaluated as follows.

The excess enthalpy for the heterogeneous region is given by Eq. (*3*), which can be rewritten as:

$$H^{\mathrm{E}}(x_1^{\mathrm{F}}, b) = H^{\mathrm{E}}(\hat{x}_1, b)\frac{x_1^{\mathrm{F}} - \hat{z}_1}{\hat{x}_1 - \hat{z}_1} + H^{\mathrm{E}}(\hat{z}_1, b)\frac{\hat{x}_1 - x_1^{\mathrm{F}}}{\hat{x}_1 - \hat{z}_1} \ . \qquad (10)$$

For $\mathrm{d}H^{\mathrm{E}}/\mathrm{d}b_k$ it is obtained from this equation that:

$$\begin{aligned}\frac{\mathrm{d}H^{\mathrm{E}}}{\mathrm{d}b_k} = &\left[\left(\frac{\partial H^{\mathrm{E}}(x_1)}{\partial b_k}\right)_{x_1} + \left(\frac{\partial H^{\mathrm{E}}(x_1)}{\partial x_1}\right)_b \frac{\mathrm{d}\hat{x}_1}{\mathrm{d}b_k}\right]\frac{x_1^{\mathrm{F}} - \hat{z}_1}{\hat{x}_1 - \hat{z}_1} + \\ &+ \frac{H^{\mathrm{E}}(\hat{x}_1)}{(\hat{x}_1 - \hat{z}_1)^2}\left[-\frac{\mathrm{d}\hat{z}_1}{\mathrm{d}b_k}\left(\hat{x}_1 - \hat{z}_1\right) - (x_1^{\mathrm{F}} - \hat{z}_1)\left(\frac{\mathrm{d}\hat{x}_1}{\mathrm{d}b_k} - \frac{\mathrm{d}\hat{z}_1}{\mathrm{d}b_k}\right)\right] + \\ &+ \left[\left(\frac{\partial H^{\mathrm{E}}(z_1)}{\partial b_k}\right)_{z_1} + \left(\frac{\partial H^{\mathrm{E}}(z_1)}{\partial z_1}\right)_b \frac{\mathrm{d}\hat{z}_1}{\mathrm{d}b_k}\right]\frac{\hat{x}_1 - x_1^{\mathrm{F}}}{\hat{x}_1 - \hat{z}_1} + \\ &+ \frac{H^{\mathrm{E}}(\hat{z}_1)}{(\hat{x}_1 - \hat{z}_1)^2}\left[-\frac{\mathrm{d}\hat{x}_1}{\mathrm{d}b_k}(\hat{x}_1 - \hat{z}_1) - \left(\hat{x}_1 - x_1^{\mathrm{F}}\right)\left(\frac{\mathrm{d}\hat{x}_1}{\mathrm{d}b_k} - \frac{\mathrm{d}\hat{z}_1}{\mathrm{d}b_k}\right)\right],\end{aligned} \qquad (11)$$

where the values of $\mathrm{d}\hat{x}_1/\mathrm{d}b_k$ and $\mathrm{d}\hat{z}_1/\mathrm{d}b_k$ will be determined by differentiation of the equilibrium conditions:

$$\ln \hat{x}_1 + \ln \bar{\gamma}_1\left(b, x_1\right) = \ln \hat{z}_1 + \ln \tilde{\gamma}_1\left(\boldsymbol{b}, z_1\right) , \qquad (12)$$

$$\ln \hat{x}_2 + \ln \bar{\gamma}_2\left(b, x_1\right) = \ln \hat{z}_2 + \ln \tilde{\gamma}_2\left(\boldsymbol{b}, z_1\right) , \qquad (13)$$

where $\hat{x}_1$ and $\hat{z}_1$ must be considered to be functions of parameters $\boldsymbol{b}$ (*i.e.*, for the given temperature, $\hat{x}_1 = \hat{x}_1(\boldsymbol{b})$, $\hat{z}_1 = \hat{z}_1(\boldsymbol{b})$). The set of equations obtained has the following form:

$$\begin{aligned}&\frac{1}{\hat{x}_1}\frac{\mathrm{d}\hat{x}_1}{\mathrm{d}b_k} + \left(\frac{\partial \ln \bar{\gamma}_1}{\partial b_k}\right)_x + \left(\frac{\partial \ln \bar{\gamma}_1}{\partial b_k}\right)_x \frac{\mathrm{d}\hat{x}_1}{\mathrm{d}b_k} = \\ &= \frac{1}{\hat{z}_1}\frac{\mathrm{d}\hat{z}_1}{\mathrm{d}b_k} + \left(\frac{\partial \ln \tilde{\gamma}_1}{\partial b_k}\right)_z + \left(\frac{\partial \ln \tilde{\gamma}_1}{\partial z_1}\right)_b \frac{\mathrm{d}\hat{z}_1}{\mathrm{d}b_k} ,\end{aligned} \qquad (14)$$

$$\begin{aligned}&-\frac{1}{1-\hat{x}_1}\frac{\mathrm{d}\hat{x}_1}{\mathrm{d}b_k} + \left(\frac{\partial \ln \bar{\gamma}_2}{\partial b_k}\right)_x + \left(\frac{\partial \ln \bar{\gamma}_2}{\partial x_1}\right)_b \frac{\mathrm{d}\hat{x}_1}{\mathrm{d}b_k} = \\ &= \frac{1}{1-\hat{z}_1}\frac{\mathrm{d}\hat{z}_1}{\mathrm{d}b_k} + \left(\frac{\partial \ln \tilde{\gamma}_2}{\partial b_k}\right)_z + \left(\frac{\partial \ln \tilde{\gamma}_2}{\partial z_1}\right)_b \frac{\mathrm{d}\hat{z}_1}{\mathrm{d}b_k} ,\end{aligned} \qquad (15)$$

or

$$\frac{\mathrm{d}\hat{x}_1}{\mathrm{d}b_k}\left[\frac{1}{\hat{x}_1}+\left(\frac{\partial\ln\bar{\gamma}_1}{\partial x_1}\right)_b\right]-\frac{\mathrm{d}\hat{z}_1}{\mathrm{d}b_k}\left[\frac{1}{\hat{z}_1}+\left(\frac{\partial\ln\tilde{\gamma}_1}{\partial z_1}\right)_b\right]=\left(\frac{\partial\ln\tilde{\gamma}_1}{\partial b_k}\right)_z-\left(\frac{\partial\ln\tilde{\gamma}_1}{\partial b_k}\right)_x\ , \qquad (16)$$

$$\frac{\mathrm{d}\hat{x}_1}{\mathrm{d}b_k}\left[-\frac{1}{1-\hat{x}_1}+\left(\frac{\partial\ln\bar{\gamma}_2}{\partial x_1}\right)_b\right]-\frac{\mathrm{d}\hat{z}_1}{\mathrm{d}b_k}\left[-\frac{1}{1-\hat{z}_1}+\left(\frac{\partial\ln\tilde{\gamma}_2}{\partial z_1}\right)_b\right]= =\left(\frac{\partial\ln\tilde{\gamma}_2}{\partial b_k}\right)_z-\left(\frac{\partial\ln\tilde{\gamma}_2}{\partial b_k}\right)_x\ . \qquad (17)$$

It can be pointed out that the factors on the left-hand sides of Eqs (*16*) and (*17*) are independent of the value of k. Therefore, the calculation of the required derivatives is equivalent to the solution of a set of equations with different right-hand sides.

4. Application of the Method of Least-Squares Itself

Provided that factors $\mathrm{d}H^{\mathrm{E}}/\mathrm{d}b_k$ for the heterogeneous region are known, the excess enthalpy in this region can be expressed by the following relation:

$$H^{\mathrm{E}}\left(T,x_1^{\mathrm{F}},\boldsymbol{b}\right)=H^{\mathrm{E}}\left(T,x_1^{\mathrm{F}},\boldsymbol{b}^{(0)}\right)+\frac{\mathrm{d}H^{\mathrm{E}}\left(T,x_1^{\mathrm{F}},\boldsymbol{b}^{(0)}\right)}{\mathrm{d}b_1}\Delta b_1+ +\frac{\mathrm{d}H^{\mathrm{E}}\left(T,x_1^{\mathrm{F}},\boldsymbol{b}^{(0)}\right)}{\mathrm{d}b_2}\Delta b_2+\ldots \qquad (18)$$

If this relation is introduced into Eq. (*4*) (*i.e.*, $H^{\mathrm{E}}(T,x_1^{\mathrm{F}},\boldsymbol{b}) = H^{\mathrm{E}}(T,x_1^{\mathrm{F}})^{\mathrm{calc}}$) the values of parameters $\boldsymbol{b}$ can be optimized, while the experimental data on the excess enthalpy in the heterogeneous region (*i.e.*, $H^{\mathrm{E}}(T,x_1^{\mathrm{F}})^{\mathrm{exp}}$) are employed in the calculation.

EXPERIMENTAL

Chemicals

Nitromethane was supplied by Riedel de Haen as a reagent with stated purity of 99%. Its density at 20 °C was found to be 1.13545 g cm^{-3}. Methyl *tert*-butyl ether (MTBE) was obtained from Merck. The stated purity of the reagent was 99.5%. The density determined at 25 °C was 0.73519 g cm^{-3}. Taking the stated purity into account, the measured densities correspond to the literature values of 1.13816 g cm^{-3} for nitromethane[12] and 0.7352 g cm^{-3} for MTBE (ref.[13]). Water used for the measurements was supplied by Merck as a reagent for chromatography. All the chemicals were used without further purification.

Measurement

The measurement of H^E was carried out using a flow calorimeter (Hart Scientific) and two metering pumps (Varian 8500). The equipment is described in more detail elsewhere[14].

The measurements in the nitromethane–water system were carried out either by mixing the two components directly or by diluting a homogeneous mixture of the components with water (to achieve low water concentrations). The homogeneous mixture used in the latter method was designated as the initial mixture and its mole fraction as $x^{(i)}$. The composition of this mixture was chosen to ensure its homogeneity for the whole temperature range of measurements. The final mixture was obtained by diluting the initial mixture with nitromethane and its excess enthalpy $H^E(x^{(f)})$ was calculated using the following formula:

$$H^E\left(x^{(f)}\right) = Q^D + \frac{x^{(f)}}{x^{(i)}} H^E\left(x^{(i)}\right) , \tag{19}$$

where $H^E(x^{(f)})$ and $H^E(x^{(i)})$ are the excess molar enthalpies of the final and initial mixtures, respectively. The value of Q^D is the heat of dilution generated by the mixing process and is related to the total mole amounts of the components. The $H^E(x^{(i)})$ values were calculated using the Redlich–Kister equation[1] with parameters obtained by fitting the experimental points for the direct mixing measurements of H^E. An initial mixture with a nitromethane mole fraction of $x^{(i)} = 0.96$ was used for the experiments. For the measurement at temperatures of 20, 40, 60 and 80 °C, values equal to $H^E(x^{(i)})$ of 466.5, 475.2 , 475.5 and 478.8 J mol^{-1}, respectively, were obtained.

The employed calorimetric system was tested with ethanol–water and tetrahydrofuran–water systems before being employed for the above measurements. According to the tests, the relative accuracy of measurement of H^E is about 2%.

RESULTS AND DISCUSSION

The experimental data on H^E for the nitromethane–water system and for the MTBE–water system are presented in Tables II and III, respectively.

Correlation of the Experimental Data

For thermodynamic description of mixtures, it is convenient to utilize the excess Gibbs energy which permits determination of other thermodynamic quantities (*e.g.*, activity coefficients, excess enthalpy) using relatively simple mathematical relations. In this work as previously[9,10,15–17], superposition of the Wilson[18] and Redlich–Kister[1] equations was employed for correlation of the experimental data.

$$Q = \frac{G^E}{RT} = Q_{\mathrm{Wilson}} + Q_{\mathrm{RK}} , \tag{20}$$

TABLE II
Experimental data on the excess enthalpies H^E (in J mol^{-1}) for the nitromethane (1)–water (2) system

20 °C		40 °C		50 °C		60 °C		80 °C	
x_1	H^E	x_1	H^E	x_1	H^E	x_1	H^E	x_1	H^E
0.0085	33.1	0.0173	80.5	0.0085	43.7	0.0085	57.8	0.0085	68.0
0.0173	71.3	0.0272	154.1	0.0173	97.4	0.0173	112.6	0.0173	142.7
0.0264	106.5	0.0359	201.3	0.0205	120.6	0.0173	118.1	0.0264	215.9
0.0358	127.0	0.0456	216.7	0.0358	220.4	0.0264	188.3	0.0456	371.8
0.0456	142.6	0.0663	263.2	0.0456	276.6	0.0358	263.5	0.0663	552.9
0.0663	163.7^{a}	0.1003	301.1	0.1003	374.9^{a}	0.0456	319.5	0.1003	707.5^{a}
0.1003	187.2^{a}	0.1672	365.7^{a}	0.1672	453.4^{a}	0.0663	396.9^{a}	0.1254	748.7^{a}
0.1672	229.5^{a}	0.2149	414.6^{a}	0.2507	552.8^{a}	0.1003	448.4^{a}	0.1672	844.4^{a}
0.2507	283.9^{a}	0.2507	462.5^{a}	0.2902	596.9^{a}	0.1254	485.2^{a}	0.2149	942.8^{a}
0.2902	308.6^{a}	0.2902	478.2^{a}	0.3580	673.1^{a}	0.1672	541.4^{a}	0.2507	1 016.7^{a}
0.3580	349.4^{a}	0.3580	557.9^{a}	0.5009	856.3^{a}	0.2149	608.0^{a}	0.3580	1 260.5^{a}
0.4384	407.3^{a}	0.4100	624.9^{a}	0.5009	862.0^{a}	0.2507	650.7^{a}	0.3580	1 259.5^{a}
0.5009	447.1^{a}	0.5009	717.6^{a}	0.7008	1 094.2^{a}	0.2507	663.1^{a}	0.4100	1 374.7^{a}
0.5009	449.6^{a}	0.5723	791.6^{a}	0.8641	1 246.0^{a}	0.2507	659.1^{a}	0.5009	1 578.8^{a}
0.5723	492.2^{a}	0.6547	879.3^{a}	0.8827	1 138.2	0.2902	705.5^{a}	0.5723	1 720.7^{a}
0.5723	494.0^{a}	0.7507	968.4^{a}	0.8827	1 132.7	0.3580	793.6^{a}	0.7008	1 990.2^{a}
0.7008	578.0^{a}	0.8641	1 083.0^{a}	0.8827	1 154.2	0.3580	800.2^{a}	0.7507	1 987.9
0.7008	576.1^{a}	0.8757	1 066.1^{a}	0.8893	1 078.4	0.4384	912.0^{a}	0.8049	1 727.3
0.8049	644.8^{a}	0.8934	1 061.9	0.8932	1 067.9	0.4384	912.2^{a}	0.8049	1 694.2
0.8641	689.1^{a}	0.9068	981.8	0.9213	854.4	0.5009	1 002.0^{a}	0.8049	1 737.3
0.8827	704.0^{a}	0.9290	773.9	0.9305	826.7	0.5723	1 100.4^{a}	0.8338	1 548.6
0.8932	708.3^{a}	0.9649	428.1	0.9377	724.1	0.7008	1 280.5^{a}	0.8338	1 570.7
0.9305	735.8^{a}	0.9698	382.6^{b}			0.8049	1 421.1^{a}	0.8641	1 325.3
0.9377	697.0	0.9747	329.1^{b}			0.8700	1 238.8	0.8641	1 405.2
0.9436	635.5	0.9797	269.8^{b}			0.8932	1 098.0	0.8700	1 347.4
0.9485	579.6	0.9847	206.4^{b}			0.9305	783.9	0.8700	1 279.4
0.9525	544.2	0.9898	141.3^{b}			0.9436	634.9	0.8827	1 203.7
0.9650	424.5	0.9949	71.8^{b}			0.9436	642.1	0.9305	781.1
0.9699	379.1^{b}					0.9525	562.7	0.9305	789.3
0.9748	328.7^{b}					0.9649	430.0^{b}	0.9377	724.7
0.9798	273.3^{b}					0.9698	380.9^{b}	0.9649	422.8^{b}
0.9848	213.2^{b}					0.9747	327.6^{b}	0.9698	369.0^{b}
0.9898	146.9^{b}					0.9797	270.3^{b}	0.9747	312.6^{b}
0.9949	75.9^{b}					0.9847	209.1^{b}	0.9797	254.1^{b}
						0.9898	166.6^{b}	0.9847	193.4^{b}
								0.9898	130.0^{b}
								0.9949	64.6^{b}

[a] Heterogeneous region. [b] Data obtained by diluting.

$$Q_{\mathrm{Wilson}} = -x_1 \ln\left(x_1 + x_2 A_{12}\right) - x_2 \ln\left(x_2 + x_1 A_{21}\right) , \tag{21}$$

$$A_{ij} = \frac{V_j}{V_i} \exp\left(-\frac{a_{ij}}{T_{\mathrm{R}}}\right) , \tag{22}$$

$$a_{ij} = \alpha_{ij} + \beta_{ij} T_{\mathrm{R}} + \gamma_{ij} / T_{\mathrm{R}} , \tag{23}$$

TABLE III
Experimental data on the excess enthalpies H^{E} (in J mol^{-1}) for the MTBE (1)–water (2) system

10 °C		20 °C		30 °C	
x_1	H^{E}	x_1	H^{E}	x_1	H^{E}
0.0025	–50.8	0.0025	–49.1	0.0025	–39.0
0.0030	–66.3	0.0030	–59.9	0.0030	–48.4
0.0038	–87.7	0.0038	–76.7	0.0037	–61.9
0.0060	–129.3	0.0060	–109.6	0.0038	–65.1
0.0066	–140.0	0.0078	–136.6	0.0210	–125.1
0.0078	–163.8	0.0210	–190.3[a]	0.0476	–112.0[a]
0.0120	–218.5	0.0476	–183.7[a]	0.0826	–97.2[a]
0.0826	–269.1[a]	0.0826	–165.5[a]	0.1094	–82.5[a]
0.1305	–247.5[a]	0.1094	–154.3[a]	0.1305	–74.3[a]
0.2001	–212.5[a]	0.1305	–140.9[a]	0.1305	–72.7[a]
0.3104	–144.2[a]	0.2001	–107.6[a]	0.1550	–63.4[a]
0.3751	–117.7[a]	0.3104	–61.0[a]	0.2001	–43.6[a]
0.5123	–42.1[a]	0.5123	44.7[a]	0.2593	–17.1[a]
0.6492	35.5[a]	0.6492	111.8[a]	0.3751	39.9[a]
0.7403	87.3[a]	0.7403	153.8[a]	0.5123	100.2[a]
0.8541	154.3[a]	0.8541	206.1[a]	0.6492	165.4[a]
0.8824	169.9[a]	0.8824	223.1[a]	0.7403	205.5[a]
				0.8541	255.3[a]
				0.8824	269.0[a]

[a] Heterogeneous region.

$$Q_{\mathrm{RK}} = x_1 x_2 \sum_{k=0}^{r} a_{12k} \left(x_1 - x_2 \right)^k \ , \tag{24}$$

$$a_{ijk} = \alpha_{ijk} + \beta_{ijk} T_{\mathrm{R}} + \gamma_{ijk} / T_{\mathrm{R}} \ , \tag{25}$$

TABLE IV
Data used for determination of parameters in the excess Gibbs relation, Eq. (*20*)

Data type	Temperature range	Standard deviation	References
	Nitromethane (*1*)–Water (*2*)		
H^E	20–80 °C	[a]	this work
LLE	0–105 °C	[b]	refs[12,20]
Critical point LLE		[b]	ref.[12]
VLE	21, 23, 40 °C	[b]	refs[21,22]
	MTBE (*1*)–Water (*2*)		
H^E	10–30 °C	[c]	this work
LLE	0–70 °C	[d]	refs[15,23]

[a] σ_{H^E} = 15 J mol^{-1}. [b] Ref.[17]. [c] σ_{H^E} = 10 J mol^{-1}. [d] σ_x = 0.0003, σ_z = 0.002, σ_T = 0.05 K.

TABLE V
Parameters ***b*** of the excess Gibbs relation. The values calculated for the nitromethane (1)–water (2) and MTBE (1)–water (2) systems

Nitromethane (*1*)–Water (*2*)		MTBE (*1*)–Water (*2*)	
α_{12} =	3.4071	α_{12} =	12.345
γ_{12} =	–1.7593	γ_{12} =	–11.171
α_{21} =	1.1979	α_{21} =	2.1995
γ_{12} =	1.7324	γ_{12} =	0.1[a]
α_{120} =	1.6687	α_{120} =	1.6634
β_{120} =	–1.1423		

[a] In the course of preliminary calculations this parameter value was found by way of trial. In the final phase of parameter determination the value was fixed in order to improve calculation stability.

where α_{ij}, β_{ij}, γ_{ij} α_{ijk}, β_{ijk} and γ_{ijk} are the temperature-independent system parameters (*i.e.*, the values of $\boldsymbol{b}$). Equation (*24*) is the Redlich–Kister expansion which can be included in relation (*20*) with different numbers of parameters a_{12k}. Their maximum number (*i.e.*, the value of r in Eq. (*24*)) is dependent on the system to be correlated. To improve the numerical stability during the calculation, a temperature transformation was introduced so that the actual temperature T was divided by a reference temperature T_{ref}, yielding the "reduced" temperature $T_{\mathrm{R}} = T/T_{\mathrm{ref}}$. A value of 300 K was used for T_{ref} in this work.

Equations (23) and (*25*) give the temperature dependence of the model parameters in a general form. For a particular system, these relations are always used with either β or γ equal to zero; *i.e.*, the relations are either a linear function of the temperature or a linear function of reciprocal temperature. The system to be correlated determines which of these two variants should be employed. For example, it can be derived that Eq. (*23*) with γ equal to zero cannot be successfully used for systems exhibiting a negative value of the excess heat capacity[19].

On the basis of the model defined by Eqs (*20*) to (*25*), H^{E} in the homogeneous region can be calculated from the relation

$$H^{\mathrm{E}}(x_1) = \frac{R T_{\mathrm{ref}} x_1 x_2}{T_{\mathrm{R}}} \left(\frac{A_{12}(\alpha_{12} T_{\mathrm{R}} + 2\gamma_{12})}{x_1 + A_{12} x_2} + \frac{A_{21}(\alpha_{21} T_{\mathrm{R}} + 2\gamma_{21})}{x_2 + A_{21} x_1} \right) + $$

$$+ \left(-T_{\mathrm{R}} \sum_{k=0}^{r} \left(\beta_{12k} T_{\mathrm{R}}^2 - \gamma_{12k} \right) \left(x_1 - x_2 \right)^k \right) \qquad (26)$$

with $x_2 = 1 - x_1$. For H^{E} in the heterogeneous region, Eq. (3) has to be applied.

To determine the system parameters, H^{E} data were complemented with other available thermodynamic data. They are summarised in Table IV together with the corresponding errors σ_{v_i} used in the objective function.

As it was already mentioned, the calculation of parameters in Eqs (*20*) to (*25*) was carried out in two subsequent steps. First, the parameters were calculated using a method[9,10] based on the accessible data for the homogeneous region (including H^{E} data). In the second step, the term defined by relationship (*4*) was included in the objective function and the parameters obtained from the first step were further corrected. The parameter values obtained for the two systems are given in Table V.

Figures 2 and 3 depict the very good agreement achieved for the calculated and measured values of H^E, while Figs 4 and 5 depict similar agreement for the values of mutual solubility (*i.e.*, LLE). The compliances are very good and, for H^E, the average deviations in the homogeneous region and heterogeneous region are 27 and 35 J mol^{-1}, respectively, in the nitromethane–water system, and, similarly, 12 and 10 J mol^{-1} in the MTBE–water system.

The described calculation procedure should also bring out the following advantage. A quite acceptable description of the liquid–liquid equilibrium for a particular system should be obtained as the result of correlation of the excess enthalpy data containing values both from the homogeneous and heterogeneous regions. Therefore, an attempt was made to calculate the pa-

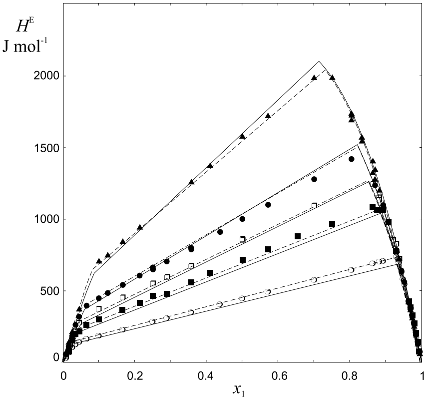

FIG. 2
Comparison of the experimental and calculated excess enthalpies H^E in the system nitromethane (1)–water (2). Experimental data: ❍ 20 °C, ■ 40 °C, ❐ 50 °C, ● 60 °C, ▲ 80 °C; ——— calculated values based on the correlation of all the experimental data (see Table IV), ---------- correlation based on the excess enthalpy data alone

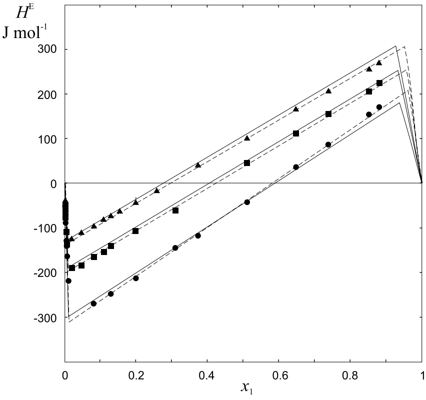

FIG. 3
Comparison of the experimental and calculated excess enthalpies H^E in the system MTBE (1)–water (2). Experimental data: ● 10 °C, ■ 20 °C, ▲ 30 °C; ——— calculated values based on the correlation of all the experimental data (see Table IV), ---------- correlation based on the excess enthalpy data alone

rameters in Eqs (*20*) to (*25*) on the basis of the H^E data for the studied systems alone. The calculation results are depicted in Figs 2 to 5. It appears that a better fit is achieved for the excess enthalpy at the expense of mutual solubility data. However, as can be seen in Fig. 4, the predicted curve of the mutual solubility for the nitromethane–water system exhibits a critical temperature, which is 7 °C higher than the experimental value. Taking into account the fact that the nearest measured isotherm of the system (80 °C) is as far as 25 °C from the critical temperature, this result is quite acceptable.

The similar prediction of LLE for the MTBE–water system (Fig. 5) does not yield good results for the part of the LLE curve corresponding to the MTBE-rich phase. This can be due to the fact that no experimental data have been obtained in this homogeneous region.

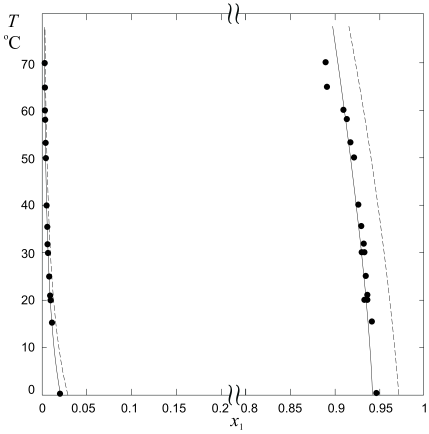

FIG. 4

Comparison of the experimental and calculated data $\hat{x}_1$ and $\hat{z}_1$ in the system nitromethane (1)–water (2). ● Experimental data[12,20]; ——calculated values based on the correlation of all the experimental data (see Table IV), - - - - - prediction based on the correlation of the excess enthalpy data alone

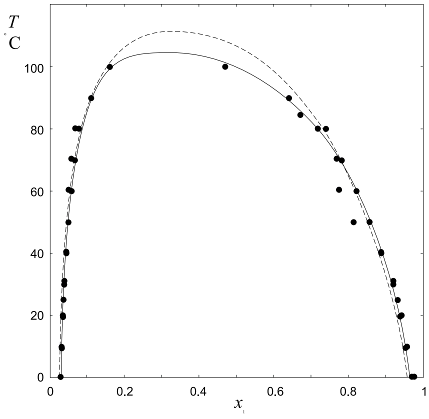

FIG. 5

Comparison of the experimental and calculated data $\hat{x}_1$ and $\hat{z}_1$ in the system MTBE (1)–water (2). ● Experimental data[15,23]; —— calculated values based on the correlation of all the experimental data (see Table IV), - - - - - prediction based on the correlation of the excess enthalpy data alone

CONCLUSION

Experimental data on H^E for the heterogeneous regions in binary systems can be obtained in the same way as for the homogeneous region. All this data then comprise information about the liquid–liquid equilibria. Taking this into account, the data in the heterogeneous regions should not be rejected, but should rather be employed for thermodynamic description of the heterogeneous system.

A procedure has been developed for inclusion of the excess enthalpy data for the heterogeneous region. It can be similarly applied to other data. For example, in the determination of liquid–vapour equilibria it is possible to measure the pressure as a function of the composition in both the homogeneous and heterogeneous regions. The values obtained could also be included in the objective function using a similar expression to that for the excess enthalpy (*4*).

At this point we would like to stress the importance of H^E data for the heterogeneous systems. Their existence makes it possible to describe the temperature dependence of the excess Gibbs energy and thus to predict the mutual solubility. In contrast, using only H^E data for the homogeneous systems (*e.g.*, refs[24,25]) for determination parameters $G^E(T,x_1,\boldsymbol{b})$ may be misleading[26].

SYMBOLS

$\bar{a}_i$, $\tilde{a}_i$	activities of the *i*-th component in the first and the second liquid phase, Eqs (*6*) and (*7*)
a_{ij}	temperature dependent parameters of the Wilson equation, Eq. (*23*)
a_{ijk}	temperature dependent parameters of the Redlich–Kister equation, Eq. (*25*)
A_{ij}	temperature dependent parameters of the Wilson equation, Eq. (*22*)
$\boldsymbol{b}$	parameters in relations for excess Gibbs energy
$\boldsymbol{b}^{(o)}$	the first approximation of the parameters $\boldsymbol{b}$
F	objective function, Eq. (*1*)
$F_{H,\mathrm{het}}$	contribution of the objective function corresponding to excess enthalpy data in the heterogeneous region
$G^E(T,x_1,\boldsymbol{b})$	excess Gibbs energy (a function of T, x_1 and $\boldsymbol{b}$), J mol^{-1}
$H^E(x_1)$	excess enthalpy in the homogeneous region (a function x_1), J mol^{-1}
$H^E(x_1^F)$	excess enthalpy in the heterogeneous region (a function x_1^F), J mol^{-1}
$H^E(\hat{x}_1)$, $H^E(\hat{z}_1)$	excess enthalpy corresponding to the LLE composition, J mol^{-1}
$n^{(1)}$, $n^{(2)}$	amount of the first and the second liquid phase, mol
Q	dimensionless excess Gibbs energy, Eq. (*20*)
Q^D	heat of dilution, J mol^{-1}
Q_{Wilson}, Q_{RK}	contribution to Q based on the Wilson and Redlich–Kister equations, Eqs (*21*) and (*24*)
r	number of terms in the Redlich–Kister equation

x_1, z_1	mole fractions of the component 1
$\hat{x}_1^{\mathrm{new}}$, $\hat{x}_1^{\mathrm{old}}$	new and old approximation of $\hat{x}_1$ in the first coexisting phase
$\hat{z}_1^{\mathrm{new}}$, $\hat{z}_1^{\mathrm{old}}$	new and old approximation of $\hat{z}_1$ in the second coexisting phase
$\hat{x}_1$, $\hat{z}_1$	composition of coexisting liquid phases in mole fraction of the component 1
x_1^{F}	feed composition, Eq. (*2*)
$x^{(\mathrm{i})}$, $x^{(\mathrm{f})}$	composition of the initial and final mixtures, Eq. (*19*)
T	temperature, K
T_{R}	reduced temperature $T_{\mathrm{R}} = T/T_{\mathrm{ref}}$
T_{ref}	reference temperature (T_{ref} = 300 K in this work), K
V_i	liquid molar volume of the *i*-th component, mol cm^{-3}, Eq. (*22*)
v_i^{exp}, v_i^{calc}	experimental and calculated values of a variable v_i used in the objective function, Eq. (*1*)
$\bar{\gamma}_i$, $\tilde{\gamma}_i$	activity coefficients of the *i*-th component in the first and the second liquid phase, Eqs (*14*) and (*15*)
α_{ij}, β_{ij}, γ_{ij}	temperature independent parameters of the Wilson equation (involved in ***b***), Eq. (*23*)
α_{ijk}, β_{ijk}, γ_{ijk}	temperature independent parameters of the Redlich–Kister equation (involved in ***b***), Eq. (*25*)
ϕ	relative amount of the first liquid phase, Eq. (*2*)
η, μ	relaxation parameters in Eq. (*5*)
$\sigma_{H_{\mathrm{het}}}$	estimated error of experimental data (standard deviation) on excess enthalpy in the heterogeneous region, J mol^{-1}, Eq. (*4*)
σ_{v_i}	estimated error of experimental data (standard deviation) on the variable ν_i , Eq. (*1*)

Abbreviations

MTBE	methyl *tert*-butyl ether
LLE	liquid–liquid equilibrium
MML	method of maximum likelihood
MLS	method of least-squares

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