

EFFECT OF THE COURSE OF THE SECOND DERIVATIVE  
OF GIBBS' ENERGY IN BINARY MIXTURES  
ON THE LIQUID-LIQUID EQUILIBRIUM IN TERNARY SYSTEM\*

Josef P. NOVÁK, Jaroslav MATOUŠ, Josef ŠOBR and Jiří PICK

*Department of Physical Chemistry,*

*Prague Institute of Chemical Technology, 166 28 Prague 6*

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The effect of the course of  $G_{11}(x_1)$  in binary systems is studied on the binodal curve shape, the extent of heterogeneous region and the inclination of tie-lines in the ternary system. The effect of individual quantities is shown both on model calculations and on the systems acetonitrile-benzene-n-heptane, water-benzene-ethanol and water-benzene-2-propanol. The UNIQUAC and the modified Wilson equations were employed for calculating.

Phase splitting of a system into two or more liquid phases is conditioned by a certain degree of non-ideality whose quantitative measure in a binary system is the second derivative of Gibbs' energy with respect to composition<sup>1</sup>, *i.e.*

$$G_{11} = [\partial^2(G^M/RT)/\partial x_1^2]_{T,P}. \quad (1)$$

In homogeneous systems in the entire concentration range, the condition<sup>2-5</sup>

$$G_{11} > 0 \quad (2)$$

must hold. In heterogeneous systems in a certain concentration range (in so-called labile region), the condition (2) is not fulfilled.

In case of multicomponent systems it is necessary to take a quantity  $D$  as a quantitative measure of deviations from ideality, where

$$D = \begin{vmatrix} G_{11} & G_{12} & \dots & G_{1(N-1)} \\ G_{12} & G_{22} & \dots & G_{2(N-1)} \\ \vdots & & & \\ G_{1(N-1)} & \dots & G_{(N-1)(N-1)} \end{vmatrix}. \quad (3)$$

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For a homogeneous system it must again hold<sup>2-4</sup> in the entire concentration range

$$D > 0, \quad (4)$$

whereas in a heterogeneous system the condition (4) is not fulfilled in a certain concentration range.

To be able to carry out qualified predictions of the non-ideality of multicomponent systems (and so also the liquid-liquid equilibrium) on the basis of binary data, it is necessary that the deviations from ideality of the every binary systems should be represented correctly, *i.e.* the course of  $G11(x_1)$  should be represented quantitatively, especially in the vicinity of its minimum. As it has been shown previously<sup>6,7</sup>, on usual evaluating the correlation equation parameters we obtain such a set of parameters which give more or less shifted course of  $G11(x_1)$ . In such a case we cannot expect a quantitatively correct description of non-ideality even for multicomponent systems. Considering that the liquid-liquid equilibrium is more sensitive to small changes in the course of activity coefficients than the vapour-liquid equilibrium, it is necessary to take into account the quantitative measure of non-ideality, *i.e.* the course of  $G11(x_1)$ , in evaluating the parameters.

From this point of view it is possible to explain the relatively little success when predicting liquid-liquid equilibria in ternary systems on the basis of binary data only. Usually it is necessary to evaluate the parameters also by means of the data on composition of coexisting phases in ternary system<sup>8-11</sup>.

In this work we should like to show the connections between the  $G11(x_1)$  course of individual binary systems and the area and shape of heterogeneous region as well as the course of tie-lines in ternary heterogeneous system.

#### *Analysis of the Effect of $G11(x_1)$ of Binary Systems on Liquid-Liquid Equilibrium in the Ternary System*

The effect of  $G11$  of binary systems on the area and shape of the heterogeneous region was summarized into several rules which are given below and demonstrated in Figs 1-6. The figures correspond to the model computations carried out on the basis of the modified Wilson equation<sup>26</sup>

$$G^E/(RT) = - \sum_{i=1}^3 x_i \ln \sum_{j=1}^3 x_j A_{ij} + b_{13} x_1 x_3, \quad A_{ii} = A_{jj} = 1, \quad (5)$$

(the binary system 1-3 is assumed to be heterogeneous). The presented modification of the Wilson equation consists in adding the term  $b_{13} x_1 x_3$  for heterogeneous binary systems (here just 1-3) or for those ones which are on the critical isotherm. For  $b_{13} = 0$  we get the original Wilson equation. At  $b_{13} > 0$  Eq. (5) can be used also for the here considered heterogeneous ternary systems.

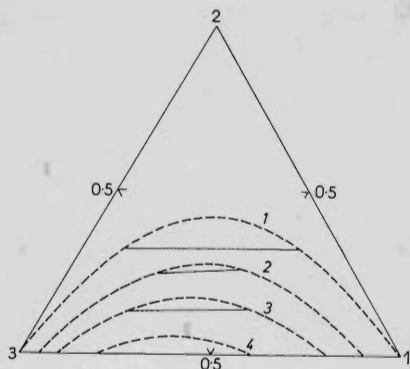


FIG. 1

Effect of mutual solubility of components on the extent of heterogeneous region. For binary systems it is:  $(x_2)_0 = 0.35$ ,  $(G11)_{x_0} = 0.5$  and  $b_{13} = 1.0$ . 1  $\bar{x}_1^0 = 0.001$ ,  $\bar{x}_1^0 = 0.998$ ; 2  $\bar{x}_1^0 = 0.05$ ,  $\bar{x}_1^0 = 0.9$ ; 3  $\bar{x}_1^0 = 0.1$ ,  $\bar{x}_1^0 = 0.8$ ; 4  $\bar{x}_1^0 = 0.2$ ,  $\bar{x}_1^0 = 0.6$

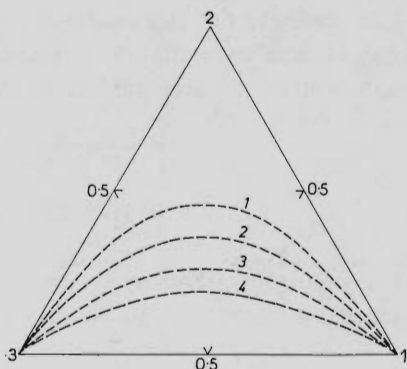


FIG. 2

Effect of the parameter  $b_{13}$  in a binary heterogeneous system on the extent of heterogeneous region. For binary systems it is:  $(x_2)_0 = 0.35$ ,  $(G11)_{x_0} = 1.5$  and  $\bar{x}_1^0 = 0.001$ ,  $\bar{x}_1^0 = 0.998$ . 1  $b_{13} = 1.5$ , 2  $b_{13} = 0.8$ , 3  $b_{13} = 0.4$ , 4  $b_{13} = 0.2$

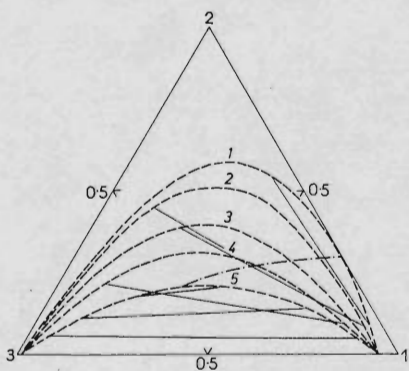


FIG. 3

Effect of  $(G11)_{x_0}$  in the binary system 1—2 on the extent of heterogeneous region. For binary systems it is: 1—2  $(x_2)_0 = 0.3$ ; 1—3  $\bar{x}_1^0 = 0.1$ ,  $\bar{x}_1^0 = 0.95$ ,  $b_{13} = 0.6$ ; 2—3  $(x_2)_0 = 0.65$ ,  $(G11)_{x_0} = 2.0$ . 5  $(G11)_{x_0,1-2} = 3.0$ , 4  $(G11)_{x_0,1-2} = 1$ , 3  $(G11)_{x_0,1-2} = 0.5$ , 2  $(G11)_{x_0,1-2} = 0.2$ , 1  $(G11)_{x_0,1-2} = 0$ ; - - - - critical curve

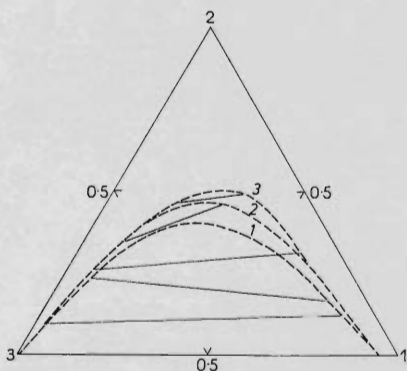


FIG. 4

Effect of  $(x_2)_0$  in the binary system 2—3 on the extent of heterogeneous region. For binary systems it is: 1—2  $(x_2)_0 = 0.35$ ,  $(G11)_{x_0} = 0.5$ ; 1—3  $\bar{x}_1^0 = 0.01$ ,  $\bar{x}_1^0 = 0.95$ ,  $b_{13} = 0.6$ ; 2—3  $(G11)_{x_0} = 0.5$ . 1  $(x_2)_{0,2-3} = 0.2$ , 2  $(x_2)_{0,2-3} = 0.5$ , 3  $(x_2)_{0,2-3} = 0.8$

The parameters of this equation were determined in binary homogeneous systems on the basis of the minimum of the curve  $G11(x_1)$  (obtained from the experimental data on vapour-liquid equilibrium) by solving the system of equations

$$[\partial^2(G^M/RT)/\partial x_1^2]_{x_1=x_0} = (G11)_{x_0, \text{exp}}, \quad (6)$$

$$[\partial^3(G^M/RT)/\partial x_1^3]_{x_1=x_0} = 0.$$

In the heterogeneous binary system 1–3, the parameters were determined on the basis of mutual solubility, *i.e.* by solving the system of equations

$$\begin{aligned} \bar{a}_1(\bar{x}_1^0) &= \bar{a}_1(\bar{x}_1^0), \\ \bar{a}_3(\bar{x}_1^0) &= \bar{a}_3(\bar{x}_1^0) \end{aligned} \quad (7)$$

for chosen values of  $b_{13}$ .

The extent of heterogeneous region depends primarily on mutual solubility of components in the heterogeneous binary system. The less the substances are mutually miscible, the larger will be the two-phase region. In Fig. 1 an example of four binodal curves is presented which were calculated for different mutual solubili-

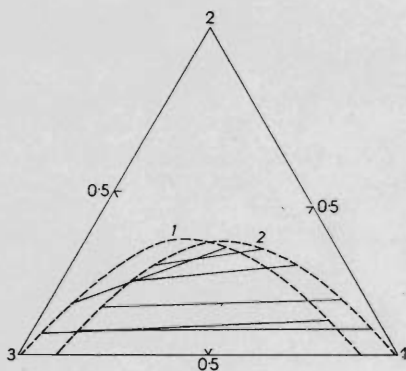


FIG. 5

Effect of asymmetric solubility on the inclination of tie-lines. Properties of binary systems: 1–2  $(x_2)_0 = 0.3$ ,  $(G11)_{x_0} = 0.5$ ; 2–3  $(x_2)_0 = 0.3$ ,  $(G11)_{x_0} = 0.4$ ; 1–3  $b_{13} = 1.0$ . 1  $\bar{x}_1^0 = 0.01$ ,  $\bar{x}_1^0 = 0.9$ ; 2  $\bar{x}_1^0 = 0.1$ ,  $\bar{x}_1^0 = 0.99$

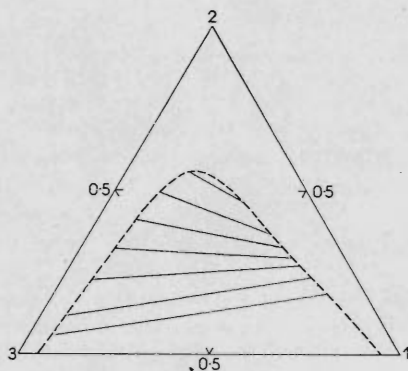


FIG. 6

Course of binodal curve and tie-lines in a system with different values  $(x_2)_0$  for homogeneous binary systems at their identical non-ideality. Properties of binary systems: 1–2  $(x_2)_0 = 0.8$ ,  $(G11)_{x_0} = 0.2$ ; 1–3  $\bar{x}_1^0 = 0.05$ ,  $\bar{x}_1^0 = 0.95$ ,  $b_{13} = 0.5$ ; 2–3  $(x_2)_0 = 0.2$ ,  $(G11)_{x_0} = 0.2$

ties, the properties of the homogeneous binary systems 1-2 and 1-3 not having been changed in single cases.

The values of mutual solubility themselves  $\bar{x}_1$  and  $\bar{x}_2$ , however, do not determine the extent of heterogeneous region for it depends also on a hypothetical course of  $G_{11}(x_1)$  inside the heterogeneous region. The lower the values  $G_{11}(x_1)$  will be inside the heterogeneous region of binary system, the larger will be the heterogeneous region in the ternary system. Considering that this hypothetical course in the heterogeneous region cannot be found out, we are entirely dependent on model calculations. In case of the modified Wilson equation we can easily choose the magnitude of  $G_{11}(x_1)$  inside the heterogeneous region by the parameter  $b_{13}$ . The values of  $G_{11}$  at minimum are inversely proportional to the value  $b_{13}$  and for  $b_{13}$  approaching zero the value of  $(G_{11})_{x_0}$  will also approach zero (analogous property has a modification of the Wilson equation, too, proposed by Hiranuma<sup>12</sup> and recently applied to the liquid-liquid equilibrium<sup>13</sup> as well). In Fig. 2 we present the computations of equilibrium curves for different values  $b_{13}$  from which it is evident that the effect of  $b_{13}$  is very expressive. It is important yet to draw attention to the fact that it is necessary, on using other equations, to prefer convex course of  $G_{11}(x_1)$  (ref.<sup>14</sup>).

The extent of the heterogeneous region is as well inversely proportional to the values  $(G_{11})_{x_0}$  in the homogeneous systems 1-2 and 2-3. The effect of the  $(G_{11})_{x_0}$  value increase in the systems which are at the end of miscibility. This fact is also in agreement with the analysis which was carried out for a regular solution<sup>15</sup>. If the system 1-2 occurs on the critical isotherm then the binodal curve touches the side of triangle corresponding to the binary system 1-2. Several computed curves illustrating this effect are shown in Fig. 3. The curve 1 depicts the case when, also in the binary system 1-2, the term  $b_{12}x_1x_2$  with  $b_{12} = 0.1$  was used, whereby  $(G_{11})_{x_0} = 0$  at  $(x_2)_{0,1-2} = 0.3$  was reached.

The effect of the  $G_{11}(x_1)$  course in homogeneous systems is, however, closely connected with the value of the minimum position,  $x_0$ . A shift of the  $(G_{11})_{x_0}$  minimum to higher content of component 2, *i.e.* larger  $(x_2)_0$  leads to a shift of binodal curve towards component 2. This effect is illustrated in Fig. 4. In spite of the value  $(x_2)_0$  having been increased from 0.2 to 0.8 in the system 2-3, the shift of binodal curve is relatively small. This effect is conditioned in addition by the extent of non-ideality of both homogeneous systems. With more ideal systems the effect of  $x_0$  is even smaller.

A considerable effect of  $(G_{11})_{x_0}$  on the extent of the heterogeneous region appears even in the case when both homogeneous binary systems 1-2 and 2-3 exhibit practically the same non-ideality ( $(x_2)_{0,1-2} = (x_2)_{0,2-3}$  and  $(G_{11})_{x_0,1-2} = (G_{11})_{x_0,2-3}$ ). These results contrast with the behaviour of regular solution in which the course of binodal curve in a similar case ( $b_{12} = b_{23} = b$ ) has not been, in a certain extent of  $b$ , influenced by this value<sup>1</sup>.

The inclination of tie-lines is primarily influenced by the difference in non-ideality

of the homogeneous systems 1–2 and 2–3 which is expressed quantitatively by the value  $(G11)_{x_0}$ . At the same or very close values  $(G11)_{x_0}$ , the effect of asymmetry in solubility of substances in the binary system 1–3 and the effect of values  $(x_2)_{0,1-2}$  and  $(x_2)_{0,2-3}$  in the binary systems become further evident.

The tie-lines are inclined, at sufficiently large difference in  $(G11)_{x_0}$  in the homogeneous systems, to the less ideal system, which is best evident in Fig. 3. In case of the curves 1–4, for which  $(G11)_{x_0,1-2} < (G11)_{x_0,2-3}$  holds, the tie-lines are inclined towards the binary system 1–2. For the curve 5 it is just the other way round (except the vicinity of the system 1–3, where a different value of  $x_0$  in homogeneous systems plays role).

The effect of asymmetric solubility in the binary system 1–3 can be expressed as follows: Let us assume that  $\bar{x}_1^0 < \bar{x}_3^0 = 1 - \bar{x}_1^0$ , which means that the substance 1 dissolves in the substance 3 less than the substance 3 in the substance 1. This fact can be interpreted also in this way that the mixture is less ideal in the vicinity of substance 3, which manifests itself effectively in the same way as if the system 2–3 were less ideal. This effect is demonstrated in Fig. 5. In case of the first curve, the inclination of tie-lines is larger than for the curve 2, *viz.* for that reason that the system 2–3 has lower value of  $(G11)_{x_0}$  than the system 1–2 and, moreover, in this case the substance 1 is less soluble in the substance 3 than the substance 3 in the substance 1. For the second curve the effect of lower value of  $(G11)_{x_0}$  in the system 2–3 is partly compensated by unsymmetry in the mutual solubility but it does not suffice to turn over the inclination of tie-lines in spite of the difference in  $(G11)_{x_0}$  in the homogeneous systems is only 0.1.

The effect of the position of the  $G11$  minimum of binary homogeneous systems on the inclination of tie-lines manifests itself as well at “small” differences in  $(G11)_{x_0}$  (with mildly non-ideal systems these differences can be larger than in case of strongly non-ideal ones) of these homogeneous systems or at small differences in symmetry of mutual solubility or on their compensating. In the vicinity of the binary system 1–3 holds that the slope of the tie-line is positive as far as  $(x_2)_{0,2-3} < (x_2)_{0,1-2}$  and *vice versa*. Also this fact will appear to be conceivable if we realize that on the critical isotherm at the point  $(x_2)_0$ , the critical point would be and the slope of tie-lines would be infinite. Similar conclusions could be drawn in the opposite case if the system 1–2 dominated. In case of further tie-lines the second homogeneous system may make its way and the inclination of tie-lines can even turn over. These facts can be watched in Fig. 6 representing the system in which  $(x_2)_{0,2-3} = 0.2$ ,  $(x_2)_{0,1-2} = 0.8$ . The slope of conodes is positive at first (small  $x_2$ ) then successively runs through the maximum, decreases and through zero passes to negative values. Such a course is brought about by considerably different values of  $(x_2)_0$  for both homogeneous systems at their identical non-ideality ( $(G11)_{x_0,1-2} = (G11)_{x_0,2-3}$ ).

The given rules can be demonstrated not only by these model computations but also by actual systems. The fact that the extent of heterogeneous region is above all

(unless we consider strongly non-ideal homogeneous systems) a function of the heterogeneous system, follows from Fig. 7. There the binodal curves for the water (1)–benzene(3)–organic solvent(2) systems<sup>16</sup> are plotted. Except four solvents (acetaldehyde, acetonitrile, 1,4-dioxane and acetone), the maximum content of the organic solvent on the binodal curve is in comparatively narrow range  $(x_2)_{\max} \in (0.38; 0.50)$ . A larger heterogeneous region in systems with acetonitrile, 1,4-dioxane and acetone can be explained by the fact that these three substances form much more non-ideal solutions with water<sup>7</sup> than *e.g.* ethanol and, moreover, by shifting the position of the  $G_{11}$  minimum towards higher concentration of organic solvent, which contributes to the shift of binodal curve towards organic solvent. A similar effect manifests itself evidently with acetaldehyde but the present vapour–liquid equilibrium experimental data do not allow to determine  $x_0$  and  $(G_{11})_{x_0}$  with sufficient accuracy (at  $x_1 = 0.5$ ,  $G_{11}$  is 0.5 to 1.0).

The effect of unequal value of  $(G_{11})_{x_0}$  on the inclination of tie-lines can be shown by an example of the water(1)–benzene(3)–ethanol(2) and water(1)–benzene(3)–2-propanol(2) systems in Fig. 8. In the first ternary system, the ethanol(2)–benzene(3) binary system is more nonideal than water(1)–ethanol(2) system and the tie-lines

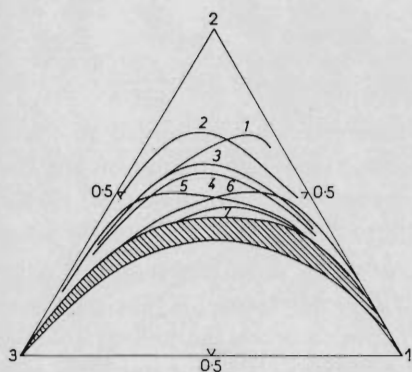


FIG. 7

Course of binodal curve in systems water(1)–organic solvent(2)–benzene(3). 1 acetonitrile, 2 acetaldehyde, 3 1,4-dioxane, 4 acetone, 5 butyric acid, 6 acetic acid, 7 1-propanol. Binodal curves with the following substances fall into the hatched band: 2-propanol, 2-methyl-2-propanol, pyridine,  $\alpha$ -picoline, ethanol, dimethylformamide, morpholine

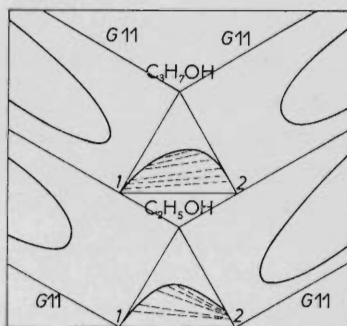


FIG. 8

Illustration of the effect of non-ideality of the homogeneous systems 1–2 and 2–3 on the inclination of tie-lines in systems water(1)–benzene(3) with ethanol and 2-propanol

are also inclined to the system (2–3). In the second case, on the contrary, the water (1)–2-propanol(2) binary system is more non ideal than 2-propanol(2)–benzene(3) system and the tie-lines have an opposite inclination.

*Correlation of the Liquid–Liquid Equilibrium Data on Using the G11( $x_1$ ) Course*

The calculations carried out in the foregoing part have been without any direct relation to reality. Now we will apply the results given above to three concrete systems: a) acetonitrile(1)–benzene(2)–n-heptane(3) (ref.<sup>19</sup>), b) water (1)–ethanol(2)–benzene(3) (ref.<sup>17</sup>), c) water(1)–2-propanol(2)–benzene(3) (ref.<sup>18</sup>).

For the computations we made use of the UNIQUAC equation<sup>20</sup>

$$G^E/(RT) = \sum_{i=1}^N x_i \ln(\phi_i/x_i) + (z/2) \sum_{i=1}^N q_i x_i \ln(\theta_i/\phi_i) + \\ - \sum_{i=1}^N q_i x_i \ln \sum_{j=1}^N \theta_j \tau_{ji}, \quad (8)$$

$$\phi_i = r_i x_i / \sum_{j=1}^N r_j x_j, \quad \theta_i = q_i x_i / \sum_{j=1}^N q_j x_j,$$

$$\tau_{ij} = \exp(-a_{ij}/T), \quad a_{ii} = a_{jj} = 0 \quad (9)$$

and the previously presented modified Wilson equation (5).

When computing the correlation equation parameters we proceeded so that in binary homogeneous systems the course of  $G11(x_1)$  (ref.<sup>7</sup>) was found on the basis of experimental vapour–liquid equilibrium data and the parameters of the  $G11(x_1)$  minimum were determined graphically. On the basis of these values, two sought parameters ( $a_{ij}$  and/or  $\tau_{ij}$  in the UNIQUAC equation,  $A_{ij}$  in the modified Wilson equation) were determined by solving the system of equations (6). The parameters in the heterogeneous binary system 1–3 were found from the mutual solubility of substances 1 and 3 by solving the system of equations (7). The parameters of the UNIQUAC equation are fully determined by these data. In case of the modified Wilson equation, the computations were carried out for several values of  $b_{13}$ .

*Acetonitrile(1)–Benzene(2)–n-Heptane(3) System at 45°C*

On the basis of experimental data<sup>19,21</sup> we determined for the acetonitrile(1)–benzene(2) and benzene(2)–n-heptane(3) these values:  $(x_2)_{0,1-2} = 0.52 \pm 0.02$ ,  $(G11)_{x_0} = 2.20 \pm 0.03$  and  $(x_2)_{0,2-3} = 0.53 \pm 0.05$ ,  $(G11)_{x_0} = 3.1 \pm 0.1$ , respectively. From these values and from mutual solubility,  $\bar{x}_1^0 = 0.1016$ ,  $\bar{x}_1^0 = 0.9372$  (ref.<sup>19</sup>), the parameters given in Table I were calculated. The binodal curve determined on the



basis of these parameters is plotted in Fig. 9. It is evident that the heterogeneous region is larger than it corresponds to the experimental data. The curve determined by Anderson and coworkers<sup>8</sup> is given in Fig. 9 as well. They found the parameters on the basis of vapour-liquid and liquid-liquid equilibria. It can be seen that the agreement is better but the modelled heterogeneous region is a little larger than reality in the vicinity of the critical point.

The parameters of the modified Wilson equation are presented also in Table I. In the acetonitrile(1)-n-heptane(3) binary system, three values of  $b_{13}$  were used and the result is evident from Fig. 10. The lower values of  $b_{13}$  diminish conspicuously the extent of heterogeneous region (also the  $G_{11}(x_1)$  minimum is increased in the heterogeneous region from  $-1.65$  through  $-1.25$  to  $-0.62$ ). At  $b_{13} = 0.4$  we get very good agreement with the experimental data. In the acetonitrile(1)-benzene(2) system we also reached very good agreement in the azeotrope composition ( $y_{az} = 0.463$ , ref.<sup>19</sup>;  $y_{az} = 0.457$  (?), ref.<sup>21</sup>;  $y_{az} = 0.466$ , ref.<sup>22</sup>;  $y_{az,calc} = 0.477$ ). Similarly, also the deviation in composition of the heterogeneous azeotrope in the acetonitrile(1)-n-heptane(3) system was very small ( $y_{az} = 0.6456$ , ref.<sup>19</sup>;  $y_{az,calc} = 0.6505$ ).

The liquid-liquid and liquid-vapour equilibria in this system have been correlated recently by Schult and coworkers<sup>13</sup> with good results by another modification of the Wilson equation<sup>12</sup>.

#### *Systems Water(1)-Benzene(3) with Ethanol and 2-Propanol*

Smoothed coordinates of the  $G_{11}(x_1)$  minimum of homogeneous binary systems<sup>7</sup> are presented in Table II. The values of  $x_0$  and  $(G_{11})_{x_0}$  for the first two systems are

TABLE I

Parameters of binary systems on applying the UNIQUAC and modified Wilson equations in the acetonitrile(1)-benzene(2)-n-heptane(3) system at 45°C

Curve	$i-j$	$(x_2)_0$ or $\bar{x}_1^0$	$(G_{11})_{x_0}$ or $\bar{x}_1^0$	$a_{ij}$ or $A_{ij}$	$a_{ji}$ or $A_{ji}$	$b_{13}$
9a	1-2	0.48	2.20	-7.63 K	159.1 K	—
	1-3	0.1016	0.9372	17.1 K	570.7 K	—
	2-3	0.53	3.10	-60.7 K	120.1 K	—
10a	1-2	0.48	2.20	0.6738	0.5087	0
	1-3	0.1016	0.9372	0.8926	0.3846	2
	2-3	0.53	3.10	1.090	0.5205	0
10b	1-3 <sup>a</sup>	0.1016	0.9372	0.3464	0.2123	1
10c	1-3 <sup>a</sup>	0.1016	0.9372	0.1466	0.09567	0.4

<sup>a</sup> The cases 1-2 and 2-3 are the same as for the curve 10a.

subject to an absolute error about 0.03 and 0.08, respectively. In the mixtures with 2-propanol there is a greater error (approximately double). The values in the water(1)-ethanol(2) system were determined on the basis of the correlation by Larkin and

TABLE II

Coordinates of the  $G_{11}(x_1)$  minimum in the systems of ethanol and 2-propanol with benzene and water

System	$t, ^\circ\text{C}$	$(x_2)_0$	$(G_{11})_{x_0}$
Water(1)-ethanol(2)	25	0.35	1.23
	50	0.35	1.42
Ethanol(2)-benzene(3)	25	0.32	0.60
	50	0.39	0.90
Water(1)-2-propanol(2)	25	0.30	0.73
	50	0.30	0.80
2-Propanol(2)-benzene(3)	25	0.43	1.06
	50	0.43	1.30

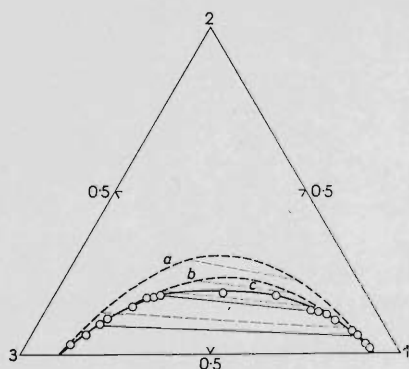


FIG. 9

Application of the UNIQUAC equation to the acetonitrile(1)-benzene(2)-n-heptane(3) system at 45°C. *a* course computed on the basis of  $G_{11}(x_1)$  minima, *b* course computed on the basis of the Anderson and Prausnitz parameters, *c* experimental data

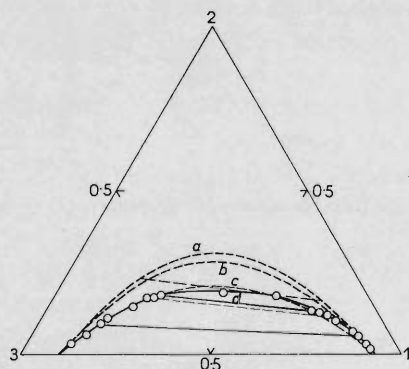


FIG. 10

Application of the modified Wilson equation to the acetonitrile(1)-benzene(2)-n-heptane(3) system at 45°C for different values  $b_{13}$ . *a*  $b_{13} = 2$ , *b*  $b_{13} = 1$ , *c*  $b_{13} = 0.4$ , *d* experimental data

Pemberton<sup>23</sup>. The data on the solubility of water and benzene were taken from the work by Polák and coworkers<sup>24</sup> ( $\bar{x}_1^0 = 0.003$ ,  $\bar{x}_1^0 = 0.9996$ ).

When the calculations were carried out in the water(1)–ethanol(2)–benzene(3) system with the UNIQUAC equation and with the parameters determined on the basis of the minimum of  $G11(x_1)$  curve, the system was represented as a three-phase one, which does not correspond to the reality – see Fig. 11 (and also ref.<sup>10</sup>). On using higher values of  $(G11)_{x_0}$  we succeeded in removing this discrepancy. When using an increased mutual solubility of benzene and water (to five times as much),

TABLE III  
Parameters of binary systems on applying the UNIQUAC and modified Wilson equations

Curve	$i-j$	$(x_2)_0$ or $\bar{x}_1^0$	$(G11)_{x_0}$ or $\bar{x}_1^0$	$a_{ij}$ or $A_{ij}$	$a_{ji}$ or $A_{ji}$	$b_{ij}$
Water(1)–ethanol(2)–benzene(3)						
11a	1–2	0.35	1.23	103.9 K	41.9 K	—
	1–3	0.015	0.998	203.2 K	576.4 K	—
	2–3	0.32	0.60	–83.6 K	428.7 K	—
11b	1–2	0.35	1.42	122.5 K	17.8 K	—
	1–3	0.015	0.998	203.2 K	576.4 K	—
	2–3	0.39	0.90	–64.4 K	369.2 K	—
12a	1–2	0.35	1.23	0.6904	0.1460	0
	1–3	0.003	0.9996	0.00838	0.00111	0.6
	2–3	0.32	0.60	0.0842	0.4536	0
12b	2–3 <sup>a</sup>	0.39	0.90	0.1675	0.4845	0
Water(1)–2-propanol(2)–benzene(3)						
13a	1–2	0.30	1.1	20.8 K	163.8 K	—
	1–3	0.015	0.998	203.2 K	576.4 K	—
	2–3	0.43	1.4	–15.5 K	194.0 K	—
14a	1–2	0.3	0.6	0.4776	0.0723	0
	1–3	0.003	0.9996	0.01174	0.001552	0.8
	2–3	0.43	1.3	0.2646	0.5507	0
14b	1–3 <sup>b</sup>	0.003	0.9996	0.00838	0.00111	0.6
14c	1–3 <sup>b</sup>	0.003	0.9996	0.003075	0.0004084	0.2

<sup>a</sup> The cases 1–3 and 1–2 are the same as for the curve 12a; <sup>b</sup> the cases 1–2 and 2–3 are the same as for the curve 14a.

an on the whole satisfactory agreement with experiment was reached — see Fig. 11. The corresponding parameters of the binary systems are given in Table III.

It would be certainly possible to attain better agreement with experiment by a further shifting of minima in both binary homogeneous systems but it was not carried out any more. When applying the modified Wilson equation, it proved that in the water(1)–benzene(3) system it was possible to start from the experimental values on mutual solubility if we used the value  $b_{13} = 0.6$ . The computed curve with the parameters obtained on the basis of values in Table II is plotted in Fig. 12. The inclination of tie-lines in the vicinity of the critical point is too large (curve *a*) and was considerably improved on using the higher value  $(G_{11})_{x_0} = 0.90$  in the ethanol(2)–benzene(3) system which corresponds to the temperature of 50°C. The agreement of calculated and measured values in this second variant is very good. Only the course of binodal curve in the vicinity of the binary system ethanol–water remains unsatisfactory.

The best agreement in the water(1)–2-propanol(2)–benzene(3) system on using the UNIQUAC equation was attained when the parameters given in the second part of Table III were used. It was necessary to take the mutual solubility of benzene and water five times as much than corresponds to the experiment. Although the values  $(G_{11})_{x_0}$  were increased as well as the mutual solubility of water and benzene, the calculated heterogeneous region exceeded the experimental one (Fig. 13). The computation was again complicated by the occurrence of three-phase region, which was

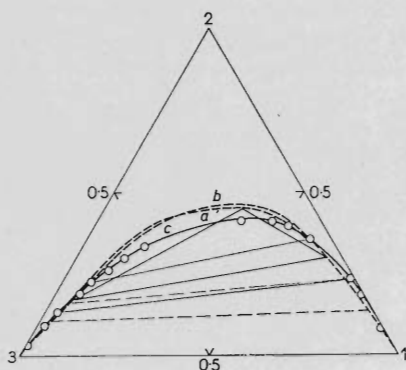


FIG. 11

Application of the UNIQUAC equation to the water(1)–ethanol(2)–benzene(3) system at 25°C. *a*, *b* calculated curves, *c* experimental data

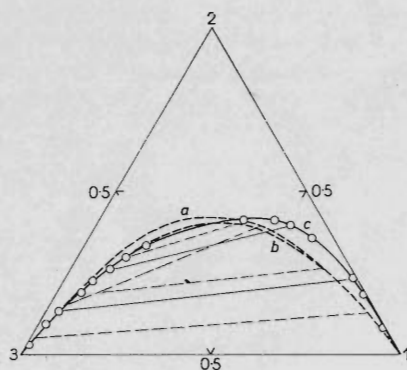


FIG. 12

Application of the modified Wilson equation to the water(1)–ethanol(2)–benzene(3) system at 25°C. *a*, *b* calculated curves, *c* experimental data

overcome by an increase of  $(G11)_{x_0}$  in the 2-propanol(2)–benzene(3) system above the value 1.3.

On applying the modified Wilson equation it was found that it was not necessary to change the previously obtained parameters in the water(1)–benzene(3) system or the value  $b_{13}$  to obtain a satisfactory representation of the binodal curve. For a good representation of tie-lines (Fig. 14) it was necessary to alter the parameters of binary systems (Table III). The altered values, however, still fall into the range delimited by experimental errors.

## DISCUSSION

It is evident from the foregoing analysis that the course of  $G11(x_1)$  of corresponding binary systems influences considerably the extent of heterogeneous region as well as the inclination of tie-lines in ternary system. On the basis of the knowledge of  $G11(x_1)$  in binary systems it is possible to judge whether the prediction of the liquid–liquid equilibrium in ternary system based on binary data only will be or will not be possible. For instance, the prediction of liquid–liquid equilibrium appears to be very difficult in case of strongly non-ideal binary systems because low values of  $G11$  are not usually determined in homogeneous systems with such an accuracy which is necessary with regard to its great effect on binodal curve (Fig. 3). The possibility of prediction can be still made more difficult in the cases when both homogeneous

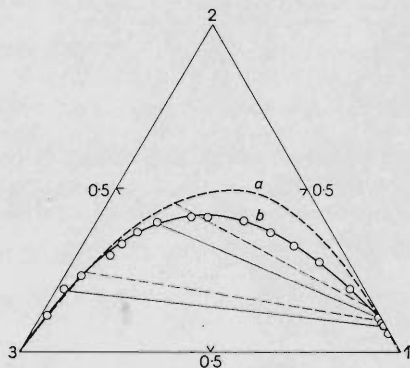


FIG. 13

Application of the UNIQUAC equation to the water(1)–2-propanol(2)–benzene(3) system at 25°C. *a* calculated curve, *b* experimental data

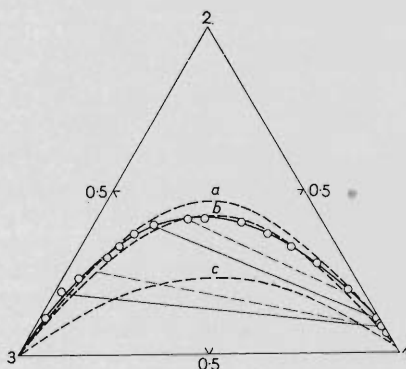


FIG. 14

Application of the modified Wilson equation to the water(1)–2-propanol(2)–benzene(3) system at 25°C for different values  $b_{13}$ . *a*  $b_{13} = 0.8$ , *b*  $b_{13} = 0.6$ , *c*  $b_{13} = 0.2$ ,  $\circ-\circ-\circ$  experimental data

systems are strongly non-ideal. On the other side, the possibility of a good prediction shows in the cases when one binary system is weakly and the second mildly non-ideal and if the heterogeneous binary system is described well (*e.g.* from the correlation of other heterogeneous systems).

The modified Wilson equation proved to be good in applications, thanks to its high flexibility which is a consequence of introducing the third parameter when describing the binary heterogeneous system. The flexibility of this equation manifests itself favourably in the fact that the difficulties are removed which have often occurred<sup>8,14</sup> on correlating the systems with relatively small heterogeneous regions.

The present results show that the third parameter used represents 10–15% of the value following from the application of regular solution theory. For expressing the mutual solubility in the case of the regular solution it holds<sup>1,25</sup>.

$$b = (1 - 2x_1)^{-1} \ln [(1 - x_1)/x_1], \quad (10)$$

where  $x_1 < 0.5$  expresses the mole fraction of component 1 in the equilibrium phase rich in component 2. So *e.g.* in the acetonitrile(1)–n-heptane(3) system we would get (see Table I)  $\bar{b} = (2.73 + 3.09)/2 = 2.91$  whereas the optimum  $b_{13}$  determined on the basis of data on liquid–liquid equilibrium in the ternary system was  $b_{13} = 0.4$  ( $\approx 14\%$ ). In the water–benzene system (Table III) the corresponding values amount to  $\bar{b} = (5.84 + 7.82)/2 = 6.8$  and  $b_{13} = 0.6$  ( $\approx 9\%$ ).

#### LIST OF SYMBOLS

$A_{ij}, a_{ij}$	parameters of Eq. (5) or (9), respectively
$b_{ij}$	parameter of Eq. (5)
$D$	determinant defined by Eq. (3)
$G$	Gibbs' (molar) energy
$G11$	$= \partial^2(G^M/RT)/\partial x_1^2$ , second derivative of Gibbs' energy with respect to composition
$(G11)_{x_0}, (G11)_{x_0,2-3}$	ordinate of $G11(x_1)$ minimum and of minimum of second derivative of Gibbs' energy in system 2–3, respectively
$i, j$	component, summation index
$M$	(superscript) mixing quantity
$N$	number of components
$P$	pressure
$q$	parameter characterizing surface of molecule
$R$	gas constant
$r$	parameter characterizing volume of molecule
$T$	temperature
$z$	coordination number ( $z = 10$ in Eq. (9))
$x$	mole fraction
$\bar{x}_1^0, \bar{x}_1^0$	mole fraction of component 1 in coexisting phases of binary heterogeneous system 1–3

- $x_0, (x_2)_{0,2-3}$  coordinates of minimum of dependence  $G_{11}(x_1)$  or mole fraction of component 2 in mixture for composition which corresponds to minimum of second derivative of Gibbs' energy with respect to composition in system 2—3, respectively
- $\phi, \theta, \tau$  quantities defined in Eq. (9)

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