LIQUID-LIQUID EQUILIBRIUM. MODELLING THE TEMPERATURE DEPENDENCE OF MUTUAL SOLUBILITY OF LIQUIDS

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Dedicated to the Academician J. Mostecký on the occasion of his 60th birthday.

The applicability of the modified Wilson equation to correlation of the temperature dependence of mutual solubility of liquids is demonstrated. The position of the critical point is fixed, and the linear dependence of parameters on temperature is used in calculating. The method was applied with success to the aqueous solutions of 1-butanol, isobutyl alcohol, phenol and 2-butanone and to the nonaqueous system cyclohexane-methanol.

The analytical representation of the temperature dependence of mutual solubility has been dealt with in a number of works[1-10]. Kehlen[9] in his extensive work used the Redlich-Kister equation containing as much as five temperature dependent parameters. This large number of parameters brought about considerable demands on experimental data. Besides the data on mutual solubilities, data on heat of mixing or even C_p^E were used, too. The merit of this procedure is, of course, a rigorous thermodynamic description of the system investigated. A substantial shortcoming in the Kehlen method is, however, the Redlich-Kister equation itself which, unless a large number of parameters is used, does not yield a description of sufficient quality for the systems with unsymmetrically located critical point, which are above all aqueous systems. For instance it was shown[11] that the three-parameter Redlich-Kister equation cannot be used for systems with $x_c \notin (0{\cdot}235, 0{\cdot}765)$ where x_c is the mole fraction of component at composition corresponding to the minimum of the second-order derivative of the Gibbs energy and consequently also to the critical point. Kehlen[9] himself recommeded not to use even the five-constant Redlich-Kister equation outside the interval $x_c \in (0{\cdot}3, 0{\cdot}7)$.

The applicability of the UNIQUAC and NRTL equations was partly dealt with by Sørensen and coworkers[10] (see also ref.[7,8]). These authors concluded that the temperature dependence included in these equations can bring out the mutual solubility only qualitatively. When considering the linear temperature dependence of energy parameters, one obtains already roughly reasonable description but quantitatively the agreement is not sufficient, especially in the vicinity of the critical point.

The-three-parameter Wilson equation[12] (with a multiplying factor) was as well used for correlating mutual solubilities[6]. The results of the correlaticns were, however, only in qualitative agreement with experimental data.

In this work we deal with use of the modified Wilson equation[14] for the description of the temperature dependence of mutual solubility. It is shown that on using the linear temperature dependence of the energy parameters a_{ij} and the parameter b, it is possible to correlate very well experimental data.

With the aim of confrontation of the results obtained, the $T - x - \bar{x}$ data given in the book by Sørensen and Arlt[15] were smoothed in the following systems: 1-butanol(1)–water(2), isobutyl alcohol(1)–water(2), phenol(1)–water(2), 2-butanone(1)–water(2), benzene(1)–water(2) and cyclohexane(1)–methanol(2). Even though these systems pertain to the very often measured ones, the agreement between the data of different authors is not often best. In Fig. 1 we give the smoothed values of solubility for the system 2-butanone(1)–water(2), and the line segments in dicate the scatter of experimental data of different authors (the greatest weight was given to the data by Campbell and coworkers[13]). The critical temperatures and the composition at the critical point of these systems are summarized in Table I.

The systems selected are especially demanding on the correlation. In the first four systems, the content of nonaqueous component at the critical point lies in the interval 10–13 mol.%. The system benzene(1)–water(2) represents, on the contrary, a pair of components with low mutual solubility, and the measured data are far from the critical region. The last (nonaqueous) system is, on the contrary, relatively symmetric, and should not make difficulties (avoiding the immediate vicinity of the critical point) in correlation.

THEORETICAL

The modified Wilson equation[14] has been used for the thermodynamic description of the above-mentioned binary systems:

$$G^E/RT = -x_1 \ln(x_1 + A_{12}x_2) - x_2 \ln(x_2 + A_{21}x_1) + bx_1x_2 ,$$
$$A_{ij} = (V_j^L/V_i^L) \exp(-a_{ij}/T) , \qquad (1)$$

TABLE I

Coordinates of critical points of the systems selected

System	t^c, °C	x_1^c
1-Butanol(1)–water(2)	124·9	0·109
Isobutanol(1)–water(2)	133·1	0·116
Phenol(1)–water(2)	65·9	0·098
2-Butanone(1)–water(2)	143·0	0·175
Cyclohexane(1)–methanol(2)	45·5	0·49

where G^E is the excess Gibbs energy, T the absolute temperature, x_i the mole fraction of component i ($i = 1, 2$), V_i^L the molar volume of pure substance i in the liquid state (for calculating, the values given by Gmehling and Onken[16] were used and considered as temperature independent), $\boldsymbol{R}$ is the gas constant, a_{ij}, b are parameters.

The values of parameters a_{ij} in dependence on temperature are given in Fig. 2 as calculated in the system 1-butanol(1)–water(2) on the basis of corresponding values of solubility by solving the equilibrium conditions

$$a_i(\bar{x}_1) = a_i(\bar{\bar{x}}_1)\,, \quad i = 1, 2 \tag{2}$$

and for a given value of the parameter b (0·5 and 1·0). It can be seen from the figure that the obtained temperature dependence of parameters has at constant b a linear character except the nearest vicinity of the critical point. The binodal curve is, however, enormously sensitive to the values of parameters, which is illustrated by the curves *1*, *2*, *3* in Fig. 3. The curve *1* corresponds to the parameters which were calculated on the basis of the critical point (by solving Eqs (*5*) – see below) with a para-

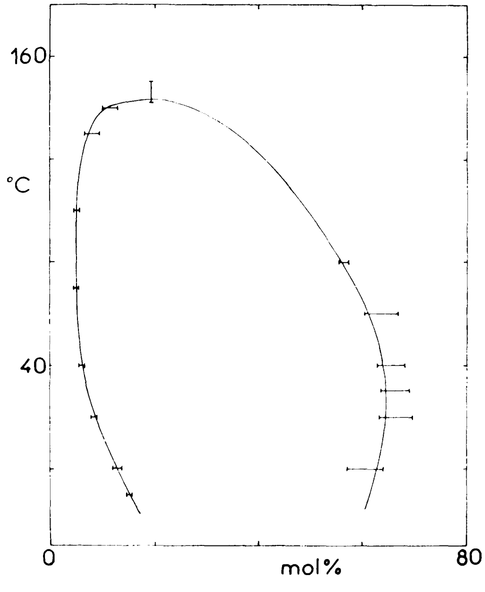

FIG. 1

Mutual solubility in the 2-butanone(1)–water(2) system

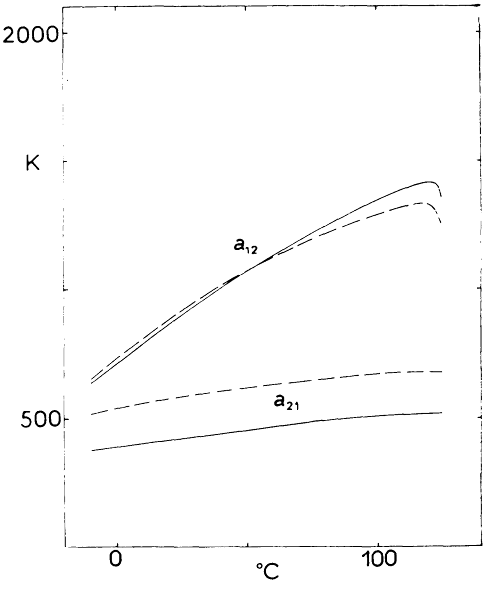

FIG. 2

Temperature dependence of parameters a_{12} and a_{21} (in K) in the 1-butanol(1)–water(2) system which were determined by solving Eq. (*2*) for $b = 0·5$ (– – – –) and $b = 1·0$ (———)

meter $b = 0{\cdot}7$. The curve *2* corresponds to the linear dependence of parameters a_{ij} on temperature

$$a_{ij} = \alpha_{ij} + \beta_{ij}T, \qquad (3)$$

the parameters α_{ij} and β_{ij} having been calculated from the values determined at the temperature of 20°C and at the critical temperature ($b = 0{\cdot}7$). The curve *3* was obtained as well with a linear dependence of a_{ij} on temperature; the parameters α_{ij} and β_{ij} were determined from the values of a_{ij} obtained from mutual solubility at 20°C and 93°C (the normal boiling point of the mixture). At these two temperatures, the absolute agreement is also reached, however, the critical temperature

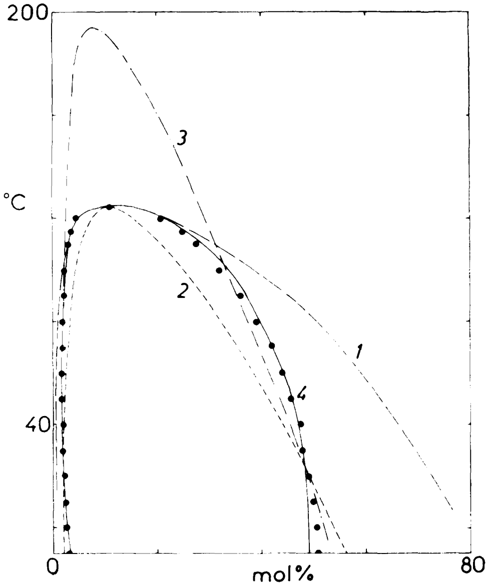

FIG. 3

Comparison of the experimental and calculated binodal curves in the 1-butanol(1)–water(2) system: *1* parameters a_{12}^c, a_{21}^c from Table II ($b = 0{\cdot}7$) used, *2* linear dependence (*3*) used: α_{ij} and β_{ij} calculated from values in Table II and from mutual solubility at 20°C (Fig. 2), *3* linear dependence (*3*) used: α_{ij} and β_{ij} calculated on the basis of a_{ij} determined from mutual solubility at 20 and 93°C, *4* parameters from Table III

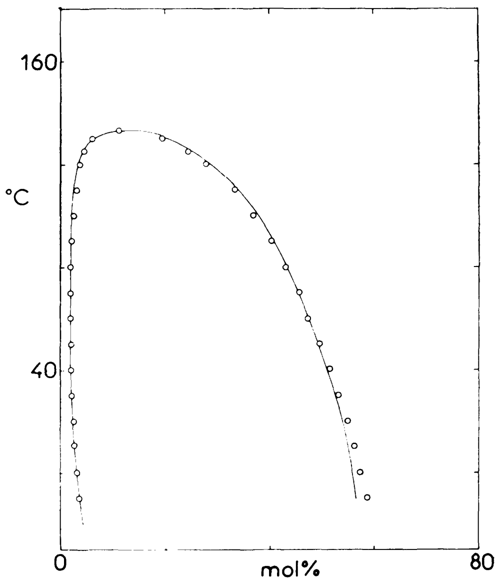

FIG. 4

Comparison of the experimental and calculated binodal curve in the isobutanol(1)–water(2) system is in this case 70°C higher than that which corresponds to the reality. These results confirm fully the experience of other authors[6–8,10].

An analysis of the results of correlation attained showed that it would have been suitable to consider even the third parameter b as temperature dependent. For the sake of simplicity the dependence

$$b = \alpha + \beta T \tag{4}$$

was chosen. The dependences (*3*) and (*4*) involve altogether 6 parameters to describe the temperature dependence of mutual solubility.

When calculating these parameters by the least-squares method, it is possible to minimize either the difference in activities of components of coexisting phases or directly in calculated and experimental compositions. The first way is very simple but as it can be shown[17], it is very ineffective in the critical region where the dependence of activities on composition is very flat. On the contrary, the minimization of the difference of experimental and calculated compositions prefers the critical region, and put down points at concentration ends.

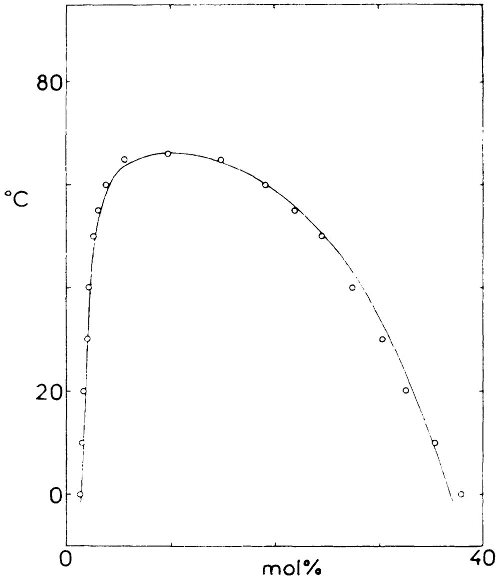

FIG. 5

Comparison of the experimental and calculated binodal curve in the phenol(1)–water(2) system

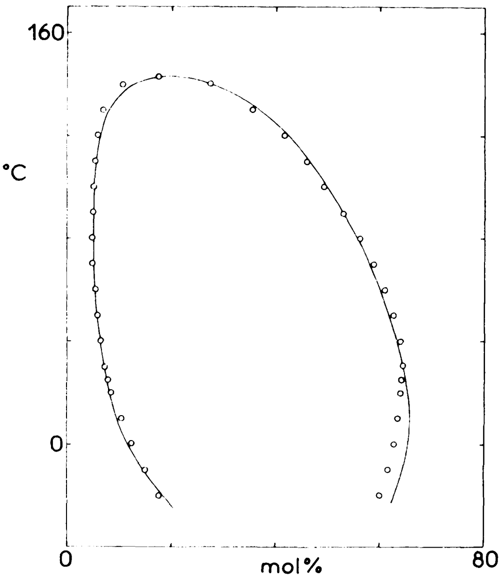

FIG. 6

Comparison of the experimental and calculated binodal curve in the 2-butanone(1)–water(2) system

For determining the parameters, the procedure given below was therefore chosen which is an effective compromise of both the foregoing methods. Its great advantage consists in the fact that it ensures not only the position of critical point but also diminishes the number of optimized parameters, which increases the stability of computation.

On the basis of the critical temperature T^c and composition x_1^c, the parameters a_{12}^c, a_{21}^c were computed by solving the equations valid at the critical point[10,17]:

$$(\partial \ln a_1/\partial x_1)_c = 0\,, \quad (\partial^2 \ln a_1/\partial x_1^2)_c = 0 \tag{5}$$

or

$$(G11)_c = 0\,, \quad (\partial G11/\partial x_1)_c = 0\,, \tag{6}$$

where

$$G11 = \partial^2(G^M/RT)/\partial x_1^2 = x_2(\partial \ln a_1/\partial x_1) \tag{7}$$

is the second-order derivative of the Gibbs energy with respect to composition. Let the chosen parameter b used in solving Eqs (5) or (6) be denoted by b^c. The parameters obtained in this way in the 1-butanol(1)–water(2) system are given in Table II.

By fixing the parameters at the critical point (it can generally be another temperature at which we know the parameters, unless *e.g.* we know the critical point) we get

TABLE II

Calculated values of a_{12}^c and a_{21}^c in dependence on the parameter b^c in the 1-butanol(1)–water(2) system ($t^c = 124.9°C$, $x_1^c = 0.109$)

b^c	a_{12}^c	a_{21}^c
0·5	1 256·5	683·8
0·6	1 252·6	641·6
0·7	1 259·2	605·4
0·8	1 276·5	573·6
0·9	1 306·7	545·1
0·95	1 327·9	531·9
1·00	1 357·8	519·3
1·05	1 393·9	507·2
1·10	1 442·1	495·7
1·15	1 509·8	484·6
1·20	1 625·7	473·9
1·25[a]	1 945·2	463·6

[a] For $b^c \geqq 1.30$ the solution of system of Eqs (5) or (6) was never more found.

from Eqs (*3*) and (*4*) the relations for the dependence of parameters a_{12}, a_{21}, b on temperature:

$$\begin{aligned} a_{12} &= a_{12}^{c} + \beta_{12}(T - T^{c}) \,, \\ a_{21} &= a_{21}^{c} + \beta_{21}(T - T^{c}) \,, \\ b &= b^{c} + \beta(T - T^{c}) \,, \end{aligned} \tag{8}$$

where the parameters β_{12}, β_{21} and β remain as the unknown quantities. With regard to the fact that the critical point is automatically fixed in this way, it is possible to use in optimization β_{12}, β_{21}, β a simpler procedure which minimizes the difference of component activities in both phases. Thus, we obtain the optimum parameters β_{12}, β_{21}, β for a chosen value of b^{c}. By choosing different b^{c}, such a set of parameters can be obtained which yields a minimum deviation.

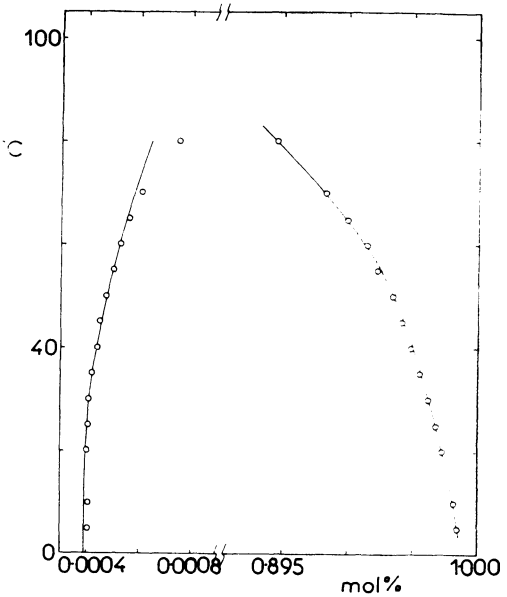

Fig. 7

Comparison of the experimental and calculated binodal curve in the benzene(1)–water(2) system

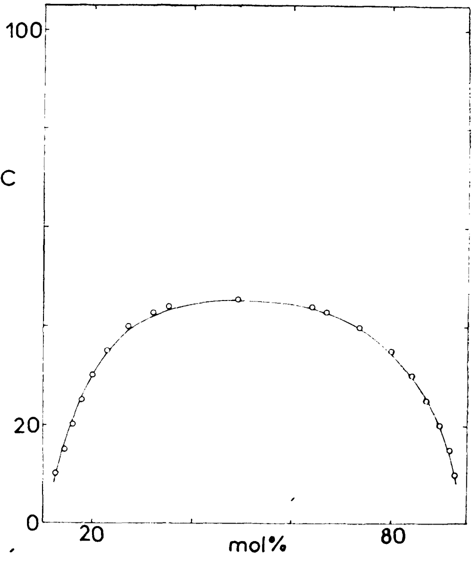

Fig. 8

Comparison of the experimental and calculated binodal curve in the cyclohexane(1)–methanol(2) system

TABLE III

Calculated values of parameters of the modified Wilson equation

System	n	α_{12}	β_{12}	α_{21}	β_{21}	α	$\beta . 10^3$	b^c	$S_1 . 10^2$	$S_2 . 10^2$
1-Butanol(1)-water(2)	22	−633·00	5·20437	806·17	−0·77998	−1·22967	5·8527	1·10	1·27	0·39
Isobutanol(1)-water(2)	18	−758·53	5·31798	807·07	−0·72953	−1·03288	5·2502	1·10	1·17	0·30
Phenol(1)-water(2)	13	271·54	2·96610	602·60	−0·57751	−1·15120	6·3448	1·10	1·29	0·80
2-Butanone(1)-water(2)	15	−718·20	5·04586	1 218·5	−1·56606	−1·15121	5·0458	1·10	1·25	0·61
Benzene(1)-water(2)[a]	14	−983·09	7·60675	1 422·6	0·74019	4·42055	−10·867	0·80	0·026	0·0032
Cyclohexane(1)- -methanol(2)	11	32·34	1·78415	1 931·6	−2·29596	0·45091	− 1·3366	0·025	1·15	1·36

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[a] When calculating the temperature dependence of parameters, the parameters determined from mutual solubility at 25°C were used instead of the critical ones.

RESULTS OF CORRELATION

The curves calculated in terms of the parameters which are summarized in Table III are plotted in Figs 3–8. In this table we as well give the mean deviation of the calculated and experimental compositions of both coexisting phases, S

$$S = [\sum(x_{1,\text{exp}} - x_{1,\text{calc}})^2/n]^{1/2}\,, \qquad (9)$$

where n stands for the number of experimental points. The value S_1 refers to the phase rich in component 1 and S_2 to that rich in component 2. The dependence of S_1 and S_2 on the chosen parameter b^c is given in Fig. 9. It is evident that the minimum is reached in both cases at $b^c = 1{\cdot}10$.

It follows from the results obtained that the agreement of calculated values with the values used for calculating is practically within the range of experimental errors. The highest deviations, especially in case of the systems phenol–water and cyclohexane–methanol, occur in the immediate vicinity of the critical point. The calculated binodal curve has always exhibited greater curvature than the curve corresponding to the experimental data.

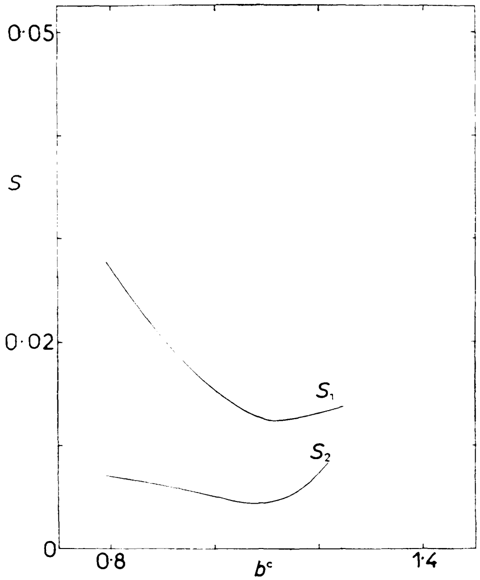

FIG. 9

Dependence of S_1 and S_2 in the 1-butanol(1)–water(2) system on the value of b^c chosen

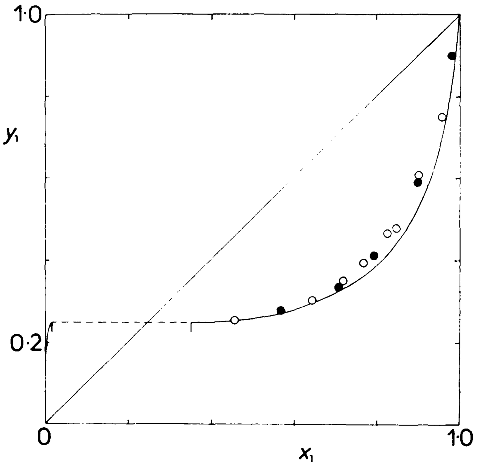

FIG. 10

Comparison of the calculated and experimental (○ Boublík[19], ● Ellis[20]) compositions of the vapour phase in the 1-butanol(1)–water(2) system at normal pressure

For the 1-butanol(1)–water(2) system, the physical significance of constants was in addition verified by comparing the calculated and experimental y–x curves at normal pressure (Fig. 10) and heat of mixing at the temperature $T = 303{\cdot}15$ K (Fig. 11). The agreement in composition of the vapour phase in homogeneous region is less satisfactory because Eq. (*1*) gives for asymmetric systems higher values of activity coefficients. The prediction of heat of mixing, however, can be considered excellent.

For the benzene(1)–water(2) system, the optimization of b^c was not carried out but such a value of b^c (0·8) was used which gave the optimum results when describing the vapour–liquid and liquid–liquid equilibria in the ternary system ethanol–water–benzene and 2-propanol–water–benzene[23].

In the cyclohexane(1)–methanol(2) system, the obtained dependence of S_1 and S_2 on b^c was very flat, and the value $b^c = 0{\cdot}025$ was chosen with regard to a good agreement in heat of mixing (Fig. 12). The calculated values of excess Gibbs energy at the temperature of 333·15 K are on the average 6% higher than those published

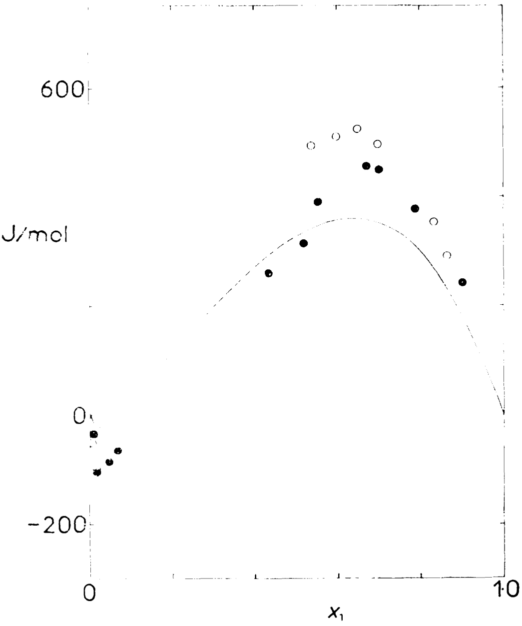

FIG. 11

Comparison of the calculated and experimental (○ Goodwin[21], ● Belousov[22]) heats of mixing in the 1-butanol(1)–water(2) system at 303·1 K

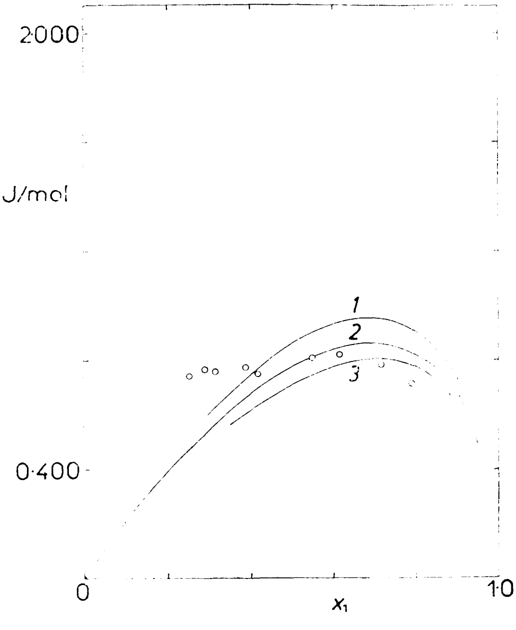

FIG. 12

Dependence of heat of mixing in the cyclohexane(1)–methanol(2) system on the value b^c chosen (○ Belousov[24]): *1* $b^c = 0{\cdot}03$, *2* $b^c = 0{\cdot}025$, *3* $b^c = 0{\cdot}02$

by Campbell and coworkers[25]. The values of limiting activity coefficients obtained at 46°C amount to: $\gamma_1^\infty = 44{\cdot}2$ and $\gamma_2^\infty = 40{\cdot}0$, and are in good agreement with the values which were read from a diagram reported by Campbell[25]: $\gamma_1^\infty = 56$, $\gamma_2^\infty = 31{\cdot}6$.

DISCUSSION

The procedure used in this work has some common features with the correlation method[18] proposed previously which takes into account the course of $G11$ and fixes the coordinates of the $G11(x_1)$ minimum, respectively, when correlating the concentration course of activity coefficients (above all in systems with high positive deviations from Raoult's law). Thus, the thermodynamic description of nonideality obtained ensured quantitatively and qualitatively the experimental reality.

Utilization of the existing dependences between physical quantities consisting in assigning infinite weight to certain key points not only increases the stability of parameter calculations of an empirical relation, but also improves considerably the quality of thermodynamic description. During the correlation of experimental data itself appears whether the empirical relation employed is sufficiently flexible to comply with all the constraining conditions and at the same time to reproduce satisfactorily the data. We assume that this aim has been reached in this work. The binodal curve is described with very good accuracy, and the prediction of other quantities is in good agreement with experiment.

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