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## ESTIMATION OF THE VAPOUR-LIQUID EQUILIBRIUM DATA OF $N$ -COMPONENT SYSTEM BY A MODIFIED METHOD OF BINARY CONTRIBUTIONS\*

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A method is proposed making it possible to calculate excess quantities of a multicomponent system on the basis of knowledge of this excess quantity for the constituent binary systems. The method is applied to the calculation of vapour-liquid equilibrium data of multicomponent systems.

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The equilibrium data of multicomponent mixtures are very important for the technologic practice. They are needed for calculating the processes such as *e.g.* rectification, extraction, *etc.* The experimental equilibrium data of  $N$ -component system occur in the literature, naturally, most often in case of  $N = 2$ , far less in case of  $N = 3$  and only exceptionally for  $N > 3$ . Therefore great attention is paid to the estimation methods which enable one to determine the equilibrium values of multicomponent systems on the basis of more easily available data.

In this work a method is derived which makes it possible to calculate the excess quantities  $Q$  in  $N$ -component system on the basis of knowledge of the same excess quantity for the constituent binary systems. The quantity  $Q$  can be *e.g.* excess Gibbs energy, heat of mixing, excess volume, *etc.* The proposed method is applied to the calculation of vapour-liquid equilibrium data of multicomponent system because in this region there exist most experimental data enabling to test the method proposed. The results obtained by the Wilson equation<sup>1</sup> and by the UNIFAC method<sup>2</sup> are given as well for comparison. The impulse to the derivation of the method proposed were the works due to Scatchard and coworkers<sup>3</sup> (estimation and correlation of heats of mixing), Ramalho and Ruel<sup>4</sup> (estimation and correlation of heats of mixing) and Jacob and Fitzner<sup>5</sup> (estimation and correlation of excess Gibbs energy of alloys). This work is reassumed by Prchal and coworkers<sup>6</sup> (testing estimation methods for heats of mixing) and Cibulka<sup>7</sup> (testing estimation methods for excess volume of liquid mixtures).

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## THEORETICAL

The original method of binary contributions has the form

$$Q(\mathbf{x}) = \sum_{i < j}^N Q_{ij}(x_i, x_j), \quad (1)$$

where  $Q$  is the excess quantity of the  $N$ -component system and  $Q_{ij}$  is the same excess quantity of the binary system  $(i)-(j)$ . The vector  $\mathbf{x} = (x_1, x_2, \dots, x_N)$  is the vector of mole fractions in the  $N$ -component system. For the sake of simplicity of the record, the temperature and pressure dependence of excess quantities is for the present neglected. It is evident that Eq. (1) fulfils the boundary conditions  $Q \rightarrow Q_{ij}$  if  $x_i + x_j \rightarrow 1$  and, consequently,  $Q \rightarrow 0$  if  $x_i \rightarrow 1$ .

A drawback of the method (1) consists in the fact that the value of  $Q_{ij}$  is determined from the non-physical values of mole fractions  $x_i$  and  $x_j$  because  $x_i + x_j = 1$  does not hold for  $N > 2$ . This leads to some paradoxical results: Let us consider a binary system  $(i)-(j)$  which is described by the two-parameter Redlich-Kister equation

$$Q_{ij} = x_i x_j (a_{ij} + b_{ij}(x_i - x_j)) \quad (2)$$

and simultaneously by the two-parameter Margules equation

$$Q_{ij} = x_i x_j (A_{ij} x_i + B_{ij} x_j), \quad (3)$$

where  $a_{ij}$ ,  $b_{ij}$ ,  $A_{ij}$  and  $B_{ij}$  are constants. Both the equations are equivalent for a binary system for, with regard to the validity of the relation  $x_i + x_j = 1$ , it is possible to derive the relations

$$A_{ij} = a_{ij} + b_{ij}, \quad B_{ij} = a_{ij} - b_{ij}. \quad (4)$$

Thus, it is indifferent whether Eq. (2) or (3) is used for reduction of experimental binary data. Now let us consider the case  $N > 2$ . If we insert Eq. (4) into Eq. (3) we obtain

$$\begin{aligned} Q_{ij}^{\text{MG}} &= x_i x_j ((a_{ij} + b_{ij}) x_i + (a_{ij} - b_{ij}) x_j) = \\ &= x_i x_j (a_{ij}(x_i + x_j) + b_{ij}(x_i - x_j)) = \\ &= Q_{ij}^{\text{RK}} - (1 - x_i - x_j) a_{ij} x_i x_j, \end{aligned} \quad (5)$$

where the index MG or RK denotes the Margules or Redlich-Kister equation, respectively. In the ternary system we have (Eq. (1))

$$Q(x_1, x_2, x_3) = Q_{12}(x_1, x_2) + Q_{13}(x_1, x_3) + Q_{23}(x_2, x_3). \quad (6)$$

If we insert Eq. (5) into (6) we get

$$Q^{\text{MG}} = Q^{\text{RK}} - x_1 x_2 x_3 (a_{12} + a_{13} + a_{23}). \quad (7)$$

Relation (7) contains a paradoxical result. Even if we have chosen two equivalent equations for the description of binary systems, the calculated values for the ternary system are different in both cases.

To eliminate the mentioned failure we have considered the function  $Q$  in the form

$$Q(\mathbf{x}) = \sum_{i < j}^N p_{ij}(\mathbf{x}) Q_{ij}(x_i^*, x_j^*), \quad (8)$$

where  $p_{ij}(\mathbf{x})$  are unknown functions and it holds  $x_i^* + x_j^* = 1$  for an arbitrary pair  $i, j$  ( $i \neq j$ ). To determine the functions  $p_{ij}(\mathbf{x})$  we have used the principle of solution regularity conservation: If each binary solution is regular (*i.e.*  $Q_{ij} = a_{ij}x_i x_j$  for all the pairs  $i-j$ ) then also the corresponding  $N$ -component solution is regular,

*i.e.*  $Q = \sum_{i < j}^N a_{ij}x_i x_j$ . The statistical-thermodynamic interpretation of this principle is as follows<sup>8</sup>: If random mixing between an arbitrary pair of molecules takes place then the corresponding group of  $N$  molecules mixes randomly, too. If we "insert" the principle of solution regularity conservation into Eq. (8) we obtain the relation

$$\sum_{i < j}^N a_{ij}x_i x_j = \sum_{i < j}^N p_{ij}(\mathbf{x}) a_{ij}x_i^* x_j^* \quad (9)$$

which can be rearranged into the form

$$\sum_{i < j}^N a_{ij}[x_i x_j - p_{ij}(\mathbf{x}) x_i^* x_j^*] = 0. \quad (10)$$

Since Eq. (10) must hold for any values of parameters  $a_{ij}$ , the functions  $p_{ij}$  are given by the expressions

$$p_{ij}(\mathbf{x}) = x_i x_j / x_i^* x_j^* \quad (11)$$

which implies the relation for function  $Q$  in the form

$$Q(\mathbf{x}) = \sum_{i < j}^N \frac{x_i x_j}{x_i^* x_j^*} Q_{ij}(x_i^*, x_j^*). \quad (12)$$

The values of composition  $x_i^*, x_j^* = 1 - x_i^*$  of binary solution ( $i$ )-(j) can be chosen in many ways. Some possibilities are depicted in Fig. 1. In the first variant

(Fig. 1a) we choose such a binary point whose distance from the point  $\mathbf{x}$  is smaller than that of the other binary points. If we denote the distance of the  $N$ -component point  $\mathbf{x}$  from the binary point  $\mathbf{x}^*$  by a symbol  $q(\mathbf{x}, \mathbf{x}^*)$  then we have

$$q^2 = \sum_{k \neq i, j}^N x_k^2 + (x_i - x_i^*)^2 + (x_j - 1 + x_i^*)^2. \quad (13)$$

From the condition  $dq^2/dx_i^* = 0$  it follows

$$x_i^* = (1 + x_i - x_j)/2, \quad x_j^* = 1 - x_i^* = (1 + x_j - x_i)/2. \quad (14)$$

If we insert Eq. (14) into Eq. (12) we obtain the expression for calculating the function  $Q$ :

$$Q(\mathbf{x}) = \sum_{i < j}^N \frac{4x_i x_j}{1 - (x_i - x_j)^2} Q_{ij} \left( \frac{1 + x_i - x_j}{2}, \frac{1 + x_j - x_i}{2} \right). \quad (15)$$

It follows  $x_i^* - x_j^* = x_i - x_j$  from Eq. (14) which means that the value  $x_i - x_j$  is constant on the line segment  $\overline{\mathbf{x}, \mathbf{x}^*}$ . Therefore Eq. (15) is identical with Eq. (1) when the individual binary systems are described by the Redlich-Kister equation

$$Q_{ij}^{\text{RK}} = x_i x_j (a_{ij} + b_{ij}(x_i - x_j) + c_{ij}(x_i - x_j)^2 + \dots). \quad (16)$$

Another possible choice of composition of binary solution is evident from Fig. 1b. On the line segment  $\overline{\mathbf{x}, \mathbf{x}^*}$  there is a constant ratio  $x_i/x_j$  in this case and we have

$$x_i^* = \frac{x_i}{x_i + x_j}, \quad x_j^* = 1 - x_i^* = \frac{x_j}{x_i + x_j}. \quad (17)$$

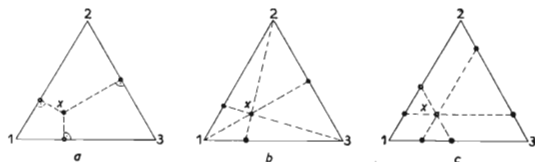


FIG. 1

Different possibilities of choosing the binary points

On inserting Eq. (17) into Eq. (12) we obtain a relation for function  $Q$  in the form

$$Q(\mathbf{x}) = \sum_{i < j}^N (x_i + x_j)^2 Q_{ij} \left( \frac{x_i}{x_i + x_j}, \frac{x_j}{x_i + x_j} \right). \quad (18)$$

And finally the third variant is illustrated in Fig. 1c. Unlike the foregoing two cases we include in this case two data of each binary system into the calculation:

$$\begin{aligned} x_i^{*,1} &= x_i, & x_j^{*,1} &= 1 - x_i, \\ x_i^{*,2} &= 1 - x_j, & x_j^{*,2} &= x_j. \end{aligned} \quad (19)$$

Since both the binary points are considered equally significant, it holds

$$Q(\mathbf{x}) = \frac{1}{2} \sum_{i < j}^N \left[ \frac{x_j}{1 - x_i} Q_{ij}(x_i, 1 - x_i) + \frac{x_i}{1 - x_j} Q_{ij}(1 - x_j, x_j) \right]. \quad (20)$$

An advantage of the prediction relations of type (12) is that binary systems need not be described by the same correlation equation.

#### *Application to the Calculation of Vapour-Liquid Equilibrium of N-Component System*

The conditions of the vapour-liquid phase equilibrium in  $N$ -component system can be written in the form

$$f_i^{(l)} = f_i^{(g)}, \quad i = 1, 2, \dots, N, \quad (21)$$

where  $f_i^{(l)}$  and  $f_i^{(g)}$  are fugacities of the  $i$ -th component in the liquid and the vapour phase, respectively. It follows<sup>9</sup> from the well-known thermodynamic relations

$$\begin{aligned} f_i^{(g)} &= y_i P v_i^{(g)}, \\ f_i^{(l)} &= \gamma_i x_i P_i^0 \delta_i^{(0,l)}, \quad i = 1, 2, \dots, N, \end{aligned} \quad (22)$$

where  $x_i$  and  $y_i$  are the mole fractions of the  $i$ -th component in the liquid and the vapour phase, respectively,  $P$  is the total pressure,  $P_i^0$  the saturated vapour pressure of the pure  $i$ -th component at the system temperature  $T$ ,  $v_i^{(g)}$  is the fugacity coefficient of the  $i$ -th component in the gas mixture at the system temperature and pressure,  $\delta_i^{(0,l)}$  is the correction for the pressure dependence of fugacity of pure component  $i$  and  $\gamma_i$  is the activity coefficient. Assuming that the values of the second virial coefficients are sufficient to describe the  $P$ - $V$ - $T$  behaviour of the gas mixture, Eq. (22) can be rewritten into the form<sup>9</sup>

$$y_i P \varphi_i = \gamma_i x_i P_i^0, \quad i = 1, 2, \dots, N \quad (23)$$

where, for the correction factor  $\varphi_i = v_i^{(g)}/\delta_i^{(0,l)}$ , we have

$$\ln \varphi_i = \frac{P}{RT} \left[ 2 \sum_{j=1}^N y_j B_{ij} - \sum_{i=1}^N \sum_{j=1}^N y_i y_j B_{ij} - \frac{B_{ii} P_i^0 + v_i^{(l)} (P - P_i^0)}{P} \right],$$

$$i = 1, 2, \dots, N, \quad (24)$$

where  $B_{ij} = B_{ij}(T)$  are the second virial coefficients,  $v_i^{(l)}$  is the molar volume of the  $i$ -th component in the liquid phase at the system temperature and  $R$  is the gas constant.

From thermodynamic relations for partial molar quantities follows

$$\ln \gamma_k = Q + \frac{\partial Q}{\partial x_k} - \sum_{i=1}^{N-1} x_i \frac{\partial Q}{\partial x_i}, \quad k = 1, 2, \dots, N-1$$

$$\ln \gamma_N = Q - \sum_{i=1}^{N-1} x_i \frac{\partial Q}{\partial x_i}, \quad (25)$$

where

$$Q = \sum_{i=1}^N x_i \ln \gamma_i \quad (26)$$

is the dimensionless molar excess Gibbs energy. The values of derivatives on the right-hand side of Eq. (25) are determined at a fixed value of the system temperature and pressure and at the restraining condition

$$x_N = 1 - \sum_{i=1}^{N-1} x_i. \quad (27)$$

To test Eqs (15), (18) and (20) we chose 31 ternary systems, 2 quaternary systems and 1 quinary system. The ternary systems were chosen so that all possible combinations of polar ( $P$ ) and non-polar ( $N$ ) components should be evenly represented, i.e. the systems  $NNN$ ,  $NNP$ ,  $NPP$  and  $PPP$ . Even though Eqs (15), (18), (20) make it possible to choose various correlation equations to reduce binary data, the Wilson equation<sup>1</sup> was chosen uniformly for all the systems:

$$Q = -x_1 \ln(x_1 + A_{12}x_2) - x_2 \ln(x_2 + A_{21}x_1), \quad (28)$$

$$A_{ij} = \frac{v_j}{v_i} \exp\left(-\frac{c_{ij}}{RT}\right),$$

where  $v_i$  is the molar volume of the  $i$ -th component in the liquid phase and  $c_{ij}$  is a constant. This choice makes it possible to compare the results of the proposed method with those obtained in terms of the multicomponent Wilson equation. As a criterion function for calculating the parameters  $c_{12}$  and  $c_{21}$ , the sum of squares of unweighted deviations in  $\ln(\gamma_1/\gamma_2)_{\text{exp}} - \ln(\gamma_1/\gamma_2)_{\text{calc}}$  was chosen. The virial coefficients needed to describe the  $P$ - $V$ - $T$  behaviour of gas mixtures were determined by the generalized method proposed by Hayden and O'Connell<sup>10</sup>. The values of saturated vapour pressures were calculated from the Antoine equation. Parameters of this equation were taken from the literature<sup>11,12</sup>. The linear dependence of molar volume of pure component in the liquid phase on temperature was established from the data reported in the Timmermans monograph<sup>13</sup>. Overall 74 binary systems, which constitute the above-mentioned 34 multicomponent systems tested, were treated in this way.

First let us deal with the calculation of the value of the dimensionless molar excess Gibbs energy  $Q$  in terms of the general relation (12). Let us consider an isobaric or isothermal multicomponent system with the given composition of the liquid phase  $\mathbf{x} = (x_1, x_2, \dots, x_N)$ . First the binary points  $x_i^*$ ,  $x_j^* = 1 - x_i^*$  are determined for each pair  $i$ - $j$  ( $i < j$ ), i.e. one of Eqs (15), (18) or (20) is chosen. Further we must attach a value of temperature (isobaric system) or pressure (isothermal system) to each binary point. Without detriment of generality let us consider the binary system (1)-(2). It follows from Eq. (23) for  $N = 2$

$$P = \frac{\gamma_1 x_1^* P_1^0(T)}{\varphi_1} + \frac{\gamma_2 x_2^* P_2^0(T)}{\varphi_2}. \quad (29)$$

From Eq. (29) we calculate the temperature  $T$  (isobaric system) or the pressure  $P$  (isothermal system) which belongs to the binary point  $x_1^*$ ,  $x_2^*$ . The relation for calculating the activity coefficients  $\gamma_1$  and  $\gamma_2$  in binary system can be determined from Eq. (25). It holds

$$\ln \gamma_1 = Q + x_2 \partial Q / \partial x_1, \quad \ln \gamma_2 = Q - x_1 \partial Q / \partial x_1. \quad (30)$$

On inserting Eq. (28) into (30) we obtain the relation for calculating activity coefficients in binary system from the Wilson equation and this relation is inserted into Eq. (29). Consequently Eq. (29) contains only one unknown quantity -  $T$  or  $P$  (the values of composition of gas mixture needed for calculating the corrections  $\varphi_1$  and  $\varphi_2$  are determined from the relation  $y_i = \gamma_i x_i^* P_i^0 / P$ ). So all the quantities are determined which are needed for calculating the value of function  $Q(\mathbf{x})$  from Eq. (12).

To calculate the composition of the gas phase and temperature (or pressure) of the  $N$ -component system (Eq. (23)) it is yet necessary to determine the values of activity coefficients  $\gamma_i$  ( $i = 1, 2, \dots, N$ ) from Eq. (25). The values of derivatives

on the right-hand side of Eq. (25) were determined numerically in this work from the relation

$$\frac{\partial Q}{\partial x_i} = \frac{Q(x_i + h, x_N - h) - Q(x_i - h, x_N + h)}{2h}, \quad i = 1, 2, \dots, N - 1 \quad (31)$$

where  $Q(x_i + h, x_N - h)$  is the value of function  $Q$  at the point  $(x_1, \dots, x_{i-1}, x_i + h, x_{i+1}, \dots, x_{N-1}, x_N - h)$ . Relation (31) was chosen on the basis of the following consideration: Let us consider a sufficiently smooth function of one variable  $f(x)$ . We can easily derive from the Taylor formula that

$$f'(x) = \frac{f(x + h) - f(x - h)}{2h} + \frac{1}{6}h^2 f'''(\xi), \quad (32)$$

where  $\xi \in (x - h, x + h)$ . If the function  $f(x)$  is a quadratic function of the variable  $x$  (i.e.  $f'''(\xi) = 0$ ) then for every  $x$  and every  $h$  holds

$$f'(x) = \frac{f(x + h) - f(x - h)}{2h}. \quad (33)$$

Thus, if the considered solution were regular (i.e.  $Q = \sum_{i < j} a_{ij} x_i x_j$ ) then Eq. (31) would hold precisely. Strictly speaking it would be sufficient if the solution were regular in a certain neighbourhood of the point  $\mathbf{x}$ . The concrete calculations which were performed showed that the value on the right-hand side of Eq. (31) is practically constant for  $h \in (0.0001, 0.01)$ . In this work  $h = 0.001$  was chosen. An advantage of this procedure is numerically easy determination of derivatives required on the assumption that the temperature and pressure dependence of the function  $Q$  is neglected. It holds obviously

$$\left(\frac{\partial Q}{\partial x_i}\right)_T = \left(\frac{\partial Q}{\partial x_i}\right)_{T,P} + \left(\frac{\partial Q}{\partial P}\right)_T \left(\frac{\partial P}{\partial x_i}\right)_T, \quad (34)$$

$$\left(\frac{\partial Q}{\partial x_i}\right)_P = \left(\frac{\partial Q}{\partial x_i}\right)_{T,P} + \left(\frac{\partial Q}{\partial T}\right)_P \left(\frac{\partial T}{\partial x_i}\right)_P$$

and

$$(\partial Q/\partial P)_T = v^E/RT, \quad (\partial Q/\partial T)_P = -\kappa^E/RT^2, \quad (35)$$

where  $v^E$  is the excess molar volume and  $\kappa^E$  is the molar heat of mixing. By using the procedure according to Eq. (31) we determine the values of derivatives either



at constant temperature (isothermal system) or only at constant pressure (isobaric system) whereas the given derivatives in Eq. (25) are meant at constant temperature and pressure.

By inserting Eq. (31) into (25) we determine the values of activity coefficients. The value of temperature or pressure is then calculated from the equation which results from adding the equilibrium conditions (23)

$$P = \sum_{i=1}^N \gamma_i x_i P_i^0(T) / \varphi_i \quad (36)$$

As a criterion of quality of the methods tested we chose the deviations  $\Delta y$ ,  $\Delta T$  (isobaric system) and  $\Delta P$  (isothermal system) defined by the relations

$$\Delta y = \sum_{k=1}^L \sum_{i=1}^N |y_{i,k}^{\text{calc}} - y_{i,k}^{\text{exp}}| / LN$$

$$\Delta T = \sum_{k=1}^L |T_k^{\text{calc}} - T_k^{\text{exp}}| / L, \quad \Delta P = \sum_{k=1}^L |P_k^{\text{calc}} - P_k^{\text{exp}}| / L, \quad (37)$$

where  $L$  is the number of experimental points in  $N$ -component system.

To compare the estimation methods based on Eq. (12) with other methods the same calculation was carried out for the given set of multicomponent systems by means of the multicomponent Wilson equation<sup>1</sup>

$$Q = - \sum_{i=1}^N x_i \ln \left( \sum_{j=1}^N x_j A_{ij} \right), \quad (38)$$

$$A_{ii} = 1, \quad A_{ij} = \frac{v_j}{v_i} \exp(-c_{ij}/RT), \quad i \neq j$$

which includes only the binary parameters  $c_{ij}$  which were determined from binary data (Eq. (28)).

The results are presented in Table I. The data in the first to fourth columns are evident. The fourth and fifth columns include the values calculated in terms of Eq. (37). The best result is given in the first line (this is meant as the comparison of results of Eqs (15), (18) and (20)) and the worst one in the second line. The value obtained on using the Wilson equation (38) is given in the third line. Most systems are identical with those which have been used by Fredenslund, Gmehling and Rasmussen<sup>2</sup> as testing systems for the UNIFAC method. In such a case the fourth line includes the values which have been given by those authors cited. The last column lists the

TABLE I  
Results of the prediction of vapour-liquid equilibrium data

Number of system	System	$P$ , kPa $T$ , K	Number of points	$\Delta y$	$\Delta T$ , K [ $\Delta P$ , kPa]	Ref.
1	benzene(1)- methylcyclopentane(2)- n-hexane(3)	101.32 kPa	54	0.0042 (18) 0.0044 (15) 0.0061 (W)	0.12 (15) 0.13 (20) 0.73 (W)	33, 30, 56, 63
2	n-hexane(1)-1-hexene(2)- 1,4-dioxane(3)	101.32 kPa	16	0.0077 (18) 0.0077 (20) 0.0064 (W)	0.33 (20) 0.35 (18) 1.05 (W)	46, 46, 46, 46
3	cyclohexane(1)- cyclohexene(2)- 1,2-dichloro ethane(3)	101.32 kPa	43	0.0138 (15) 0.0139 (18) 0.012 (W) 0.012 (U)	2.45 (18) 2.47 (20) 1.97 (W) 0.6 (U)	40, 40, 40, 40
4	ethanol(1)- methylcyclopentane(2)- n-hexane(3)	101.32 kPa	54	0.0108 (20) 0.0140 (15) 0.0091 (W)	0.32 (20) 0.46 (15) 0.45 (W)	53, 50, 56, 64
5	ethanol(1)- benzene(2)-cyclohexane(3)	101.32 kPa	56	0.0162 (20) 0.0177 (15) 0.0133 (W)	1.02 (20) 1.12 (15) 1.0 (W)	26, 41, 24, 65
6	ethanol(1)-benzene(2)- n-heptane(3)	53.33 kPa	50	0.0209 (20) 0.0232 (15) 0.0155 (W) 0.032 (U)	0.86 (20) 1.0 (15) 0.63 (W) 2.1 (U)	27, 49, 27, 27
7	benzene(1)-ethanol(2)- n-hexane(3)	101.32 kPa	7	0.0126 (20) 0.0160 (15) 0.0060 (W)	0.89 (18) 1.24 (15) 0.58 (W)	26, 30, 50, 66
8	ethanol(1)- 1,2-dichloroethane(2)- benzene(3)	313.5 K	63	0.0087 (18) 0.0098 (15) 0.0079 (W) 0.011 (U)	0.41 (18) 0.53 (20) 0.69 (W) 0.72 (U)	28, 28, 25, 28
9	benzene(1)-n-heptane(2)- 1-propanol(3)	348.15 K	77	0.0149 (20) 0.0165 (18) 0.0122 (W) 0.018 (U)	1.56 (20) 1.75 (15) 1.43 (W) 1.33 (U)	29, 29, 29, 67

TABLE I  
(Continued)

Number of system	System	$P$ , kPa $T$ , K	Number of points	$\Delta y$	$\Delta T$ , K [ $\Delta P$ , kPa]	Ref.
10	tetrachloromethane(1)- cyclohexane(2)- 2-propanol(3)	101.32 kPa	60	0.0285 (18) 0.0304 (15) 0.0265 (W) 0.027 (U)	1.25 (18) 1.33 (15) 1.16 (W) 1.4 (U)	43, 61, 42, 43
11	tetrachloromethane(1)- benzene(2)-2-propanol(3)	101.32 kPa	39	0.0068 (18) 0.009 (15) 0.0052 (W) 0.011 (U)	0.41 (18) 0.48 (15) 0.36 (W) 0.6 (U)	35, 61, 34, 61
12	n-hexane(1)-benzene(2)- 1-butanol(3)	101.32 kPa	57	0.0196 (20) 0.0205 (15) 0.0188 (W)	0.75 (20) 0.86 (15) 0.82 (W)	30, 36, 23, 36
13	methyl acetate(1)- benzene(2)-cyclohexane(3)	101.32 kPa	60	0.0058 (18) 0.0059 (20) 0.0054 (W) 0.011 (U)	0.23 (20) 0.23 (18) 0.30 (W) 0.3 (U)	31, 24, 24, 24
14	acetone(1)- tetrachloromethane(2)- benzene(3)	101.32 kPa	58	0.0056 (15) 0.0059 (18) 0.0054 (W) 0.010 (U)	0.45 (20) 0.46 (18) 0.45 (W) 0.7 (U)	20, 14, 35, 68
15	benzene(1)-n-heptane(2)- acetonitrile(3)	101.32 kPa	36	0.0252 (20) 0.0322 (15) 0.0308 (W) 0.023 (U)	0.69 (20) 0.88 (15) 0.84 (W) 1.3 (U)	21, 21, 21, 21
16	acetonitrile(1)- benzene(2)-n-heptane(3)	318.15 K	51	0.0211 (20) 0.0240 (18) 0.0181 (W) 0.02 (U)	1.81 (20) 2.03 (18) 1.12 (W) 1.73 (U)	22, 22, 22, 22
17	ethanol(1)-water(2)- 1,4-dioxane(3)	101.32 kPa	19	0.0194 (20) 0.0217 (18) 0.0176 (W) 0.022 (U)	1.54 (15) 1.66 (20) 1.21 (W) 1.1 (U)	54, 45, 47, 47
18	2,3-dimethylbutane(1)- methanol(2)- chloroform(3)	101.32 kPa	20	0.0161 (20) 0.0198 (18) 0.0078 (W)	0.86 (20) 1.14 (15) 0.20 (W)	44, 15, 55, 44

TABLE I  
 (Continued)

Number of system	System	$P$ , kPa $T$ , K	Number of points	$\Delta y$	$\Delta T$ , K [ $\Delta P$ , kPa]	Ref.
19	acetone(1)-chloroform(2)- 2,3-dimethylbutane(2)	101.32 kPa	19	0.0104 (15) 0.0106 (18) 0.0074 (W) 0.020 (U)	0.56 (18) 0.57 (20) 0.27 (W) 1.3 (U)	17, 15, 15, 69
20	2,3-dimethylbutane(1)- methanol(2)-acetone(3)	101.32 kPa	27	0.0073 (15) 0.0097 (18) 0.0051 (W) 0.016 (U)	0.33 (20) 0.41 (18) 0.36 (W) 0.50 (U)	44, 15, 16, 15
21	methyl acetate(1)- chloroform(2)-benzene(3)	101.32 kPa	91	0.0034 (15) 0.0036 (18) 0.0038 (W) 0.007 (U)	0.17 (15) 0.18 (20) 0.16 (W) 0.2 (U)	31, 31, 31, 31
22	acetone(1)-methanol(2)- ethanol(3)	101.32 kPa	91	0.0077 (15) 0.0079 (18) 0.007 (W) 0.014 (U)	0.24 (15) 0.26 (18) 0.2 (W) 0.7 (U)	16, 16, 52, 16
23	acetone(1)-methanol(2)- 2-propanol(3)	101.32 kPa	21	0.0082 (20) 0.0084 (18) 0.012 (W) 0.010 (U)	0.32 (20) 0.34 (18) 0.97 (W) 0.3 (U)	16, 18, 58, 18
24	acetone(1)-methanol(2)- 2-propanol(3)	328.15 K	27	0.0068 (20) 0.0070 (18) 0.0081 (W)	0.95 (20) 0.97 (15) 0.86 (W)	18, 18, 18, 18
25	chloroform(1)-acetone(2)- ethanol(3)	101.32 kPa	25	0.0101 (15) 0.0116 (18) 0.0225 (W) 0.013 (U)	0.36 (15) 0.43 (18) 1.12 (W) 0.7 (U)	17, 51, 16, 70
26	n-butanone(1)- 2-propanol(2)-water(3)	101.32 kPa	15	0.0152 (15) 0.0176 (18) 0.0119 (W) 0.017 (U)	0.84 (15) 0.90 (18) 0.56 (W) 0.7 (U)	34, 39, 62, 71
27	chloroform(1)- methanol(2)- ethyl acetate(3)	101.32 kPa	71	0.0118 (18) 0.0129 (20) 0.0107 (W) 0.011 (U)	0.77 (18) 0.84 (20) 0.66 (W) 0.6 (U)	55, 55, 55, 55

TABLE I  
(Continued)

Number of system	System	$P$ , kPa $T$ , K	Number of points	$\Delta y$	$\Delta T$ , K [ $\Delta P$ , kPa]	Ref.
28	chloroform(1)- methanol(2)- methyl acetate(3)	101.32 kPa	13	0.0077 (20) 0.0083 (18) 0.0080 (W)	0.39 (18) 0.44 (15) 0.44 (W)	55, 31, 31, 32
29	ethyl acetate(1)- ethanol(2)-water(3)	343.15 K	9	0.0129 (18) 0.0159 (15) 0.0219 (W) 0.041 (U)	1.01 (18) 1.28 (20) 2.43 (W) 9.2 (U)	48, 48, 48, 48
30	methanol(1)-ethanol(2)- water(3)	101.32 kPa	28	0.0206 (18) 0.0221 (15) 0.0325 (W) 0.029 (U)	1.05 (18) 1.22 (15) 1.47 (W) 1.3 (U)	52, 59, 54, 52
31	water(1)-1-propanol(2)- 1-butanol(3)	101.32 kPa	16	0.0271 (15) 0.0298 (20) 0.0147 (W) 0.018 (U)	2.5 (15) 3.0 (18) 0.6 (W) 0.3 (U)	60, 38, 37, 72
32	n-hexane(1)- methylcyclopentane(2)- ethanol(3)-benzene(4)	101.32 kPa	20	0.0127 (20) 0.0160 (18) 0.0067 (W)	1.63 (20) 1.99 (18) 0.76 (W)	56, 50, 30 53, 33, 26 63
33	benzene(1)- chloroform(2)- methanol(3)- methyl acetate(4)	101.32 kPa	29	0.0052 (18) 0.0055 (20) 0.0064 (W)	0.30 (18) 0.32 (20) 0.37 (W)	31, 32, 31 55, 31, 57 32
34	acetone(1)-benzene(2)- chloroform(3)- methanol(4)- methyl acetate(5)	101.32 kPa	15	0.0059 (18) 0.0067 (20) 0.0070 (W)	0.18 (18) 0.27 (20) 0.31 (W)	14, 17, 16, 19 32

literature sources of the binary and multicomponent experimental data. In case of the ternary systems, the first citation refers to the system (1)-(2), the second one to the system (1)-(3), the third one to the system (2)-(3) and finally the fourth one to the system (1)-(2)-(3).

## DISCUSSION

The difficulties connected with testing the method proposed consist among others in the fact that the binary and multicomponent experimental data are often mutually inconsistent. There are only very few cases when the binary and multicomponent data, too, were measured by the same authors. To eliminate at least partly the effect of the inconsistency mentioned, all the binary data were reduced by the Wilson equation (28), which makes it possible to compare the results of the method proposed with those reached by means of the multicomponent Wilson equation (38). An increase of deviations between the experimental and calculated value in case of lower content (less than 10%) of alcohol in the mixture manifests itself clearly in case of systems alcohol-non-polar component-non-polar component. Similarly with systems 16, 18, 19, 20, 22, 26, 27, 30, 31 and 32 the largest deviations appear in case of a low content of one of components, which proves likely the mutual inconsistency of the binary and ternary data.

From overall number of thirty four systems tested, a deviation  $\Delta y < 0.01$  was attained for fifteen systems,  $\Delta y < 0.02$  for thirteen systems and for remaining six ones, the deviation in the vapour phase composition is lower than 0.03. The scatter of results obtained from Eqs (15), (18) and (20) is surprisingly small. For systems *NNP* and *NPP* the best agreement is shown with Eq. (20) and the worst with Eq. (15). For systems *PPP*, Eq. (18) yields rather better results. In case of *NNN* systems, Eqs (15), (18) and (20) are equivalent. On the average, Eq. (20) yields the best results.

The comparison of results of Eqs (15), (18) and (20) with the Wilson multicomponent equation (38) purports mildly in favour of the Wilson equation. In case of the limited miscibility of systems (*e.g.* 26 and 31) the use of the Wilson equation is not physically correct even though just for these systems the Wilson equation yielded very good results. The results obtained by the UNIFAC equation were available<sup>2</sup> for 22 ternary systems. This method yields worse results, however, its indisputable advantage consists in the universality of calculating the activity coefficients.

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