
**LIQUID-LIQUID EQUILIBRIUM
IN THE WATER-ETHANOL-TOLUENE SYSTEM.
CORRELATION OF EQUILIBRIUM DATA**

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Liquid-liquid equilibrium data in the water-ethanol-toluene system were correlated by the superposition of the Wilson and Redlich-Kister equations with a ternary term. The correlation of both homogeneous binary systems was taken from the literature. The ternary liquid-liquid equilibrium data were at all temperatures satisfactorily described on using only three ternary parameters determined from the equilibrium data at 50°C. The parameters obtained by the correlation yield also a good estimate of boiling point and composition of homogeneous azeotropic mixture.

When undertaking the thermodynamic description of equilibrium data of ternary and multicomponent systems, especially in connection with liquid-liquid equilibrium, we meet with the following three problems: (i) what correlation relation to apply, (ii) how to insert binary data into the correlation relation, (iii) which parameters to determine from the data of ternary and multicomponent systems?

The choice of the correlation relationship is the essential problem but hitherto not solved. On principle, the correlation relations may be divided into two groups. To the first group belong the "classical" equations (Margules, van Laar, Redlich-Kister, etc. — in more detail see Hála and coworkers¹) which are to be derived from the Wohl expansion². These equations contain in addition to the binary parameters also those ones which can be determined only from the ternary data, and designated henceforth as ternary parameters. To the second group pertain the relations based on the local composition concept (the Wilson, NRTL, UNIQUAC equations — for further information see refs^{3,4}) which consider only the interactions between pairs of molecules and consequently do not contain ternary parameters. The fact that these relations do not contain ternary parameters is often qualified as an advantage of these equations for such equations do not formally require ternary data, and the prediction of behaviour of multicomponent systems consists only in binary subsystems.

In case of vapour-liquid equilibrium it has been proved that it is possible to predict successfully the behaviour of multicomponent systems only on the basis of binary

data^{3,5-10}. However, the application of these equations to the liquid-liquid equilibrium data, which are more sensitive to the $G^E(T, x)$ dependence, has no longer been so successful^{8,11-13}. This fact made Surový and coworkers¹⁴ insert a ternary term even into the relations stemming from the local composition concept.

Here, however, it is necessary to emphasize that more substantial differences in the data correlation by single equations occur in binary systems only with the mildly and strongly nonideal ones. In weakly nonideal systems, the differences in the description by single equations are negligible¹⁵.

The correlation relations used hitherto are substantially empirical, and one may hardly expect the equation chosen to describe, in limits of experimental errors, the behaviour of all the binary subsystems composing the given multicomponent system. The correlation relation selected for the given binary system should describe the measured data as truly as possible (both qualitatively and quantitatively). For these reasons it is not possible to regard as ideal the practice when all the binary subsystems are a priori correlated by the same equation.

The phase equilibrium data in binary subsystems can be involved in the correlation of equilibrium data of multicomponent systems in principle in two ways: directly or indirectly (the alternative when the data are not accepted at all, is not considered because it is without any substantiation).

In case of the direct inclusion of equilibrium binary data we determine all the parameters simultaneously on the basis of binary and ternary data. This procedure was used, e.g., by Anderson and Prausnitz⁸. The indirect mode of inclusion of binary data consists in that on the basis of ternary data, the parameters of binary subsystems are determined which were not (or could not be) determined on the basis of data of the respective binary subsystem. From the statistical point of view, the direct inclusion of binary data is correct but it is not suitable from the practical point of view. In case of a rigorous approach we should actualize the respective binary parameters on measuring every new ternary system with the given binary subsystem. As we do not "improve" the description of behaviour of pure substances on the basis of correlation of binary systems, it is not advantageous "to improve" the description of binary subsystems on the basis of multicomponent systems. It is necessary to note as well that the indirect inclusion of binary data of multicomponent systems in case of the equations based on the local composition concept (which do not contain ternary parameters) is groundless for it is nothing to optimize.

From the above-mentioned discussion follows also the answer to the third question. It is necessary to establish above all the ternary parameters — as far as the correlation relation contains them — and then the parameters of the binary subsystems which have not been determined with sufficient accuracy and at the same time the equilibrium data in the ternary system are significantly influenced by these parameters. For instance, it is useless to determine, on the basis of the liquid-liquid

equilibrium data, the parameters of those binary subsystems which exhibit only small deviations from ideality because these parameters do not nearly affect the liquid-liquid equilibrium^{4,16}.

The studied system water(1)-ethanol(2)-toluene(3) represents a suitable basis for verifying the consistence of the vapour-liquid and liquid-liquid equilibrium experimental data and so also the possibility of simultaneous correlation of equilibrium data. First the correlation of equilibrium data of the binary subsystems and finally of the ternary system itself is discussed.

Correlation of Binary Subsystems

Water(1)-ethanol(2). This system has been studied experimentally many times¹⁷, and the data were correlated by various equations. To attain sufficiently precise reproduction of experimental data (vapour-liquid equilibrium, composition of azeotropic point, limiting activity coefficients, heat of mixing), it is not sufficient to employ the usually used correlation equations. Larkin and Pemberton¹⁸, as well as Pemberton and Mash¹⁹ used the orthogonal polynomials with temperature-dependent parameters for the correlation. A similar procedure was used by Kolbe and Gmehling²⁰ who applied the Legendre polynomials. Their correlation was transformed to the Redlich-Kister equation²¹ in the form

$$G^E/(RT) = x_1 x_2 \sum_{i=1}^5 A_{12i} (x_1 - x_2)^{i-1}. \quad (1)$$

Parameters A_{12i} are temperature dependent, and the constants of this dependence are given in Table I. This correlation makes the thermodynamic description of behaviour of this system possible in the whole concentration range and within the temperature of 30–150°C.

Ethanol(2)-toluene(3). Vapour-liquid equilibrium of this system has also been measured by a number of authors — see Gmehling and coworkers¹⁷, quite recently by Oracz and Kolasinska²² as well. The limiting activity coefficients for this system report Tieggs and coworkers²³ and Thomas and coworkers²⁴. Nagata and Yamada²⁵ recommend for the simultaneous correlation of G^E and H^E the Wilson equation²⁶ with the temperature dependent parameters

$$a_{23}/K = 1\,832.8 - 3.1467 T/K, \quad (2)$$

$$a_{32}/K = 89.69 - 0.1156 T/K.$$

In spite of a mild disagreement of experimental and correlated limiting activity coefficients of ethanol (see below), this correlation was applied further because

other relations verified by Nagata and Yamada²⁵ yielded worse results. The virtue was also the finding that this correlation describes well the value of $\partial^2 G_m / \partial x_1^2$ in the neighbourhood of its minimum.

Water(1)-toluene(3). Experimental data on liquid-liquid equilibrium of this heterogeneous system are summarized by Sørensen and Arlt²⁷ who also recommend the optimum values of mutual solubility from 0 to 25°C. For higher temperatures there exist only the data by Tarasenkov and Polozniceva²⁸ on the solubility of water in toluene. To obtain thermodynamic description of this system in the temperature interval 0 to 90°C, the data on mutual solubility at higher temperatures than those reported by Sørensen and Arlt²⁷ are needed. The data on mutual solubility of water and toluene were estimated for this purpose on the basis of the solubility data in the water-benzene and water-ethylbenzene systems published by Tsonopoulos and Wilson²⁹ and Heidman and coworkers³⁰ from the relation

$$\ln x_T = (\ln x_B + \ln x_{EB})/2 \quad (3a)$$

or

$$x_T = (x_B x_{EB})^{1/2}. \quad (3b)$$

Here x_T gives the mole fraction of toluene (water) in the aqueous (toluene-rich) phase in the water-toluene system at the given temperature, x_B the mole fraction of benzene (water) in the aqueous (benzene-rich) phase in the water-benzene system at the same temperature. Analogous meaning stands for x_{EB} for the ethylbenzene-water system. The derivation of this relation is in Appendix 1.

TABLE I

Parameters for the dependence of constants of the Redlich-Kister equation in the water(1)-ethanol(2) system on absolute temperature [$A_{12i} = A_{12i(1)} + A_{12i(2)}(T_0/T) + A_{12i(3)} \ln(T/T_0) + A_{12i(4)}(T/T_0)$, $T_0 = 373.15$ K]

<i>i</i>	$A_{12i(1)}$	$A_{12i(2)}$	$A_{12i(3)}$	$A_{12i(4)}$
1	6.012867	-10.922972	-17.56731	6.110625
2	-2.452920	1.143357	0.0106675	0.935025
3	2.523675	-9.512025	-16.367100	7.124700
4	-3.356440	28.390575	53.671200	-25.129550
5	3.492037	-3.846762	-3.799950	0.382375
6	-0.441504	-24.438172	-49.937737	24.904845

The obtained values on mutual solubility are given in Table II and in Figs 1 and 2 (along with further literature data). The agreement of estimated and experimental data may be considered to be very good. The upper limit of applicability of Eq. (3) may be regarded 90°C for above this temperature the solubility of water in toluene exceeds 1%. Even at the temperature of 100°C, the difference of experimental data by Anderson and Prausnitz³¹ and estimated ones amounts to 6.7% (solubility of toluene in water) and 17% (solubility of water in toluene).

On the basis of the estimated data, the constants of the modified Wilson equation⁴ were calculated for this system by minimizing the difference in activities of components in equilibrium phases⁴. The parameters obtained are as follows

$$\begin{aligned} a_{13}/K &= -395.48 + 7.0509 T/K, \\ a_{31}/K &= 1\,733.2 + 0.22224 T/K, \\ A_{131} &= 3.22971 - 0.0076055 T/K. \end{aligned} \quad (4)$$

TABLE II

Estimated and literature values of mutual solubility of water(1) and toluene(3) ($\delta x = x_{exp} - x_{calc}$)

t^0 , C	$x_1 \cdot 10^4$	$x_3 \cdot 10^3$	$\delta x_1 \cdot 10^4$ ^a	$\delta x_3 \cdot 10^3$ ^a
0	1.070	1.194	0.106	0.082
10 ^b	1.42	1.09	—	—
10	1.058	1.719	0.041	0.051
20 ^b	1.13	2.16	—	—
20	1.081	2.427	0.00	0.00
30	1.134	3.365	-0.024	-0.071
40	1.218	4.589	-0.032	-0.071
50	1.336	6.170	-0.024	-0.15
60	1.492	8.17	-0.003	-0.22
70	1.693	10.7	0.033	-0.15
80	1.947	13.8	0.078	0.22
90	2.267	17.8	0.130	1.11
100	2.667	22.5	0.171	3.02
99.14 ^c	2.86	19.2	—	—

^a Deviations from estimated and calculated values according to the modified Wilson equation with parameters (4), ^b see ref.²⁷, ^c see ref.³¹.

Distribution Coefficient K_2

With respect to the small mutual solubility of water and toluene, this ternary system is an ideal model to verify the consistence of experimental data on liquid-liquid and vapour-liquid equilibria and consequently to judge the suitability of the correlation relation used. The distribution coefficient of ethanol is defined by the relation

$$K_2 = \frac{(x_2)_{\text{aqueous phase}}}{(x_2)_{\text{toluene phase}}} = \frac{(\gamma_2)_{\text{toluene phase}}}{(\gamma_2)_{\text{aqueous phase}}} \quad (5)$$

In case of a low mutual solubility, for limiting value of distribution coefficient holds the relation

$$K_2^0 = \lim_{x_2 \rightarrow 0} K_2 = \frac{(\gamma_2^\infty)_{\text{toluene phase}}}{(\gamma_2^\infty)_{\text{aqueous phase}}} = \frac{(\gamma_2^\infty)_{\text{toluene}}}{(\gamma_2^\infty)_{\text{water}}} \quad (6)$$

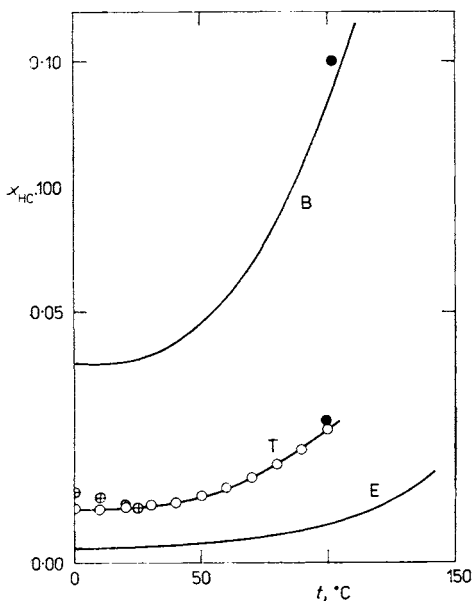


FIG. 1

Solubility of benzene²⁹ B, ethylbenzene³⁰ E, and estimated of toluene T in water (⊕ data by Sørensen and Arlt²⁷, ● data by Anderson and Prausnitz³¹)

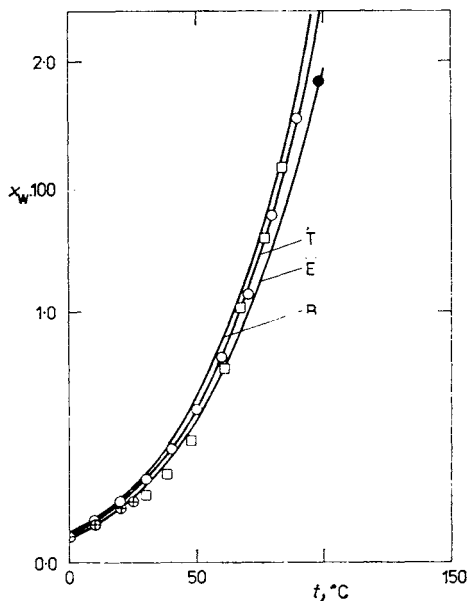


FIG. 2

Solubility of water in benzene²⁹ B, ethylbenzene³⁰ E, and estimated in toluene T (⊕ Sørensen, Arlt²⁷, □ Tarasenkova and Polozniceva²⁸, ● Anderson and Prausnitz³¹)

where $(\gamma_2^\infty)_{\text{toluene}}$ and $(\gamma_2^\infty)_{\text{water}}$ are the limiting activity coefficients of ethanol in toluene and in water. The literature limiting activity coefficients of ethanol in water and in toluene are summarized in Table III along with the values of γ_2^∞ in water and in toluene calculated on the basis of the correlation relations of Larkin and Pemberton¹⁸, Kolbe and Gmehling²⁰, and Nagata and Yamada²⁵. It is apparent from the given values that the γ_2^∞ values following from the data by Larkin and Pemberton¹⁸ and Kolbe and Gmehling²⁰ differ at lower temperatures. The values of γ_2^∞ calculated from the Wilson equation for the ethanol–toluene system are rather higher than the experimental ones. In case of the Wilson equation, we meet with this effect very often.

When comparing K_2^0 estimated on the basis of limiting activity coefficients at 25°C with the value of K_2^0 following from the data by Washburn and coworkers³², considerable discrepancy is evident. On the other hand it is possible to state good

TABLE III

Values of limiting activity coefficient of ethanol in the binary systems water–ethanol and ethanol–toluene and of limiting distribution coefficient

<i>t</i> , °C	Limiting activity coefficient γ_2^∞				Limiting distribution coefficient		
	H ₂ O(1)–ethanol(2)		ethanol(2)–toluene(3)		K_2^{0a}	K_2^{0b}	K_2^{0c}
	Ref. ¹⁸	Ref. ²⁰	Ref. ²⁵	Refs ^{22–24}			
5	—	1.97	28.9	—	—	14.7	9.2 ^d
20	—	2.81	21.1	—	—	7.51	—
25	3.83	3.10	19.0	18.4 ^e	4.96	6.12	5.8 ^d
25	—	—	—	—	—	—	12 ^f
28.3	—	—	—	14.9 ^e	—	—	—
30	4.10	—	17.1	—	4.17	—	—
40	—	3.96	14.1	10.0 ^g	—	3.56	—
50	5.00	4.48	11.7	—	2.36	2.63	2.75 ^d
69.5	—	—	—	6.95 ^h	—	—	—
70	5.62	5.36	8.30	—	1.49	1.57	—
81.5	—	—	—	6.30 ^e	—	—	—
84.3	—	—	—	—	—	—	1.13 ⁱ
90	5.95	5.93	6.16	—	1.04	1.04	—
107.8	—	—	—	4.39 ^h	—	—	—

^a Distribution coefficient calculated from Eq. (6) on the basis of limiting activity coefficients of ethanol (see refs^{18,25}), ^b distribution coefficient calculated from Eq. (6) on the basis of limiting activity coefficients of ethanol (see refs^{20,25}), ^c distribution coefficient determined on the basis of liquid–liquid equilibrium data, ^d see ref.³⁴, ^e see ref.²³, ^f see ref.³², ^g see ref.²², ^h see ref.²⁴, ⁱ see ref.³³.

agreement of the estimated limiting distribution coefficients with the values determined by Arzhanov and coworkers³³ and those determined in our preceding work³⁴.

Correlation of Equilibrium Data in the Ternary System

To correlate data in this system, the superposition of the Wilson²⁶ and Redlich-Kister²¹ equations with a ternary term,

$$Q = G^E/(RT) = Q_{\text{Redl. Kist.}} + Q_{\text{Wilson}} + Q_{\text{tern}}, \quad (7)$$

was used. For N -component system holds

$$Q_{\text{Wilson}} = - \sum_{i=1}^N x_i \ln \sum_{j=1}^N x_j A_{ij}^W, \quad (8)$$

$$A_{ij}^W = (V_j^L/V_i^L) \exp(-a_{ij}/T), \quad (9)$$

$$Q_{\text{Redl. Kist.}} = \sum_{i=1}^{N-1} \sum_{j>i}^N x_i x_j \sum_{m=1}^{b_{ij}} A_{ijm} (x_i - x_j)^{m-1}, \quad (10)$$

$$Q_{\text{tern}} = \sum_{i=1}^{N-2} \sum_{j>i}^{N-1} \sum_{k>j}^N x_i x_j x_k (C_{ijk} x_i + C_{ikj} x_j + C_{ikj} x_k), \quad (11)$$

where b_{ij} is the number of terms (parameters) in the binary system $i - j$. Molar volumes and the Antoine equation constants are given in Table IV. The expression for the activity coefficient of the i -th component is given in Appendix 2. The relations for $\partial \ln \gamma_i / \partial x_j$ needed when applying the Newton method for calculating the composition of coexisting phases are given in monograph⁴ for the Wilson equation, and for the Redlich-Kister equation with the ternary term they will be published³⁶.

The correlation of both homogeneous binary systems, as it has been given, was taken from the literature^{20,25}. In the water-ethanol system it was the correlation by Kolbe and Gmehling²⁰. The respective constants are summarized in Table I.

TABLE IV

Molar volumes in the liquid phase V_{mi}^L (taken from the monograph by Gmehling and coworkers¹⁷) and constants of the Antoine vapour pressure equation ($\ln(p/\text{kPa}) = A - B/(C + t/^\circ\text{C})$)

Substance	$V_{mi}^L, \text{cm}^3 \text{mol}^{-1}$	A	B	C	Ref.
Toluene	106.85	14.01415	3 106.47	220.0	35
Ethanol	58.68	16.75508	3 718.97	228.14	35
Water	18.07	16.32931	3 841.72	228.0	40

Considering that the Redlich–Kister equation fully reproduces the nonideal behaviour of this system, the contribution of the Wilson equation to the excess energy was annulled, or better, at all temperatures the calculations were carried out with values

$$A_{12}^W = A_{21}^W = 1. \quad (12)$$

For the ethanol–toluene system, the Wilson equation was used with the parameters determined by Nagata and Yamada²⁵. The constants of the Redlich–Kister equation, which would in expansion (7)–(10) belong to this system, were considered to be zero (the Wilson equation fully reproduces the behaviour of this system). In the heterogeneous system water–toluene, the modified Wilson equation⁴ was employed with parameters (4) determined on the basis of estimated data on mutual solubility. Application of the Redlich–Kister equation to this system failed.

Calculation of Ternary Parameters

When calculating the ternary parameters $C_{ijk(i)}$ on the basis of liquid–liquid equilibrium data, two alternatives were used. In the first case, all three parameters in Eq. (11) were considered to be of the same magnitude; then the ternary term can be written in the form

$$Q_{\text{tern}} = x_1 x_2 x_3 C. \quad (13)$$

With this alternative, parameter C was determined by way of trial. For different values of C , the objective function

$$S = \left\{ \sum_{k=1}^n S_k / (6n) \right\}^{1/2} = \\ = \left\{ \sum_{k=1}^n \left[\sum_{i=1}^3 (x'_{i,\text{exp}} - x'_{i,\text{calc}})^2 + (x''_{i,\text{exp}} - x''_{i,\text{calc}})^2 \right]_k (6n)^{-1} \right\}^{1/2}, \quad (14)$$

was evaluated, where n is the number of tie-lines. Values $x'_{i,\text{calc}}$, $x''_{i,\text{calc}}$ were determined so as to yield the minimum value of S_k for the given experimental values of $x'_{i,\text{exp}}$, $x''_{i,\text{exp}}$ (by using the Newton method⁴). The dependence of S on the values of C for single isotherms is illustrated in Fig. 3. Larger deviations for the 50°C isotherm result from the fact that two tie-lines, unlike the other isotherms, lie in the immediate proximity of the critical point.

It is evident from Fig. 3 that the consideration of the only ternary constant considerably improves the description of equilibrium data. Further it is apparent that the optimum value of C decreases with increasing temperature. If we neglect this temperature dependence and use the value $C = 1.50$ or $C = 1.10$ which cor-

respond to the temperature of 25 or 50°C, respectively, then only small deterioration in thermodynamic description for the remaining isotherms will occur — see Fig. 3.

As to the second alternative, all three ternary parameters C_{1231} , C_{1232} , C_{1233} were optimized. To determine them, a procedure minimizing the objective function (14) in terms of the Newton method⁴ was elaborated. The results obtained are summarized in Table V. Here it is necessary to point out that (especially in case of the 50°C isotherm) a considerable decrease in the objective function was observed on using all three parameters. In this case, too, the parameters determined at one temperature were applied to the other isotherms with the aim of verifying the possibility

TABLE V

Calculated values of ternary parameters and objective function S corresponding to them

t^0 , C	C_{1231}	C_{1232}	C_{1233}	S
5	2.20	2.20	2.20	0.73 ^a
25	1.599	1.574	1.355	1.15
50	1.421	1.208	0.685	2.10
5	1.599	1.574	1.353	0.83 ^b
50	1.599	1.574	1.353	2.94 ^b
5	1.421	1.208	0.685	1.44 ^c
25	1.421	1.208	0.685	2.02 ^c

^a Even with these parameters, the increments of parameters were smaller than 0.01; ^b estimation of liquid-liquid equilibrium with the parameters obtained at 25°C; ^c estimation of liquid-liquid equilibrium with the parameters obtained at 50°C.

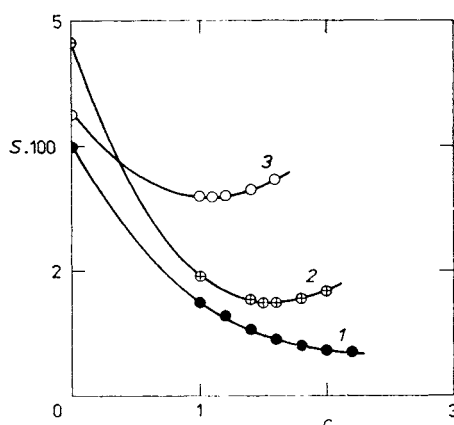


FIG. 3

Dependence of S on parameter C for single isotherms. 1 5°C, 2 25°C, 3 50°C

of predicting the liquid–liquid equilibria at the other temperatures. The results of these calculations, summarized in Table V, showed that parameters $C_{ijk(i)}$ determined on the basis of isothermal data at 5 and 25°C (not containing any equilibrium points from the critical region) predict larger heterogeneous region. The data prediction at 25°C on the basis of ternary parameters determined at 50°C can be judged in Fig. 4 where the points obtained by the titration method by Washburn and co-workers³² are plotted as well. It can be seen that the agreement of the calculated and experimental data in the critical region obtained with the ternary parameters determined at 50°C, is better than that with the ternary parameters established from the data at this temperature. For this reason we recommend the ternary parameters obtained on using the data at 50°C even for the temperature of 25°C.

DISCUSSION

In Fig. 5 we give the temperature dependence of limiting distribution coefficient K_2^0 determined from the liquid–liquid equilibrium data the by authors of this work and by Arzhanov and coworkers³³. Besides, values K_2^0 calculated from limiting activity coefficients of ethanol in water and in toluene are also plotted in Fig. 5. The values of K_2^0 following from the data by Washburn and coworkers is beyond this dependence (see our preceding work³⁴) and is probably in error. On the contrary, the values measured by us³⁴ agree well with those predicted. A larger difference occurs only at 5°C probably because both the correlation relations used for the homogeneous binary subsystems^{20,25} are in this case applied outside the temperature range from which the parameters were determined.

The used superposition of the Wilson and Redlich–Kister equations, as far as it is based only on binary contributions, is not sufficient to get a good description of

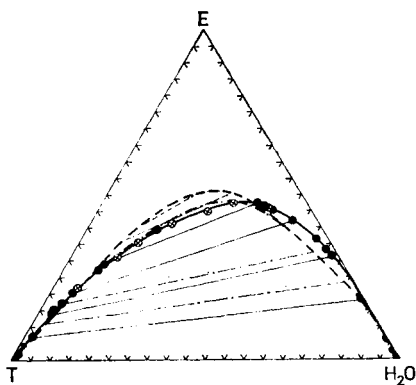


FIG. 4

Correlation and prediction of equilibrium data at 25°C. ● ——— experimental data obtained in paper³⁴, ⊕ data by Washburn and coworkers³² determined by the titration method, — — — equilibrium curve calculated on the basis of ternary parameters determined at 25°C, - - - - equilibrium curve calculated on the basis of ternary parameters determined from the data at 50°C

equilibrium data in the ternary system but is necessary to add even the ternary term. The application of as few as one ternary constant considerably improves the thermodynamic description of equilibrium data.

The superposition of the Wilson and Redlich-Kister equations was applied because the parameters of these equations were available for both the binary subsystems and at the same time well reproduced the measured data. In other systems, the possibility is not excluded of obtaining better results by combining other equations. The main advantage of the superposition used is regarded by us in the fact that it keeps in the

TABLE VI

Boiling point and composition of azeotropic mixture in the water(1)-ethanol(2)-toluene(3) system under normal pressure

Source	$t, ^\circ\text{C}$	x_1	x_2	x_3
Ogorodnikov and coworkers ³⁹	74.4	0.326	0.432	0.242
Arzhanov and coworkers ³³	74.4	0.335	0.404	0.261
Řířná and coworkers ³⁴	74.4	0.304	0.436	0.260
Calculated in this work on the basis of liquid-liquid equilibrium at 50°C	75.4 ₅	0.277 ₅	0.472 ₅	0.250

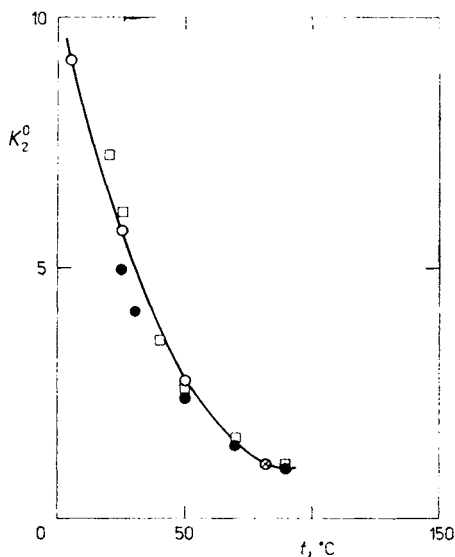


FIG. 5

Dependence of distribution coefficient K_2^0 on temperature, \circ paper³⁴, \bullet estimation on the basis of limiting activity coefficient of ethanol in toluene²⁵ and in water¹⁸, \square estimation on the basis of limiting activity coefficient of ethanol in toluene²⁵ and in water²⁰, \circ Arzhanov and coworkers³³

highest degree the information on respective binary subsystems and in the same time, it enables one to use multiparameter correlation^{21,37,38} of binary subsystems when describing multicomponent mixtures.

To verify the applicability of our correlation, the boiling point and composition of the azeotropic mixture, which lies in the homogeneous region, were calculated (the verification using the vapour-liquid equilibrium data by Arzhanov and co-workers³³ was not carried out because of their internal inconsistency and probably little accuracy). The boiling temperature and composition of azeotropic mixture under normal pressure found experimentally and calculated in terms of the ternary parameters determined at 50°C are given in Table VI. Despite this agreement is not excellent, it is so far good as to confirm the adequacy of the correlation applied and the possibility of the simultaneous description of liquid-liquid and vapour-liquid equilibria.

APPENDIX 1

Derivation of Eq. (3)

Relation (3) can be derived in terms of the assumption of additivity of group contributions for $\ln \gamma_i$, i.e.

$$\begin{aligned} \ln \gamma_i &= \ln \gamma(\text{toluene}) = \ln \gamma(\text{benzene ring} + \text{CH}_3) = \\ &\doteq [\ln \gamma(\text{benzene}) + \ln \gamma(\text{benzene ring} + \text{CH}_2 + \text{CH}_3)]/2. \end{aligned} \quad (A1-1)$$

In group contribution methods in residual terms, the contributions for CH_2 and CH_3 are not distinguished, and consequently the logarithm of activity coefficient of toluene is to be approximated by the arithmetic mean of logarithms of limiting activity coefficients of benzene and ethylbenzene. In case of low solubilities, activity coefficient corresponds to the reciprocal value of mole fraction, and relation (3) is obtained from Eq. (A1-1).

APPENDIX 2

Relation for the Activity Coefficient of the i -th Component in case of the Superposition of the Wilson and Redlich-Kister Equations

For the activity coefficient of the i -th component in N -component system holds the general relation⁴

$$\ln \gamma_i = Q + (\partial Q / \partial x_i) - \sum_{j=1}^N x_j (\partial Q / \partial x_j), \quad (A2-1)$$

where $(\partial Q/\partial x_i)$ and/or $(\partial Q/\partial x_j)$ represent so-called non-physical derivatives which are obtained without respecting the constraint $\sum_{i=1}^N x_i = 1$. From relations (7)–(11) it is possible to derive the following relation

$$\begin{aligned}
 (\partial Q/\partial x_s) = & -\ln \sum_{j=1}^N x_j A_{sj}^W - \sum_{k=1}^N x_k A_{ks}^W / \left(\sum_{j=1}^N x_j A_{kj}^W \right) + \\
 & + \sum_{j=s+1}^N x_j A_{sjl} + \sum_{p=2}^{b_{sj}} A_{sjp} (x_s - x_j)^{(p-2)} (p x_s - x_j) + \\
 & + \sum_{i=1}^{s-1} x_i A_{isl} + \sum_{p=2}^{b_{is}} A_{isp} (x_i - x_s)^{(p-2)} (x_i - p x_s) + \\
 & + \sum_{j=s+1}^{N-1} \sum_{k=j+1}^N x_j x_k (2x_s C_{sjks} + x_j C_{sjkj} + x_k C_{sjkk}) + \\
 & + \sum_{i=1}^{s-1} \sum_{k=s+1}^N x_i x_k (x_i C_{iskl} + 2x_s C_{isks} + x_k C_{iskk}) + \\
 & + \sum_{i=1}^{s-2} \sum_{j=i+1}^{s-1} x_i x_j (x_i C_{ijsl} + x_j C_{ijsj} + 2x_s C_{ijss}), \quad s = 1, 2, \dots, N. \quad (A2-2)
 \end{aligned}$$

By evaluating all N derivatives and inserting the respective values into (A2-1), the activity coefficients of all the components are obtained.

LIST OF SYMBOLS

A_{ij}^W, A_i^W	parameters of Wilson equation (8), (9)
A_{ijk}	k -th parameter (temperature dependent) of Redlich-Kister equation (10)
a_{ij}, a_{ji}	parameters of Wilson equation (9)
b_{ij}	number of parameters of Redlich-Kister equation in binary system $i-j$
$C_{ijk(i)}$	i -th ternary parameter in ternary system $i-j-k$ (11)
C	ternary parameter (13)
G^E	molar excess Gibbs energy
H^E	molar excess enthalpy
K_2	distribution coefficient of component 2, see (5)
K_2^0	limiting distribution coefficient of component 2, see (6)
N	number of components
Q	dimensionless excess Gibbs energy
S	objective function
S_k	sum of squares of deviations in mole fractions of all components in both phases at k -th tie-line, see (14)
T	absolute temperature
V_i^L	molar volume of i -th component in liquid phase
x_i	mole fraction of i -th component in liquid phase
γ_i	activity coefficient of i -th component in liquid phase
γ_i^∞	limiting activity coefficient of i -th component in liquid phase

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