LIQUID-VAPOUR EQUILIBRIUM. L.*

PREDICTION OF MULTICOMPONENT VAPOUR-LIQUID EQUILIBRIA FROM THE BINARY PARAMETERS IN SYSTEMS WITH LIMITED MISCIBILITY

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A practical test of adequacy was made of the III and IV suffix Margules equation and the Renon-Prausnitz NRTL equation for prediction of behaviour of multicomponent systems from the binary data. An extensive set of vapour-liquid equilibrium data from the literature for systems with perfect and limited miscibility of the components in the liquid phase was used for the test.

The design of industrial separation units as well as the determination of optimum operation parameters calls for the knowledge of a set of equilibrium and transport data of mixtures to be separated. A serious lack of these data exists and their determination, particularly in multicomponent systems, is both difficult and time consuming. This has stimulated an effort of chemists and chemical engineers to work out a method enabling as much as possible thorough description of complex systems on the basis of a small number, and from experimental standpoint easily available, data.

This paper deals with the problem of prediction of the behaviour of multicomponent and multiphase systems from the binary data. The methods selecting binary data as a basis of the calculation seem most adequate to the present state of theoretical knowledge. A theoretically founded expression of intermolecular forces in a mixture from the data of the pure components is not known, nor does it seem hopeful to predict the properties of mixtures on the basis of pure component properties. In contrast, statistical theories commonly assume that the binary intermolecular interactions predetermine the macroscopic properties of mixtures. It seems therefore natural to start the phenomenological prediction of phase equilibria of multicomponent systems from the binary data.

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THEORETICAL

Criterion of Equilibrium

A multicomponent and multiphase system is in the thermodynamic equilibrium if the fugacities of each component in each phase are equal. For an equilibrium between a liquid and a gas phase consequently

$$f_i^l = f_i^g\,. \tag{1}$$

On taking the state of the pure component at the temperature and pressure of the system as the standard state for the liquid phase and the component of unit fugacity as the standard state for the gas phase (this choice of standard states is convenient for mixture consisting of components which are at the temperature and pressure of the system below critical point), we can derive from Eq. (*1*) (see[39]) an exact relationship characterizing the dependence between the state variables in a system with the liquid and the gas phase at equilibrium:

$$y_i P Z_i = x_i \gamma_i P_i^0\,, \tag{2}$$

and

$$Z_i = \frac{v_i^g}{v_i^0} \exp\left\{-\int_{P_i^0}^{P} \frac{v_i^{01}}{RT}\,dP\right\} =$$

$$= \exp\left\{\int_0^P \left(\frac{\bar{v}_i^g}{RT} - \frac{1}{P}\right) dP - \int_0^{P_i^0} \left(\frac{v_i^{0g}}{RT} - \frac{1}{P}\right) dP - \int_{P_i^0}^{P} \frac{v_i^{01}}{RT}\,dP\right\}. \tag{3}$$

At moderate pressure it may be assumed that the gas phase obeys the equation of state with the 2nd virial coefficient and that the molar volume of the pure liquid component is independent of pressure. The correction factor Z_i takes then the following form[109]

$$Z_i = \exp\left\{\frac{1}{RT}(B_{ii} - v_i^{01})(P - P_i^0) + \frac{P}{RT}\left[\left(\frac{\partial B}{\partial y_i}\right)_{T,P,y_{j\neq i}} - B_{ii} - B\right]\right\}, \tag{4}$$

where $B = \sum_i \sum_j x_i y_i B_{ij}$ is the virial coefficient of the gaseous mixture.

For systems the components of which do not associate in the gas phase, the value of the factor Z_i at low pressure does not differ appreciably from unity and Eq. (*2*) may be than written as

$$y_i P = x_i \gamma_i P_i^0\,. \tag{5}$$

Activity Coefficients in Multicomponent Systems

From Eq. (*5*) it is seen that in the range of low and normal pressure the knowledge of the activity coefficients is mandatory for the calculation of phase equilibria in multicomponent systems.

It is therefore apparent that the search for a function characterizing the dependence of the activity coefficients on the state variables and, above all, on composition of the liquid phase is of prime importance in description of vapour–liquid equilibrium in multicomponent systems.

Many thermodynamically consistent equations may be found in the literature expressing the dependence of the activity coefficients on the state variables (most of them list the monographs of Hála, Pick, Fried and Vilém[39] and Prausnitz[82]). A disadvantage of the classic equations, represented first of all by the group of the Wohl expansion[116], is the requirement of the ternary eventually higher constants (Margules III and IV–suffix, Redlich-Kister) for description of a multicomponent system, or fulfilment of certain constraints between the binary constants.

The semi-theoretical Wilson[115] equation lacks these disadvantages, however, it cannot describe in principle the behaviour of systems having components of limited mutual solubility in the liquid phase. Wilson attempted to remove this drawback by introducing the third parameter. This arrangement, however, renders the calculation of polycomponent systems difficult as it requires all values of the third parameter be equal in all pertaining binary systems. Renon and Prausnitz modified Wilson's model by implementing a nonrandom parameter α (its value may be estimated by means of general rules on the basis of the character of the binary mixture and its components) and combined it with Scott's two-liquid theory[99]. The relationship obtained enables a description even systems with a limited miscibility in the liquid phase.

Another problem of characterizing the phase equilibria in multicomponent systems rests in the calculation of constants of selected empirical function. These parameters are usually coupled by simple relationships with limiting values of the activity coefficients, which may be estimated from the properties of the pure component[8,27,42,49,78]. This approach necessitates a minimum of data and it is therefore in focus of interest of chemical engineers.

The accuracy of all methods of this kind published to date is unfortunately insufficient for non-ideal systems and can be used only as a rough estimate (*e.g.* choice of extraction solvent) in case of the lack of suitable data. As the only expedient way of estimating the properties of the multicomponent system under present state of the theory of solution appears the calculation of parameters from the binary data.

RESULTS AND DISCUSSION

Correlation of the Binary Data

The vapour–liquid equilibrium data of 144 binary systems from the literature were correlated by the III- and IV-suffix Margules equation[39]

$$\log \gamma_1 = x_2^2[A_{12} + 2x_1(A_{21} - A_{12} - D_{12}) + 3x_2^2 D_{12}] ,$$

$$\log \gamma_2 = x_1^2[A_{21} + 2x_2(A_{12} - A_{21} - D_{12}) + 3x_1^2 D_{12}] , \tag{6}$$

where A_{12}, A_{21} and D_{12} are adjustable parameters*, and by the Renon-Prausnitz NRTL equation[83]

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* Relationship (*6*) is the IV-suffix equation. The III-suffix equation with parameters A_{12} and A_{21} may be obtained from (*6*) by putting $D_{12} = 0$.

$$\ln \gamma_1 = x_2^2 \left\{ \frac{\tau_{12} \exp(-\alpha_{12}\tau_{12})}{[x_1 \exp(-\alpha_{12}\tau_{12}) + x_2]^2} + \frac{\tau_{21} \exp(-2\alpha_{12}\tau_{21})}{[x_1 + x_2 \exp(-\alpha_{12}\tau_{21})]^2} 2 \right\},$$

$$\ln \gamma_2 = x_1^2 \left\{ \frac{\tau_{12} \exp(-2\alpha_{12}\tau_{12})}{[x_1 \exp(-\alpha_{12}\tau_{12}) + x_2]^2} + \frac{\tau_{21} \exp(-\alpha_{12}\tau_{21})}{[x_1 + x_2 \exp(-\alpha_{12}\tau_{21})]^2} \right\} \tag{7}$$

with τ_{12} and τ_{21} as parameters. The constant α_{12} of the NRTL equation was determined by means of the general rules[83], as well as it was calculated as the third adjustable parameter.

The values of the constants were obtained by minimizing the function

$$Q \equiv \sum_{m=1}^{n} W_m F_m^2 , \tag{8}$$

where the index m denotes the m-th experimental point, n is the number of experimental points and F_m is a function defined by

$$F_m \equiv \ln (\gamma_1/\gamma_2)_{m,exp} - \ln (\gamma_1/\gamma_2)_{m,calc} . \tag{9}$$

W_m is a weight factor assigned to the m-th experimental point from the relation[114]

$$W_m \equiv \{[(\partial F/\partial x_1)_{y_1}]_m^2 + [(\partial F/\partial y_1)_{x_1}]_m^2\}^{-1} \tag{10}$$

(index m on the right hand side of equation (*10*) indicates that the values of the derivatives were calculated in the point $[x_{1,m};\ y_{1,m}]$). The value of the weight factor has its maximum at the concentration $x_1 = y_1 = 0{\cdot}5$ and decreases towards concentration limits. Thus the points with a low concentration of one component having greater relative error are assigned a smaller weight.

The function Q was minimized by the least square method (Margules equation) and by the Marquardt method[58] (NRTL). The results of correlations of 66 isothermal and 78 isobaric (the temperature dependence of the parameter τ_{12} and τ_{21} was neglected) binary vapour–liquid equilibria based on the assumption of an ideal gas phase ($Z_i = 1$) are shown in Tables I and II. The mean values of deviations were defined as follows

$$\Delta y_1 = \sum_{m=1}^{n} \left| y_{1,m,exp} - y_{1,m,calc} \right| . \tag{11}$$

Table III summarizes the constants of equations calculated from the binary azeotropic and solubility data in the systems ethyl acetate–ethanol, ethyl acetate–water and ethanol–water. The constants of two-parameter equations (Margules II - suffix and NRTL with the generalized α_{12}) were evaluated by solving the following set of equations

$$\ln (P/P_1^0) - \ln \gamma_1 = 0 \,, \tag{12a}$$

$$\ln (P/P_2^0) - \ln \gamma_2 = 0 \,, \tag{12b}$$

(azeotropic data), or

$$\ln (x_1^{(1)}/x_1^{(2)}) - \ln (\gamma_1^{(2)}/\gamma_1^{(1)}) = 0 \,, \tag{13a}$$

$$\ln (x_2^{(1)}/x_2^{(2)}) - \ln (\gamma_2^{(2)}/\gamma_2^{(1)}) = 0 \,, \tag{13b}$$

(solubility data – indices$^{(1)}$ and $^{(2)}$ designate equilibrium liquid phases). The constants of three-parameter relations (Margules IV-suffix and NRTL with adjusted α_{12}) were evaluated by solving the set of Eqs (*12a*), (*13a*) and (*13b*) (ethyl acetate–water system).

Table IV gives the average values of the mean deviations of the calculated and experimental composition of the gas phase. This Table is supplemented by the results of correlations of the isothermal data in which the correction factor Z_i was calculated from Eq. (*4*). The necessary virial coefficients were taken over from the literature, or (in most cases) estimated by a generalized method of O'Connell and Prausnitz[74]. From comparison of the results it is apparent that the assumption often made in chemical engineering practice about an ideal behaviour of the gas phase is at moderate pressure acceptable for most of the systems.

The results summarized in Tables I, II and IV clearly indicate that of the two models with two adjustable parameters (Margules III-suffix and NRTL with the generalized α_{12}), the Renon-Prausnitz equation provides better results, while the three-parameter relations (Margules IV-suffix and NRTL with the minimalized α_{12}) follow the behaviour of the binary systems equally well.

Ternary Vapour–Liquid Equilibrium

The vapour–liquid equilibria of 41 ternary systems of different types were calculated from the binary parameters given in Tables I and II by means of the IV-suffix Margules and the NRTL equations. The relationships used have the form:
Margules IV-suffix[49]

$$\begin{aligned} \log \gamma_1 = {} & x_2^2[A_{12} + 2x_1(A_{21} - A_{12} - D_{12}) + 3x_1^2 D_{12}] + \\ & + x_3^2[A_{13} + 2x_1(A_{31} - A_{13} - D_{13}) + 3x_1^2 D_{13}] + \\ & + x_2x_3[A_{21} + A_{13} - A_{32} + 2x_3(A_{31} - A_{13}) + 2x_2(A_{32} - A_{23}) + \\ & + 3x_2x_3D_{23} - x_1(2 - 3x_1)\, C_1 - x_2(1 - 3x)\, C_2 - x_3(1 - 3x_1)\, C_3] \end{aligned} \tag{14}$$

(expressions for γ_2 and γ_3 are obtained by permuting the indices)

TABLE I

Binary Systems
NRTL Equation

Binary system	Data ref.	Temp. °C
Water–1,4-dioxane	92	88— 97
Water–propyl acetate	97	90— 98
Water–pyridine	50	50
Sulphur dioxide–benzene	9	32
Tetrachloromethane–benzene	119	50
Tetrachloromethane–benzene	30	77— 80
Tetrachloromethane–cyclohexane	89	40
Tetrachloromethane–cyclohexane	89	70
Tetrachloromethane–ethanol	4	45
Tetrachloromethane–ethanol	4	65
Tetrachloromethane–2-propanol	119	68— 79
Chloroform–1,4-dioxane	60	50
Chloroform–ethanol	86	45
Chloroform–ethanol	86	55
Chloroform–ethyl acetate	70	64— 78
Chloroform–n-hexane	54	45
Chloroform–n-hexane	54	55
Chloroform–methanol	94	50
Chloroform–methanol	70	53— 63
Chloroform–methyl isobutyl ketone	51	62—113
Nitromethane–tetrachloromethane	11	45
Methanol–benzene	90	35
Methanol–benzene	90	55
Methanol–benzene	33	57— 69
Methanol–1-butanol	43	71—102
Methanol–ethanol	3	66— 77
Methanol–ethylacetate	2	62— 75
Methanol–n-hexane	28	45
Methanol–2-propanol	32	55
Methanol–tetrachloromethane	90	35
Methanol–tetrachloromethane	90	55
Methanol–toluene	15	64— 90
Methanol–water	62	60
Methanol–water	107	65— 93
Acetonitrile–water	110	76— 95
Ethanol–benzene	108	50
Ethanol–benzene	44	55
Ethanol–benzene	113	68— 79
Ethanol–1,2-dichloroethane	108	50
Ethanol–1,4-dioxane	45	78— 99
Ethanol–n-heptane	29	30

α_{12} Estimated				α_{12} Calculated			
α_{12}	τ_{12}	τ_{21}	$\Delta y_1 . 10^4$	α_{12}	τ_{12}	τ_{21}	$\Delta y_1 . 10^4$
0·30	1·6838	0·8191	210	0·4878	1·8913	1·4084	81
0·20	5·3582	0·2405	91	0·1582	5·8243	−0·2692	53
0·47	2·2475	−0·0762	127	0·6561	2·7330	0·4148	49
0·30	−0·9564	3·6753	9	0·3287	0·1843	9·6673	6
0·30	−0·3939	0·6063	14	0·2969	−0·3967	0·6106	14
0·30	−0·0588	0·1447	23	6·2453	0·0167	0·1505	7
0·30	−0·4711	0·6709	13	0·2981	−0·4724	0·6736	13
0·30	−0·3383	0·4695	12	0·2994	−0·3384	0·4698	12
0·47	2·0291	0·7544	44	0·4856	2·0549	0·7890	44
0·47	1·7670	0·7112	20	0·5044	1·8120	0·7877	19
0·30	1·0118	0·4925	183	0·0281	1·1895	0·1535	182
0·30	0·5764	−1·2502	105	0·4301	1·5247	−1·6083	30
0·30	2·4035	−0·4622	61	0·1561	3·3480	−1·2895	58
0·30	2·4165	−0·5155	48	0·1293	3·7784	−1·6768	44
0·30	0·7569	−1·2599	13	0·3158	0·7662	−1·2461	10
0·30	0·6551	−0·1204	26	0·3670	0·6232	−0·0835	26
0·30	0·6786	−0·1742	29	0·3624	0·6662	−0·1545	28
0·30	2·1974	−0·2111	76	0·0737	5·0232	−2·5801	71
0·30	2·1416	−0·1998	49	0·2743	2·2093	−0·2778	49
0·30	0·2189	−1·2150	234	1·8737	0·6386	−1·0026	49
0·47	1·3495	1·7367	41	0·4609	1·3521	1·6865	41
0·47	1·1350	1·9245	62	0·4822	1·1788	2·0012	52
0·47	1·0746	1·8140	48	0·5062	1·1808	1·8977	45
0·47	1·4374	1·8768	175	0·4104	1·2714	1·7541	154
0·30	2·5422	−0·6901	128	0·0470	130·9200	0·3875	20
0·30	0·0093	−0·0363	112	1·2895	−0·0356	3·2536	81
0·30	0·6131	0·4652	41	0·3746	0·5879	0·5076	41
0·47	2·2697	2·4159	213	0·4316	2·3953	2·4231	15
0·30	−0·1292	0·1407	40	0·4278	−0·1292	0·1442	40
0·47	1·3373	2·3743	185	0·4763	1·4056	2·5104	149
0·47	1·1866	1·8992	198	0·4451	1·1148	1·9806	177
0·47	1·6502	1·7030	281	0·3938	1·4923	1·4914	251
0·30	0·0874	0·6496	108	0·6248	0·0166	0·8189	101
0·30	−0·3929	1·2438	24	0·2940	−0·3946	1·2561	23
0·30	0·9526	1·2828	191	0·4431	1·0217	1·7830	130
0·47	0·6316	1·6576	28	0·5131	0·7397	1·6747	28
0·47	0·8621	1·8302	63	0·4698	0·8614	1·8320	57
0·47	0·7061	1·3142	99	0·5496	0·7921	1·7314	36
0·47	0·7751	1·5972	36	0·4320	0·6858	1·6449	25
0·30	1·7423	−0·4774	134	0·2638	1·8110	−0·5265	123
0·47	1·7717	2·3258	252	0·4579	1·7001	2·2694	248

TABLE I
(*Continued*)

Binary system	Data ref.	Temp. °C
Ethanol–n-heptane	52	71– 88
Ethanol–water	63	40
Ethanol–water	24	50
Ethanol–water	63	55
Ethanol–water	63	70
Ethanol–water	85	77– 99
Acrylonitrile–acetonitrile	110	76– 81
Acrylonitrile–water	110	73– 99
Acetone–benzene	12	45
Acetone–benzene	31	58– 76
Acetone–chlorobenzene	31	59–122
Acetone–chloroform	65	25
Acetone–chloroform	94	50
Acetone–chloroform	51	59– 64
Acetone–cyclohexane	56	53– 77
Acetone–n-heptane	79	50
Acetone–methanol	94	50
Acetone–methanol	32	55
Acetone–methanol	37	56– 63
Acetone–methyl acetate	94	50
Acetone–methyl isobutyl ketone	51	59–110
Acetone–nitromethane	13	45
Acetone–2-propanol	32	55
Acetone–tetrachloromethane	12	45
Acetone–tetrachloromethane	94	50
Acetone–tetrachloromethane	1	56– 74
Acetone–water	5	25
Acetone–water	107	56– 77
Methyl acetate–methanol	94	50
Methyl acetate–methanol	104	54– 62
Methyl acetate–water	104	56– 58
1-Propanol–benzene	34	75
1-Propanol–propyl acetate	77	95– 98
1-Propanol–water	66	60
1-Propanol–water	66	87– 95
2-Propanol–water	103	81– 97
Methyl ethyl ketone–benzene	23	78– 80
Methyl ethyl ketone–cyclohexane	22	72– 77
Methyl ethyl ketone–n-heptane	99	77– 96
Methyl ethyl ketone–toluene	99	80–110
Ethyl acetate–benzene	16	77– 80
Ethyl acetate–cyclohexane	17	72– 77

α_{12} Estimated				α_{12} Calculated			
α_{12}	τ_{12}	τ_{21}	$\Delta y_1 . 10^4$	α_{12}	τ_{12}	τ_{21}	$\Delta y_1 . 10^4$
0·47	1·8098	2·0143	87	0·4723	1·8309	2·0513	81
0·30	0·5198	0·5768	20	0·4572	0·5613	0·6005	20
0·30	−0·2374	2·2202	25	0·3000	−0·2374	2·2203	25
0·30	0·3147	0·7045	23	0·5783	0·4529	0·6687	20
0·30	0·3517	0·5563	22	0·2792	0·3433	0·5599	22
0·30	−0·2003	1·8610	55	0·3008	−0·1983	1·8596	53
0·30	−0·4264	0·5374	90	−0·0292	−1·2512	1·2500	85
0·20	0·2598	3·3372	94	0·2021	0·2745	3·3270	93
0·30	−0·3733	0·8952	16	0·1971	−0·6268	1·2071	19
0·30	−0·5848	1·1789	32	0·0147	−8·1077	9·6325	39
0·30	−0·1231	0·1153	145	−1·0177	−2·9870	0·3574	83
0·30	−0·0095	−0·7869	182	0·6594	0·0426	−0·6909	204
0·30	−0·8946	0·2424	49	0·3002	−0·8944	0·2419	49
0·30	−0·4437	−0·2232	28	0·0602	−0·5442	−0·1492	26
0·20	1·8258	0·0036	125	0·1566	2·0457	−0·2163	124
0·20	2·1837	−0·2374	56	0·2000	2·1840	−0·2375	56
0·30	0·3479	0·2904	67	1·3686	0·4565	0·4285	62
0·30	0·2892	0·3860	35	0·3397	0·2788	0·3970	35
0·30	1·2068	−0·4313	50	0·3245	1·2263	−0·4349	49
0·30	0·6487	−0·4511	25	0·3027	0·6504	−0·4511	25
0·30	0·5111	−0·9832	302	10·8670	0·1129	−0·5136	120
0·30	0·4483	−0·5450	86	0·9120	0·4366	−0·4650	86
0·30	0·0832	0·5520	36	0·2993	0·0830	0·5524	36
0·30	−0·1873	1·1829	27	0·3050	−0·1805	1·1767	27
0·30	−0·0699	1·0433	29	0·9396	0·3752	0·7921	26
0·30	−0·1185	1·0725	66	0·3013	−0·1173	1·0721	66
0·30	0·9275	1·3137	134	0·5107	1·5973	1·4017	163
0·30	0·9666	1·2831	191	0·4965	1·8563	1·4127	150
0·30	0·5450	0·5819	32	0·3857	0·5744	0·5897	32
0·30	0·1174	1·0200	128	0·9816	0·8671	1·0904	71
0·20	−0·0171	2·5593	189	0·1987	−0·0175	2·5713	189
0·47	0·3565	1·3424	53	0·3926	0·3227	1·3182	60
0·30	0·3427	0·2607	10	−0·0266	0·2062	0·3665	11
0·30	−0·0277	2·3152	152	0·5478	0·6876	2·2493	110
0·30	−0·0788	2·7041	93	0·4334	0·3556	2·5276	83
0·30	−0·1368	2·4131	123	0·2988	−0·1409	2·4186	123
0·30	−0·1713	0·3811	22	0·9148	−0·1390	0·4022	11
0·20	−0·3114	1·5683	55	0·2914	−0·3088	1·5670	55
0·20	0·4659	0·7375	73	0·7668	0·7974	0·8591	45
0·30	−0·2079	0·5442	57	0·3571	−0·1695	0·5146	54
0·30	−0·1705	0·2882	7	0·5811	−0·1598	0·2912	6
0·20	0·2042	0·7172	32	0·3111	0·2123	0·7500	27

TABLE I
(*Continued*)

Binary system	Data ref.	Temp. °C
Ethyl acetate–ethanol	63	40
Ethyl acetate–ethanol	63	55
Ethyl acetate–ethanol	63	70
Ethyl acetate–ethanol	38	72— 76
Ethyl acetate–water	63	40
Ethyl acetate–water	63	55
Ethyl acetate–water	63	70
Ethyl acetate–water	26	70— 99
Diethyl ether–tetrachloromethane	106	41— 74
n-Pentane–benzene	9	—32
Perfluoro-n-hexane–n-hexane	25	35
Benzene–acetic acid	36	81—111
Benzene–aniline	59	70
Benzene–aniline	53	95—151
Benzene–chlorobenzene	31	83—126
Benzene–cyclohexane	91	70
Benzene–cyclohexane	71	77— 80
Benzene–1,2-dichloroethane	119	50
Benzene–furfural	105	82—155
Benzene–n-heptane	10	60
Benzene–n-heptane	34	75
Benzene–n-heptane	10	80
Benzene–n-heptane	95	80— 95
Benzene–2-ethoxyethanol	105	80—118
Benzene–nitromethane	112	90—108
Benzene–1-propanol	81	76— 93
Benzene–2-propanol	72	60— 70
Benzene–toluene	41	81—109
Cyclohexane–aniline	46	70
Cyclohexane–2-methoxyethanol	105	77—105
Cyclohexane–furfural	105	82—148
Cyclohexane–n-heptane	7	89— 98
Cyclohexane–methyl isobutyl ketone	20	81—111
Cyclohexane–1-propanol	64	76— 88
Cyclohexane–2-propanol	73	69— 80
Cyclohexane–toluene	68	81—108
Cyclohexane–2,2,3-trimethylbutane	40	79— 80
1-Hexene–1,4-dioxane	101	69— 88
1-Hexene–2-ethoxyethanol	101	65—111
1-Hexene–1,2,3-trichloropropane	101	66—114
1-Hexene–n-hexane	101	64— 68
Methylcyclopentane–benzene	68	71— 80

α_{12} Estimated				α_{12} Calculated			
α_{12}	τ_{12}	τ_{21}	$\Delta y_1 . 10^4$	α_{12}	τ_{12}	τ_{21}	$\Delta y_1 . 10^4$
0·30	−0·0692	1·7111	49	0·3002	−0·0685	1·7105	49
0·30	−0·1507	1·8623	55	0·3071	−0·1325	1·8450	55
0·30	−0·2017	1·9616	61	0·3314	−0·1201	1·8827	60
0·30	0·1995	0·6959	32	0·1525	0·1852	0·6729	27
0·20	1·1761	1·5857	43	0·0215	−0·5906	3·1143	43
0·20	0·8117	2·1315	43	0·0755	−0·2320	3·0587	43
0·20	0·5210	2·5111	37	0·1041	−0·3035	3·2945	36
0·20	0·6896	2·0869	800	0·4160	1·6897	2·3923	649
0·30	2·5551	−1·1848	100	0·2989	2·5551	−1·1843	100
0·30	0·0498	2·1870	20	0·3543	0·1724	2·2086	18
0·40	1·1276	1·9199	68	0·4094	1·1406	1·9869	50
0·30	−0·0176	0·6837	189	0·5363	−0·0895	1·4833	189
0·40	0·9051	−0·2562	9	0·4111	0·8998	−0·2595	9
0·30	0·0974	0·1246	35	0·2491	0·0963	0·1256	35
0·30	0·3302	−0·3830	109	−0·6003	0·3370	−0·3782	158
0·30	0·2437	0·1179	19	0·0975	0·3133	0·0442	20
0·80	0·3259	0·0551	21	0·1963	0·3874	−0·0076	21
0·20	0·0002	−0·0308	59	2·0088	10·3320	2·3636	41
0·30	1·4728	−0·4068	40	0·3061	1·5005	−0·4066	40
0·30	0·4876	−0·0801	50	0·3888	0·4554	−0·0422	50
0·30	0·3560	−0·0015	46	0·3044	0·3563	−0·0014	46
0·30	0·2087	0·0973	84	−0·2908	0·3563	−0·0699	83
0·30	0·3521	−0·0374	43	0·3933	0·3244	−0·0063	43
0·30	2·0319	−0·3186	35	0·2950	2·0275	−0·3220	37
0·30	0·9266	0·3100	102	0·8725	1·1418	0·7699	69
0·47	1·1313	0·3124	201	0·1584	1·4025	−0·0782	204
0·47	1·3496	0·5185	48	0·6139	1·4294	0·7245	28
0·30	0·4374	−0·4165	66	0·3016	0·3919	−0·3883	64
0·20	1·4297	0·8436	6	0·4152	1·6716	1·1801	5
0·20	1·0000	1·0000	410	0·4811	1·9683	4·4859	728
0·20	1·6057	0·7987	97	0·4375	1·7922	1·3215	55
0·30	−0·0994	0·1434	28	4·2972	−0·0478	0·1473	26
0·30	−0·5774	1·5929	285	0·7104	0·6362	4·1309	230
0·47	1·8758	0·6314	103	0·2088	2·1745	−0·0412	93
0·47	1·4197	0·7755	131	0·6208	1·8121	1·1026	104
0·30	−0·0065	0·2298	63	2·4670	0·0512	0·3045	57
0·30	0·2624	−0·0333	57	0·3050	0·2626	−0·0332	56
0·20	0·2335	0·5596	49	0·4764	0·1648	0·7321	44
0·20	1·7560	0·0110	87	0·2854	1·5671	0·2487	88
0·30	0·4051	0·4104	22	0·4803	0·3142	0·5292	19
0·30	−0·0069	0·0050	42	−9·5244	0·0802	−0·0852	30
0·30	−0·2963	0·6948	24	0·0220	−4·0415	4·8230	16

TABLE I
(*Continued*)

Binary system	Data ref.	Temp. °C
Methylcyclopentane–ethanol	96	60—76
n-Hexane–benzene	118	55
n-Hexane–benzene	102	70
n-Hexane–benzene	81	68—78
n-Hexane–cyclohexane	102	70
n-Hexane–cyclohexane	69	69—81
n-Hexane–1,4-dioxane	101	69—85
n-Hexane–ethanol	54	45
n-Hexane–ethanol	44	55
n-Hexane–2-ethoxyethanol	101	70—76
n-Hexane–methylcyclopentane	69	69—72
n-Hexane–1-propanol	81	66—90
n-Hexane–1,2,3-trichloropropane	101	70—113
Toluene–furfural	105	111—153
n-Heptane–aniline	87	51·5
n-Heptane–1-propanol	34	75
n-Heptane–toluene	117	99—110
2,2,4-Trimethylbutane–furfural	105	99—127
2,2,4-Trimethylbutane–toluene	105	100—110

NRTL $(C = 3)$

$$\ln \gamma_i = \frac{\sum_{j=1}^{C} x_j \tau_{ji} \exp\left(-\alpha_{ij}\tau_{ji}\right)}{\sum_{j=1}^{C} x_j \exp\left(-\alpha_{ij}\tau_{ji}\right)} + \sum_{j=1}^{C} \frac{x_j \exp\left(-\alpha_{ij}\tau_{ij}\right)}{\sum_{k=1}^{C} x_k \exp\left(-\alpha_{kj}\tau_{kj}\right)} \,.$$

$$\left[\tau_{ij} - \frac{\sum_{l=1}^{C} x_l \tau_{lj} \exp\left(-\alpha_{ij}\tau_{lj}\right)}{\sum_{k=1}^{C} x_k \exp\left(-\alpha_{kj}\tau_{kj}\right)}\right] . \qquad (15)$$

Margules equation was used in four versions which differed from each other by the method of evaluation of the ternary constants C_1, C_2 and C_3:
In version A ternary effects were entirelly neglected $(C_1 = C_2 = C_3 = 0)$, in version B estimated using the Colburn and Wohl method[18] for the ternary constant of the III-suffix equation

$$C_1 = C_2 = C_3 = {}^1/_2(A_{21} - A_{12} + A_{13} - A_{31} + A_{32} - A_{23}) \,. \qquad (16)$$

α_{12} Estimated				α_{12} Calculated			
α_{12}	τ_{12}	τ_{21}	$\Delta y_1 \,.\, 10^4$	α_{12}	τ_{21}	τ_{21}	$\Delta y_1 \,.\, 10^4$
0·47	2·1965	1·1447	97	0·4617	2·1820	1·1059	92
0·30	−0·2949	0·9482	21	0·2994	−0·2953	0·9486	21
0·30	0·5652	−0·0662	22	1·5813	0·3752	0·2331	22
0·30	−0·5909	1·2709	49	0·3026	−0·5868	1·2822	49
0·30	−0·0564	0·1214	33	0·6033	−0·0539	0·1194	33
0·30	0·0127	0·0511	38	7·5135	0·0286	0·1917	24
0·20	−0·1957	1·5167	109	0·2048	−0·1881	1·5155	109
0·47	2·5626	1·5255	91	0·4243	2·3862	1·2600	55
0·47	1·5045	1·3380	258	0·5236	1·8424	2·0417	202
0·20	2·5864	−0·4206	41	0·1430	2·9402	−0·7783	41
0·30	0·4406	−0·3388	31	0·3000	0·4406	−0·3385	31
0·47	0·9334	1·2570	228	0·5413	1·6010	1·1602	190
0·20	0·9393	0·3375	41	0·0306	1·0340	0·1649	45
0·30	−0·2244	1·3017	327	1·1173	1·9233	1·3999	184
0·20	1·7749	1·0581	1	0·2011	1·7755	1·0594	1
0·47	1·1404	1·0490	132	0·6133	1·4162	1·3587	115
0·30	−0·0956	0·3789	28	1·2872	0·0034	0·3451	21
0·20	1·2751	1·1801	91	0·3544	1·7154	1·2136	81
0·30	0·0994	0·2009	18	0·1737	0·0969	0·2001	18

In the last two versions the ternary constants were evaluated from the ternary experimental data: in version C a single constant ($C_1 = C_2 = C_3 = C$), in version D all three constants ($C_1 \neq C_2 \neq C_3$).

The method of calculation of the adjustable parameters was analogous to the correlation of the binary data, *i.e.* the following function was minimized by the least square method

$$Q = \sum_{m=1}^{n} W_{13,m} F_{13,m}^2 + \sum_{m=1}^{n} W_{23,m} F_{23,m}^2 \,, \tag{17}$$

where for example

$$F_{13,m} = \ln (\gamma_1/\gamma_3)_{m,\mathrm{exp}} - \ln (\gamma_1/\gamma_3)_{m,\mathrm{calc}} \tag{18}$$

and

$$W_{13,m} = \left\{ \left[\left(\frac{\partial F_{13}}{\partial x_1} \right)_{x_2,y_1,y_2} \right]_m^2 + \left[\left(\frac{\partial F_{13}}{\partial x_2} \right)_{x_1,y_1,y_2} \right]_m^2 + \right.$$

$$\left. + \left[\left(\frac{\partial F_{13}}{\partial y_1} \right)_{x_1,x_2,y_2} \right]_m^2 + \left[\left(\frac{\partial F_{13}}{\partial y_2} \right)_{x_1,x_2,y_1} \right]_m^2 \right\}^{-1} . \tag{19}$$

TABLE II

Binary Systems
Margules Equation

Binary system	Data ref.	Temp. °C
Water–1,4-dioxane	92	88—97
Water–propyl acetate	97	90—98
Water–pyridine	50	50
Sulphur dioxide–benzene	9	—32
Tetrachloromethane–benzene	119	50
Tetrachloromethane–benzene	30	77—80
Tetrachloromethane–cyclohexane	89	40
Tetrachloromethane–cyclohexane	89	70
Tetrachloromethane–ethanol	4	45
Tetrachloromethane–ethanol	4	65
Tetrachloromethane–2-propanol	119	68—79
Chloroform–1,4-dioxane	60	50
Chloroform–ethanol	86	45
Chloroform–ethanol	86	55
Chloroform–ethyl acetate	70	64—78
Chloroform–n-hexane	54	45
Chloroform–n-hexane	54	55
Chloroform–methanol	94	50
Chloroform–methanol	70	53—63
Chloroform–methyl isobutyl ketone	51	62—113
Nitromethane–tetrachloromethane	11	45
Methanol–benzene	90	35
Methanol–benzene	90	55
Methanol–benzene	33	57—69
Methanol–n-butanol	43	71—102
Methanol–ethanol	3	66—77
Methanol–ethyl acetate	2	62—75
Methanol–n-hexane	28	45
Methanol–2-propanol	32	55
Methanol–tetrachloromethane	90	35
Methanol–tetrachloromethane	90	55
Methanol–toluene	15	64—90
Methanol–water	62	60
Methanol–water	107	65—93
Acetonitrile–water	110	76—95
Ethanol–benzene	108	50
Ethanol–benzene	44	55
Ethanol–benzene	113	68—79
Ethanol–1,2-dichloroethane	108	50
Ethanol–1,4-dioxane	45	78—99
Ethanol–n-heptane	29	30

III-Suffix			IV-Suffix			
A_{12}	A_{21}	$\Delta y_1 \cdot 10^4$	A_{12}	A_{21}	D_{12}	$\Delta y_1 \cdot 10^4$
0·7926	0·9366	267	0·9709	1·0992	0·6170	101
0·8299	1·9430	580	0·8799	2·3815	0·8736	27
0·2309	0·6579	220	0·4266	0·9152	0·7276	119
0·5253	−0·1469	11	1·3431	0·7095	2·0457	7
0·0694	0·0467	14	0·0674	0·0444	−0·0062	14
0·0574	0·0253	8	0·0647	0·0032	0·0226	8
0·0540	0·0318	13	0·0513	0·0290	−0·0082	13
0·0406	0·0296	12	0·0407	0·0296	0·0001	12
0·5604	0·9150	146	0·6802	1·0334	0·4062	72
0·5581	0·8417	115	0·6642	0·9544	0·3417	38
0·5612	0·5834	180	0·5903	0·0619	0·1013	181
−0·3040	−0·6274	28	−0·3324	−0·6684	−0·1124	24
0·2693	0·6390	37	0·2303	0·5301	−0·2425	22
0·2474	0·6123	26	0·2053	0·5026	−0·2460	18
−0·2564	−0·4371	11	−0·2728	−0·0455	−0·0508	9
0·1751	0·2289	26	0·1744	0·2281	−0·0023	26
0·1560	0·2129	29	0·1665	0·2237	0·0324	27
0·3386	0·7628	83	0·3737	0·7978	0·1224	73
0·3402	0·7364	64	0·3806	0·7784	0·1330	53
−0·1881	−0·9221	150	−0·4677	−1·5007	−1·4272	93
0·8959	0·8105	106	1·0161	0·9237	0·4015	42
0·9420	0·7198	229	1·1017	0·8684	0·5358	89
0·9199	0·7079	189	1·0579	0·8574	0·5403	55
0·9797	0·8436	141	1·0743	0·0927	0·3936	148
0·1876	0·5204	141	0·3898	0·8475	0·9130	110
0·0020	−0·0242	107	0·0449	0·0022	0·1324	104
0·4193	0·4289	42	0·4558	0·4629	0·1035	40
1·0080	1·0026	248	1·3319	1·3292	0·9977	31
0·0101	−0·0053	40	−0·0044	−0·0239	−0·0527	39
1·0284	0·7396	448	1·2394	0·9589	0·7128	281
0·9847	0·7288	231	1·1095	0·0860	0·4532	195
0·9322	0·9135	230	0·9647	0·9716	0·1926	240
0·3504	0·1826	87	0·2488	0·0015	−0·4793	43
0·3351	0·1869	20	0·3468	0·2028	0·0455	22
0·9212	0·7113	160	1·0226	0·8020	0·3413	132
0·7999	0·5480	120	0·8971	0·6391	0·3032	46
0·8870	0·6289	100	0·9924	0·7240	0·3444	73
0·7926	0·5302	97	0·9053	0·0646	0·3694	59
0·8405	0·5841	74	0·9057	0·6538	0·2268	28
0·2259	0·4784	130	0·2362	0·0489	0·0383	128
1·0574	0·8665	493	1·2406	1·0786	0·7259	301

TABLE II
(*Continued*)

Binary system	Data ref.	Temp. °C
Ethanol–n-heptane	52	71— 88
Ethanol–water	63	40
Ethanol–water	24	50
Ethanol–water	63	55
Ethanol–water	63	70
Ethanol–water	85	77— 99
Acrylonitrile–acetonitrile	110	76— 81
Acrylonitrile–water	110	73— 99
Acetone–benzene	12	45
Acetone–benzene	31	58— 76
Acetone–chlorobenzene	31	59—122
Acetone–chloroform	65	25
Acetone–chloroform	94	50
Acetone–chloroform	51	59— 64
Acetone–cyclohexane	56	53— 77
Acetone–n-heptane	79	50
Acetone–methanol	94	50
Acetone–methanol	32	55
Acetone–methanol	37	56— 63
Acetone–methyl acetate	94	50
Acetone–methyl isobutyl ketone	51	59—110
Acetone–nitromethane	13	45
Acetone–2-propanol	32	55
Acetone–tetrachloromethane	12	45
Acetone–tetrachloromethane	94	50
Acetone–tetrachloromethane	1	56— 74
Acetone–water	5	25
Acetone–water	107	56— 77
Methyl acetate–methanol	94	50
Methyl acetate–methanol	104	54— 62
Methyl acetate–water	104	56— 58
1-Propanol–benzene	34	75
1-Propanol–propyl acetate	77	95— 98
1-Propanol–water	66	60
1-Propanol–water	66	87— 95
2-Propanol–water	103	81— 97
Methyl ethyl ketone–benzene	23	78— 80
Methyl ethyl ketone–cyclohexane	22	72— 77
Methyl ethyl ketone–n-heptane	99	77— 96
Methyl ethyl ketone–toluene	99	80—110
Ethyl acetate–benzene	16	77— 80
Ethyl acetate–cyclohexane	17	72— 77

III-Suffix			IV-Suffix			
A_{12}	A_{21}	$\Delta y_1 . 10^4$	A_{12}	A_{21}	D_{12}	$\Delta y_1 . 10^4$
0·9845	0·9136	309	1·1733	1·1184	0·7429	105
0·4407	0·4327	21	0·4532	0·4449	0·0416	20
0·7492	0·2993	71	0·8466	0·4439	0·3773	20
0·4255	0·3802	24	0·4534	0·4053	0·0892	21
0·3761	0·3551	23	0·3730	0·3521	−0·0096	24
0·6639	0·3174	80	0·7054	0·0386	0·1909	54
−0·0302	0·0655	56	−0·0180	0·0785	0·0375	56
1·5359	0·8231	109	1·5535	0·8780	0·5570	93
0·2061	0·1319	18	0·2192	0·1480	0·0465	20
0·2113	0·0974	38	0·2032	0·0872	−0·0281	38
0·1299	0·1096	162	0·0563	−0·0577	−0·5030	138
−0·2507	−0·4047	209	−0·6278	−0·7644	−0·8822	188
−0·3943	−0·2791	48	−0·3374	−0·2194	0·1670	44
−0·3088	−0·3017	26	−0·2815	−0·2785	0·0743	24
0·5283	0·7723	116	0·4436	0·0693	−0·2671	107
0·4981	0·8179	56	0·5160	0·8391	0·1706	56
0·2613	0·2661	67	0·2878	0·0297	0·0864	62
0·2829	0·2690	34	0·2893	0·2755	0·0213	36
0·1520	0·2910	51	0·1618	0·3033	0·0362	49
0·0347	0·0553	25	0·0492	0·0068	0·0419	25
0·1347	−0·7307	248	−0·1748	−1·2677	−1·3958	125
0·0010	−0·1543	43	−0·0469	−0·0230	−0·2118	25
0·2737	0·2372	36	0·2597	0·2183	−0·0536	37
0·4080	0·2658	39	0·4550	0·0317	0·1600	15
0·4082	0·2933	36	0·4500	0·3356	0·1448	24
0·3998	0·2743	64	0·4087	0·2837	0·0300	65
0·8552	0·7434	119	0·9044	0·9074	0·3848	155
0·7901	0·8967	194	0·8902	1·0214	0·4178	167
0·4507	0·4447	33	0·4811	0·0474	0·1011	31
0·4786	0·4088	122	0·6055	0·5359	0·4251	66
0·0536	0·5909	185	0·9970	0·0534	−0·1795	185
0·6502	0·4596	62	0·6861	0·4940	0·1235	64
0·2497	0·2500	11	0·2573	0·0256	0·0233	10
0·8526	0·4470	224	1·0522	0·6461	0·6864	137
0·9673	0·3963	242	1·1070	0·5723	0·6005	111
0·8659	0·3680	118	0·9287	0·4338	0·2403	116
0·0994	0·0550	11	0·1079	0·0644	0·0267	11
0·5183	0·3458	57	0·5614	0·0392	0·1433	53
0·5001	0·4763	75	0·5488	0·5310	0·1717	47
0·1407	0·1132	57	0·2170	0·0199	0·2646	56
0·0503	0·0355	6	0·0469	0·0319	−0·0115	6
0·4052	0·3457	28	0·4165	0·0357	0·0378	28

TABLE II
(*Continued*)

Binary system	Data ref.	Temp. °C
Ethyl acetate–ethanol	63	40
Ethyl acetate–ethanol	63	55
Ethyl acetate–ethanol	63	70
Ethyl acetate–ethanol	38	72— 76
Ethyl acetate–water	63	40
Ethyl acetate–water	63	55
Ethyl acetate–water	63	70
Ethyl acetate–water	26	70— 99
Diethyl ether–tetrachloromethane	106	41— 74
n-Pentane–benzene	9	— 32
Perfluoro-n-hexane–n-hexane	25	35
Benzene–acetic acid	36	81—111
Benzene–aniline	59	70
Benzene aniline	53	95—151
Benzene–chlorobenzene	31	83—126
Benzene–cyclohexane	91	70
Benzene–cyclohexane	71	77— 80
Benzene–1,2-dichloroethane	119	50
Benzene–furfural	105	82—155
Benzene–n-heptane	10	60
Benzene–n-heptane	34	75
Benzene–n-heptane	10	80
Benzene–n-heptane	95	80— 95
Benzene–2-ethoxyethanol	105	80—118
Benzene–nitromethane	112	90—108
Benzene–1-propanol	81	76 — 93
Benzene–2-propanol	72	60— 70
Benzene–toluene	41	81—109
Cyclohexane–aniline	46	70
Cyclohexane–2-methoxyethanol	105	77—105
Cyclohexane–furfural	105	82—148
Cyclohexane–n-heptane	7	89— 98
Cyclohexane–methyl isobutyl ketone	20	81—111
Cyclohexane–1-propanol	64	76— 88
Cyclohexane–2-propanol	73	69— 80
Cyclohexane–toluene	68	81—108
Cyclohexane–2,2,3-trimethylbutane	40	79— 80
1-Hexene–1,4-dioxane	101	69— 88
1-Hexene–2-ethoxyethanol	101	65—111
1-Hexene–1,2,3-trichloropropane	101	66—114
1-Hexene–n-hexane	101	64— 68
Methylcyclopentane–benzene	68	71— 80

III-Suffix			IV-Suffix			
A_{12}	A_{21}	$\Delta y_1 . 10^4$	A_{12}	A_{21}	D_{12}	$\Delta y_1 . 10^4$
0·6764	0·3891	59	0·6989	0·0413	0·1163	52
0·6925	0·3666	68	0·7314	0·4083	0·1971	58
0·6926	0·3590	88	0·7555	0·0409	0·2760	63
0·3700	0·3424	26	0·3654	0·3368	−0·0154	25
1·0927	1·0093	43	1·0895	0·0875	−3·5058	32
1·2261	0·9518	42	1·2230	0·8203	−3·3180	16
1·2949	0·8786	35	1·2930	0·0753	−3·0700	12
1·0851	0·9224	842	1·2772	1·1132	0·6223	734
−0·0712	0·2221	103	−0·0902	−0·2016	0·0567	103
0·8757	0·4455	25	0·9933	0·5424	0·3538	18
1·0225	0·7803	189	1·1373	0·8922	0·4014	66
0·4899	0·1634	153	0·2948	−0·0055	−0·5452	87
0·1391	0·2561	8	−0·0510	−0·0177	−0·7026	5
0·0956	0·0945	35	0·0168	−0·0140	−0·5103	28
0·0403	−0·0268	143	−0·0137	−0·1129	−0·2642	134
0·1512	0·1550	20	0·1630	0·1667	0·0352	18
0·1552	0·1647	21	0·1445	0·1573	−0·0234	21
0·0250	−0·0521	32	−0·0320	−0·1096	−0·1689	27
0·2164	0·4164	45	0·1843	0·3489	−0·1736	52
0·1458	0·1774	50	0·1456	0·1772	−0·0005	50
0·1380	0·1533	46	0·1438	0·0159	0·0195	46
0·1415	0·1235	83	0·1102	0·0907	−0·1058	74
0·1206	0·1365	43	0·1491	0·0167	0·0923	44
0·2887	0·6358	53	0·3316	0·6829	0·1403	34
0·4299	0·5130	107	0·4861	0·5783	0·1927	86
0·4530	0·5596	203	0·4466	0·5531	−0·0220	202
0·4937	0·6900	94	0·5902	0·7925	0·3180	30
0·0242	−0·0584	54	−0·0141	−0·1038	−0·1360	45
0·8027	0·9284	7	0·8882	1·0216	−0·0329	5
0·9227	0·6317	486	1·1859	0·0956	1·0832	593
0·8438	0·9669	101	0·9309	1·0656	0·3899	55
0·0322	0·0047	24	0·0243	−0·0042	−0·0268	23
0·3571	0·1420	282	0·2185	−0·0138	−0·4297	265
0·5575	0·8757	101	0·5695	0·8914	0·0577	99
0·6043	0·7525	190	0·7335	0·9134	0·4860	129
0·1319	0·0693	55	0·1143	0·0480	−0·0571	53
0·0909	0·0990	57	0·1123	0·0120	0·0713	56
0·3780	0·2806	44	0·3174	0·1914	−0·2416	28
0·5313	0·7286	82	0·5228	0·0706	−0·0568	79
0·3542	0·2993	19	0·3202	0·2381	−0·1697	16
0·0338	−0·0027	25	0·0281	−0·0083	−0·0170	26
0·1744	0·1240	15	0·1641	0·1128	−0·0334	14

TABLE II
(*Continued*)

Binary system	Data ref.	Temp. °C
Methylcyclopentane–ethanol	96	60— 76
n-Hexane–benzene	118	55
n-Hexane–benzene	102	70
n-Hexane–benzene	81	68— 78
n-Hexane–cyclohexane	102	70
n-Hexane–cyclohexane	69	69— 81
n-Hexane–1,4-dioxane	101	69— 85
n-Hexane–ethanol	54	45
Hexane–ethanol	44	55
n-Hexane–2-ethoxyethanol	101	70— 76
n-Hexane–methylcyclopentane	69	69— 72
n-Hexane–1-propanol	81	66— 90
n-Hexane–1,2,3-trichloropropane	101	70—113
Toluene–furfural	105	111—153
n-Heptane–aniline	87	51·5
n-Heptane–1-propanol	34	75
n-Heptane–toluene	117	99—110
2,2,4-Trimethylbutane–furfural	105	99—127
2,2,4-Trimethylbutane–toluene	105	100—110

Table V gives the values of the mean deviations in composition of the gas phase calculated from the Margules equation in all four version (A through D) and from the NRTL equation with two and three adjustable parameters per binary (versions E and F).

Table VI contains results of the calculations in the system ethyl acetate–ethanol–water at 70°C* based on the binary azeotropic and solubility data. The results indicate that the accuracy of prediction of the ternary vapour–liquid equilibrium by the NRTL equation with the constants from the binary one-point data is comparable with the accuracy of correlation based on a set of points. The same procedure applied to the Margules equation leads to considerably inferior results.

The average values of the mean deviation in composition of the gas phase are summarized in Table VII. A comparison of the results of the version A and B of the Margules equation indicates that Colburn's and Wohl's estimate of the ternary constant did not produce on average any improvement in comparison with the results

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* The results of prediction at 55 and 40°C are identical within experimental error.

III-Suffix			IV-Suffix			
A_{12}	A_{21}	$\Delta y_1 . 10^4$	A_{12}	A_{21}	D_{12}	$\Delta y_1 . 10^4$
0·7031	0·9959	204	0·8396	1·1393	0·4957	141
0·2636	0·1726	20	0·2540	0·1622	−0·0329	19
0·1765	0·2137	23	0·1908	0·0228	0·0448	21
0·2295	0·1090	53	0·2603	0·1403	0·1002	48
0·0271	0.0252	33	0·0800	0·0807	0·1617	27
0·0565	0·0186	24	0·0588	0·0210	0·0074	24
0·5533	0·3860	110	0·6206	0·4598	0·2124	111
0·7593	1·0664	141	0·8995	1·2132	0·4481	66
0·8927	0·8163	262	1·1268	0·1071	0·8215	201
0·4327	0·8404	38	0·1221	0·5644	−0·8388	24
0·0201	0·0282	31	0·0178	0·0025	−0·0071	31
0·6838	0·7810	248	0·7352	0·8488	0·1980	223
0·5098	0·5209	44	0·4463	0·0417	−0·3005	33
0·4182	0·3033	471	0·5944	0·0717	1·0730	186
0·9152	1·1410	1	1·9434	1·1557	1·2912	1
0·6913	0·7147	165	0·8149	0·8398	0·4336	117
0·1444	0·0913	21	0·1461	0·0933	0·0065	21
0·8616	1·0003	103	0·9162	1·0632	0·2054	85
0·1280	0·1261	18	0·1185	0·0115	−0·0327	17

without the constant. An interesting conclusion is that the error of predicition from the NRTL equation with nine, respectively six adjustable binary parameters is practically the same. This somewhat surprising finding is caused by the fact that in six out of total 41 processed ternary systems the nine-parameter equation yields results by more than 20% rel. worse than the six-parameter one. For a typical example – the acetone–methanol–chloroform system – the values of the molar excess free energy were calculated in the ternary system for both sets of constants (Table VIII). It has been found that the differences between the calculated values of the function in the binary systems are small (several percent at most), while the values in a major portion of the ternary diagram differ by several tens of percent. The differences in the values of activity coefficients are alike. It is therefore apparent that polycomponent thermodynamic quantities depend on the values of the NRTL parameters more markedly than the binary values. In this as well as in all similar cases at least one constant α_{ij} takes a value deviating substantially from the generalized one. An unambiguous account for this phenomenon was not found. The results of correlations of the "anomalous" binary system (in our case aceton–methanol and methanol–

chloroform) point out that the calculated values are insensitive to large variations in the values of parameters. In contrast, the variations of the experimental values of the gas phase concentration within experimental error proved that the values

TABLE III

Margules and NRTL Parameters from Binary Azeotropic and Solubility Data

System $i-j$	Temp. °C	Margules Eq. (6)			NRTL Eq. (7)			Data[a]
		A_{ij}	A_{ji}	D_{ij}	α_{ij}	τ_{ij}	τ_{ji}	
Ethyl acetate–ethanol	70	0·401	0·382	—	0·3	0·410	0·560	A
	55	0·432	0·434	—	0·3	0·501	0·568	A
	40	0·469	0·479	—	0·3	0·633	0·565	A
Ethyl acetate–water	70	1·906	0·433	—	0·2	0·030	4·520	S
					0·4	2·134	3·847	S
		2·006	1·225	1·695	0·381	1·696	3·850	AS
	55	1·895	0·529	—	0·2	0·171	4·320	S
					0·4	2·188	3·797	S
		1·987	1·239	1·607	0·382	1·802	3·777	AS
	40	1·871	0·745	—	0·2	0·396	4·035	S
					0·4	2·259	3·730	S
		1·936	1·258	1·474	0·373	1·882	3·660	AS
Ethanol–water	70	0·655	0·397	—	0·3	−0·227	2·230	A
	55	0·628	0·403	—	0·3	−0·168	1·996	A
	40	0·610	0·405	—	0·3	−0·136	1·874	A

[a] Data: A azeotropic[63]; S solubility[63]; AS azeotropic[61] (interpolated by method of Othmer and Ten Eyck[76]) and solubility[63].

TABLE IV

Binary Systems

Mean deviation ($\Delta y_1 . 100$) in vapour phase composition.

Type of systems	Vapour phase	Number of systems	NRTL Eq. (7) with α_{12}		Margules Eq. (7)	
			estim.	calc.	III-Suffix	IV-Suffix
Isothermal	ideal	66	0·63	0·53	0·87	0·56
Isobaric	ideal	78	1·06	0·90	1·20	0·91
Isothermal + isobaric	ideal	144	0·86	0·73	1·05	0·75
Isothermal	real	66	0·60	0·50	0·85	0·53

TABLE V

Ternary Vapour–Liquid Equilibria
Mean deviation ($\Delta y_1 . 100$) in vapour phase composition

Ternary system	Data ref.	Temp. °C	Margules IV-suffix Eq. (6)[a]				NRTL Eq. (7)[a]		Ternary constants Margules Eq. (6)[a]	
			A	B	C	D	E	F	C	D
Acetone–			1·8	1·9	2·2	2·3	1·9	2·2		−0·805
benzene–	55	55–78	0·8	0·8	0·9	1·1	0·7	0·9	−0·402	0·415
cyclohexane			2·3	2·2	2·2	1·9	2·0	2·4		−0·892
Mean			*1·6*	*1·6*	*1·8*	*1·8*	*1·5*	*1·9*		
Acetone–			1·7	1·8	1·4	2·9	1·2	2·1		0·267
chloroform–	51	60–112	3·1	3·1	2·9	3·4	3·5	3·5	−0·241	4·351
methyl isobutyl ketone			2·7	2·7	2·5	3·1	3·8	1·9		−4·095
Mean			*2·5*	*2·5*	*2·2*	*3·1*	*2·8*	*2·5*		
Acetone–			0·8	1·1	0·7	0·6	0·9	2·4		−0·070
methanol–	94	50	0·8	1·2	0·6	0·6	1·0	3·2	0·272	0·390
chloroform			0·8	1·3	0·5	0·5	1·0	3·0		0·489
Mean			*0·8*	*1·2*	*0·6*	*0·6*	*1·0*	*2·8*		
Acetone–			0·5	0·5	0·5	0·4	0·5	0·5		−0·314
methanol–	32	55	0·5	0·5	0·6	0·5	0·5	0·5	−0·160	−0·279
2-propanol			0·4	0·4	0·4	0·3	0·4	0·4		0·219
Mean			*0·5*	*0·5*	*0·5*	*0·4*	*0·5*	*0·5*		
Acetone–			1·0	1·1	3·2	3·2	0·7	1·4		2·380
methanol–	37	57–70	1·9	2·0	3·4	3·6	2·0	2·1	1·358	1·725
water			2·1	2·1	1·5	1·2	1·7	1·7		0·123
Mean			*1·7*	*1·7*	*2·7*	*2·6*	*1·5*	*1·7*		
Acetone–			0·6	0·6	0·7	0·9	0·6	0·6		−0·014
methyl acetate–	32	50	1·0	1·0	0·9	0·9	0·9	1·0	0·263	1·030
methanol			1·2	1·2	1·2	1·1	1·2	1·2		−0·346
Mean			*0·9*	*0·9*	*0·9*	*1·0*	*0·9*	*0·9*		
Acetone–			0·7	0·7	0·7	0·7	0·8	1·0		−0·011
tetrachloromethane–	100	57–80	0·8	0·8	0·8	0·8	0·8	0·9	−0·109	−0·452
benzene			0·6	0·6	0·6	0·6	0·6	0·7		0·153
Mean			*0·7*	*0·7*	*0·7*	*0·7*	*0·7*	*0·8*		
Acrylonitrile–			3·0	2·4	1·8	1·5	1·9	2·1		−0·485
acetonitrile–	111	71–81	3·0	2·4	1·8	1·5	1·7	1·5	0·757	0·276
water			3·1	2·7	2·4	1·7	1·7	2·0		2·163
Mean			*3·0*	*2·5*	*2·0*	*1·6*	*1·8*	*1·9*		

TABLE V
(*Continued*)

Ternary system	Data ref.	Temp. °C	Margules IV-suffix Eq. (6)^a				NRTL Eq. (7)^a		Ternary constants Margules Eq. (6)^a	
			A	B	C	D	E	F	C	D
Benzene–	105	83—108	0·4	0·5	0·4	0·4	0·4	0·6	−0·651	−0·092
cyclohexane–			0·5	0·5	0·5	0·4	0·5	0·6		−0·673
furfural			0·5	0·5	0·5	0·5	0·6	0·7		−0·958
Mean			*0·5*	*0·5*	*0·5*	*0·4*	*0·5*	*0·6*		
Benzene–	84	69— 79	1·7	1·7	1·6	1·5	1·4	1·4	0·053	0·272
cyclohexane–			2·1	2·1	2·1	2·1	1·8	1·8		0·126
n-hexane			0·7	0·7	0·7	0·8	0·6	0·6		0·007
Mean			*1·5*	*1·5*	*1·5*	*1·4*	*1·3*	*1·3*		
Benzene–	105	75— 95	4·1	3·6	3·4	3·3	3·8	3·8	−1·278	−1·067
cyclohexane–			4·3	4·0	4·7	4·3	3·2	3·2		−2·303
2-methoxyethanol			2·5	2·2	1·7	1·6	2·3	2·3		−0·567
Mean			*3·6*	*3·3*	*3·3*	*3·1*	*3·1*	*3·1*		
Benzene–	23	72— 78	0·3	0·3	0·5	0·5	0·4	0·4	−0·139	−0·397
cyclohexane–			1·1	1·1	1·1	1·2	1·2	1·1		0·060
methyl ethyl ketone			1·1	1·1	1·1	1·1	1·2	1·1		−0·045
Mean			*0·8*	*0·8*	*0·9*	*0·9*	*0·9*	*0·9*		
Benzene–	64	74— 84	0·8	1·0	0·7	0·9	0·7	1·4	−0·176	−0·193
cyclohexane–			1·7	1·7	1·7	1·4	2·1	2·0		0·567
1-propanol			2·1	2·1	2·1	1·8	2·5	2·2		−0·776
Mean			*1·5*	*1·6*	*1·5*	*1·4*	*1·8*	*1·8*		
Benzene–	35	75	2·2	2·1	2·6	2·3	1·7	1·6	−0·246	−0·993
n-heptane–			1·9	1·9	1·9	1·9	1·6	1·6		−0·506
1-propanol			2·3	2·5	2·2	1·9	2·0	1·9		0·658
Mean			*2·1*	*2·2*	*2·2*	*2·0*	*1·7*	*1·7*		
Benzene–	102	70	0·9	0·9	0·9	0·6	0·8	0·8	−0·046	−0·571
n-hexane–			0·6	0·6	0·6	0·4	0·6	0·5		0·370
cyclohexane			0·4	0·4	0·4	0·4	0·4	0·4		0·169
Mean			*0·6*	*0·6*	*0·7*	*0·5*	*0·6*	*0·6*		
Benzene–	6	69— 77	0·5	0·5	0·5	0·5	0·7	0·5	0·135	0·034
n-hexane–			0·5	0·5	0·4	0·4	0·4	0·7		0·251
methylcyclopentane			0·4	0·3	0·3	0·3	0·3	0·7		0·135
Mean			*0·5*	*0·4*	*0·4*	*0·4*	*0·5*	*0·7*		

TABLE V
(*Continued*)

Ternary system	Data ref.	Temp. °C	Margules IV-suffix Eq. (6)^a				NRTL Eq. (7)^a		Ternary constants Margules Eq. (6)^a	
			A	B	C	D	E	F	C	D
Chloroform–			1·9	1·2	0·5	0·4	1·1	1·3		0·984
methanol–	70	55—72	2·4	1·5	0·7	0·7	1·4	1·5	0·844	0·923
ethyl acetate			1·4	1·0	0·6	0·6	1·0	1·0		0·617
Mean			*1·9*	*1·3*	*0·6*	*0·5*	*1·1*	*1·3*		
Cyclohexane–			4·6	4·6	5·0	3·3	2·8	2·3		1·537
benzene–	80	70	4·5	4·6	4·0	3·2	2·8	2·3	−0·616	−1·987
aniline			0·1	0·1	0·1	0·1	0·0	0·0		−1·222
Mean			*3·0*	*3·1*	*3·0*	*2·2*	*1·9*	*1·6*		
Cyclohexane–			0·5	0·5	0·6	0·6	0·5	0·6		−0·349
n-heptane–	67	88—108	0·5	0·5	0·6	0·5	0·5	0·5	−0·071	0·037
toluene			0·7	0·7	0·7	0·7	0·7	0·7		0·074
Mean			*0·5*	*0·6*	*0·6*	*0·6*	*0·6*	*0·6*		
Ethanol–			1·1	1·1	1·1	1·0	1·0	0·9		0·291
benzene–	96	60—71	0·5	0·5	0·5	0·4	0·6	0·4	−0·033	−0·123
methylcyclopentane			0·9	1·1	0·9	0·9	0·9	0·9		−0·273
Mean			*0·8*	*0·8*	*0·8*	*0·8*	*0·8*	*0·8*		
Ethanol–			2·4	2·2	1·8	1·1	1·1	1·0		0·722
chloroform–	54	55	1·0	1·0	1·3	1·0	1·9	1·5	−0·417	−0·666
n-hexane			1·7	1·5	1·5	0·8	2·3	2·0		−1·277
Mean			*1·7*	*1·5*	*1·5*	*1·0*	*1·8*	*1·5*		
Ethanol–			1·3	1·2	1·2	0·8	0·7	0·8		0·837
1,2-dichloroethane–	108	50	0·7	0·7	0·7	0·7	0·6	0·6	0·121	−0·181
benzene			1·1	1·0	1·0	0·8	0·6	0·7		−0·393
Mean			*1·0*	*1·0*	*1·0*	0·7	*0·7*	*0·7*		
Ethanol–			1·7	1·9	1·7	1·3	1·3	1·4		−0·220
water–	92	78—86	1·8	1·6	1·9	2·0	2·1	2·0	0·288	0·719
1,4-dioxane			2·1	2·3	1·7	1·8	1·8	1·7		0·343
Mean			*1·8*	*1·9*	*1·8*	1·8	*1·7*	*1·7*		
Ethyl acetate–			1·6	1·4	2·0	1·8	1·7	1·5		−0·459
ethanol–	63	40	1·7	1·5	1·9	1·6	1·6	1·6	0·174	0·961
water			1·3	1·4	1·1	1·2	1·3	1·8		0·076
Mean			*1·5*	*1·5*	*1·7*	*1·5*	*1·5*	*1·6*		

TABLE V

(*Continued*)

Ternary system	Data ref.	Temp. °C	Margules IV-suffix Eq. (*6*)^a				NRTL Eq. (*7*)^a		Ternary constants Margules Eq. (*6*)^a	
			A	B	C	D	E	F	C	D
Ethyl acetate–			1·3	1·4	1·4	1·7	1·5	1·6		0·845
ethanol–	63	55	1·2	1·2	1·2	1·6	1·2	1·1	0·133	−0·521
water			1·4	1·4	1·4	1·1	1·3	1·4		0·045
Mean			*1·3*	*1·3*	*1·3*	*1·4*	*1·3*	*1·4*		
Ethyl acetate–			1·3	1·3	1·6	1·5	1·4	1·3		0·347
ethanol–	63	70	1·7	1·6	1·6	1·5	1·6	1·6	0·711	1·330
water			1·7	1·7	1·3	1·3	1·5	1·6		0·577
Mean			*1·5*	*1·5*	*1·5*	*1·4*	*1·5*	*1·5*		
Ethyl acetate–			3·2	3·3	3·2	2·5	2·7	2·8		2·132
ethanol–	38	70— 78	2·1	2·2	2·0	1·8	2·0	1·6	1·164	1·483
water			3·1	3·2	2·5	2·0	2·8	2·6		−0·156
Mean			*2·8*	*2·9*	*2·6*	*2·1*	*2·5*	*2·3*		
n-Hexane–			2·4	2·5	2·4	2·5	1·9	2·5		0·370
ethanol–	118	55	2·1	2·1	2·1	2·2	2·5	2·1	−0·048	−0·007
benzene			1·4	1·4	1·4	1·4	1·4	1·4		−0·445
Mean			*2·0*	*2·0*	*2·0*	*2·0*	*1·9*	*2·0*		
n-Hexane–			1·6	1·5	1·4	1·4	0·6	1·2		0·431
1-hexene–	101	65— 86	0·9	0·9	0·9	0·8	1·0	1·5	0·136	0·196
1,4-dioxane			1·0	1·0	1·0	0·9	1·1	2·0		−0·205
Mean			*1·1*	*1·1*	*1·1*	*1·0*	*0·9*	*1·6*		
n-Hexane–			6·9	6·8	6·1	5·5	2·8	2·4		−1·053
1-hexene–	101	67—109	5·4	5·3	5·2	4·6	2·6	2·4	−0·948	0·685
2-ethoxyethanol			2·2	2·2	2·0	1·7	0·9	0·9		−1·982
Mean			*4·9*	*4·8*	*4·4*	*3·9*	*2·1*	*1·9*		
n-Hexane–			1·6	1·6	1·6	1·5	1·1	1·1		0·926
1-hexene–	101	69—129	1·2	1·2	1·2	1·2	0·9	1·0	0·016	0·049
1,2,3-trichloropropane			1·7	1·7	1·7	1·6	1·5	1·4		−0·520
Mean			*1·5*	*1·5*	*1·5*	*1·4*	*1·2*	*1·2*		
Methanol–			3·4	3·3	4·3	4·5	3·9	3·3		−0·167
benzene–	14	60— 97	1·9	1·8	2·9	3·0	2·1	1·8	−0·607	−0·958
toluene			1·8	1·8	1·7	1·7	2·1	1·8		−0·536
Mean			*2·4*	*2·3*	*2·9*	*3·1*	*2·7*	*2·3*		
Methanol–			1·3	1·2	1·3	1·3	1·3	1·2		−0·226
ethanol–	48	67— 76	1·3	1·3	1·3	1·3	1·3	1·0	0·185	0·542
water			0·1	0·2	0·1	0·1	0·1	0·3		1·245
Mean			*0·9*	*0·9*	*0·9*	*0·9*	*0·9*	*0·8*		

TABLE V

(*Continued*)

Ternary system	Data ref.	Temp. °C	Margules IV-suffix Eq. (*6*)^a				NRTL Eq. (*7*)^a		Ternary constant Margules Eq. (*6*)^a	
			A	B	C	D	E	F	C	D
Methanol–			2·0	1·9	2·1	2·0	2·5	2·4		−0·400
ethanol–	21	68— 88	1·5	1·4	1·6	1·6	1·8	1·7	−0·622	−0·323
water			3·0	2·8	1·8	1·8	3·8	2·2		−0·853
Mean			*2·2*	*2·1*	*1·8*	*1·8*	*2·7*	*2·0*		
Methanol–			1·5	1·6	1·2	0·7	0·5	0·4		1·021
tetrachloromethane–	88	55	0·9	0·9	0·9	0·6	0·5	0·4	0·248	−0·415
benzene			0·7	0·8	0·5	0·2	0·3	0·2		−0·342
Mean			*1·1*	*1·1*	*0·9*	*0·5*	*0·4*	*0·3*		
Methyl acetate–			2·9	2·9	2·8	3·4	2·8	3·8		1·959
methanol–	19	55— 63	3·0	2·9	2·9	2·7	2·8	4·1	0·086	2·368
water			3·8	3·8	3·8	2·7	3·5	3·8		−3·407
Mean			*3·2*	*3·2*	*3·2*	*2·9*	*3·0*	*3·9*		
Methyl ethyl ketone–			0·4	0·5	0·4	0·4	0·4	0·2		0·067
n-heptane–	99	88—108	0·3	0·3	0·3	0·2	0·4	0·2	0·025	−0·263
toluene			0·4	0·4	0·4	0·3	0·2	0·3		0·217
Mean			*0·3*	*0·4*	*0·3*	*0·3*	*0·3*	*0·2*		
1-Propanol–			5·7	6·4	3·9	1·8	3·2	2·8		−1·093
propyl acetate–	98	88— 99	11·1	13·3	5·9	3·0	5·3	4·1	1·463	0·821
water			7·7	9·3	4·9	2·1	3·6	2·8		4·080
Mean			*8·2*	*9·7*	*4·9*	*2·3*	*4·0*	*3·2*		
Tetrachloromethane–			1·4	1·4	1·4	0·8	1·2	1·4		−1·185
benzene–	72	70— 76	1·1	1·1	1·1	0·9	1·0	1·2	−0·062	0·056
2-propanol			1·7	1·8	1·7	0·9	1·5	1·7		0·956
Mean			*1·4*	*1·4*	*1·4*	*0·9*	*1·3*	*1·4*		
Tetrachloromethane–			1·1	1·1	1·3	1·4	0·8	0·8		−0·574
ethanol–	57	50	1·3	1·3	1·0	0·7	1·8	1·8	−0·224	−0·842
benzene			1·7	1·8	1·6	1·0	2·1	2·1		0·740
Mean			*1·4*	*1·4*	*1·3*	*1·0*	*1·5*	*1·6*		
2,2,4-Trimethylbutane–			1·7	1·6	2·8	1·7	2·5	3·1		−1·841
toluene–	105	103—125	1·6	1·6	2·2	1·6	2·1	2·6	−0·630	−1·268
furfural			1·9	1·8	1·4	1·3	2·8	1·2		0·434
Mean			*1·7*	*1·7*	*2·1*	*1·5*	*2·4*	*2·3*		

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[a] A to F denote variants of calculation; description see Table VII.

TABLE VI

Prediction of Ternary Vapour–Liquid Equilibrium in System Ethyl Acetate–Ethanol–Water[63] from Binary Azeotropic and Solubility Data

Component	Mean deviation in vapour composition, mol % Margules Eq. (*6*)				NRTL Eq. (*7*)[a]			Ternary constants of Margules Eq. (*6*)[a]	
	A	B	C	D	E 1	E 2	F	C	D
Ethyl acetate	5·4	3·7	2·5	1·2	2·0	1·1	1·2		0·089
Ethanol	4·0	3·0	2·2	1·9	2·2	1·7	1·7	1·566	1·412
Water	3·3	2·7	1·9	1·4	1·6	1·4	1·3		2·860
Mean	*4·2*	*3·1*	*2·2*	*1·5*	*1·9*	*1·4*	*1·4*		

[a] Origin of binary constants: A—D 12 and 23 azeotropic data, 13 solubility data; E 1 12 and 23 azeotropic data, 13 solubility data ($\alpha_{13} = 0{\cdot}2$); E 2 12 and 23 azeotropic data, 13 solubility data ($\alpha_{13} = 0{\cdot}4$); F 12 and 23 azeotropic data, 13 azeotropic and solubility data.

TABLE VII

Ternary Systems

Mean deviation in vapour phase composition; binary parameters from vapour–liquid equilibrium data.

Type of equation	Number of parameters		$\Delta y_i \cdot 100$ number of liquid phases	
	binary	ternary	one	two
A Margules IV, Eq. (*6*)	9	0	1·5	3·2
B Margules IV[a], Eq. (*6*)	9	0	1·5	3·2
C Margules IV, Eq. (*6*)	9	1	1·4	2·5
D Margules IV, Eq. (*6*)	9	3	1·3	1·9
E NRTL, Eq. (*7*)	6	0	1·4	2·2
F NRTL, Eq. (*7*)	9	0	1·4	2·3
	Number of systems		34	7

[a] Ternary constant was estimated by method of Colburn and Wohl[18].

of parameters of the NRTL equation with the minimized α_{ij} are extraordinarily sensitive to the character of the experimental data.* In this case even the effect

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* Similar behaviour of the Wilson equation was observed by Orye and Prausnitz[76] and Hudson and van Winkle[47].

of distribution of experimental errors of the binary data or the effect of round-off error of the calculation on the values of constants in the three-parameter NRTL equation and on the results of the ternary estimate cannot be ruled out. The phenomenon observed deserves undoubtedly a more profound mathematical analysis. From a practical viewpoint it may be concluded that if an experimental check of prediction of polycomponent equilibria is missing, it is preferable to use the two-parameter NRTL equation instead of the three-parameter one.

From comparison of the results achieved by different types of equations in systems formed by components of unlimited miscibility it follows that the NRTL equation with six binary adjustable parameters and no ternary constant characterizes the vapour–liquid equilibrium on average better than the IV-suffix Margules equation with nine binary constants and no or one ternary constant and practically equally well as this equation with three ternary adjustable parameters. This rule is preserved for estimates of vapour–liquid equilibria in systems with components of limited miscibility in the liquid phase as well. The average values of the deviations, however, are lower in homogeneous systems and increase toward two-liquid region. It is therefore natural to assume that the possibility of prediction of polycomponent systems is limited by the ability of the equation to describe the equilibrium between two (or more) liquid phases.

Prediction of Liquid–Liquid Equilibrium

The composition of conjugated phases in a ternary system with one pair of components of limited solubility was found by solving the following set of equations

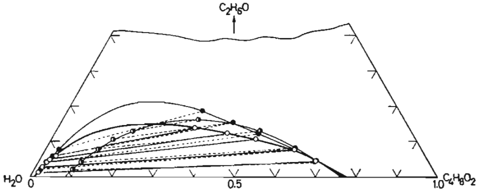

FIG. 1

Ethyl Acetate (1)–Ethanol (2)–Water (3)

Liquid–liquid equilibrium at 70°C. Comparison of experimental and calculated values of conjugated liquid phases in molefractions. ○—○ Experimental values, ●—● calculated: NRTL equation (α_{ij} calculated); constants solubility + azeotrop (1—3), liquid–vapour equilibrium (1—2, 2—3), ◑—◑ calculated: NRTL equation (α_{ij} estimated); constants liquid–vapour.

TABLE VIII

Molar Excess Free Energy ($\Delta G^E/RT \cdot 10^4$) in the System Acetone (1)–Methanol (2)–Chloroform (3) at 50°C from the NRTL Model Parameters from binary vapour–liquid equilibria. (1 step of the concentration scales = 5 mol %.)

NRTL Parameters

i–j	α_{ij}	τ_{ij}	τ_{ji}
1–2	0·3000	0·3479	0·2904
1–3	0·3000	−0·8946	0·2424
2–3	0·3000	−0·2111	2·1974

Acetone

0																				
-323	291																			
-620	-2	551																		
-892	-268	287	780																	
-1136	-506	52	545	978																
-1352	-715	-154	340	771	1145															
-1538	-894	-328	166	595	965	1281														
-1692	-1040	-470	25	453	818	1128	1386													
-1814	-1152	-577	-80	346	707	1010	1260	1461												
-1900	-1229	-648	-149	275	633	929	1170	1361	1505											
-1951	-1268	-681	-180	244	597	887	1119	1299	1431	1519										
-1963	-1268	-673	-169	254	603	886	1109	1278	1396	1470	1502									
-1935	-1226	-624	-116	306	652	928	1142	1299	1404	1463	1479	1456								
-1866	-1141	-529	-17	405	746	1016	1220	1364	1456	1499	1498	1457	1379							
-1751	-1010	-388	129	551	889	1151	1345	1478	1555	1581	1562	1502	1404	1272						
-1591	-831	-197	326	749	1083	1338	1521	1641	1703	1712	1675	1594	1475	1321	1135					
-1381	-600	47	576	1000	1330	1578	1751	1857	1903	1895	1838	1736	1595	1418	1208	968				
-1120	-316	346	882	1308	1635	1875	2037	2129	2158	2131	2054	1931	1767	1565	1330	1064	771			
-805	25	703	1248	1676	2000	2232	2382	2460	2472	2426	2327	2181	1993	1766	1505	1212	891	544		
-433	426	1123	1677	2108	2429	2653	2792	2854	2848	2781	2660	2490	2276	2023	1734	1413	1063	687	287	
0	891	1608	2174	2608	2926	3142	3268	3314	3289	3201	3057	2861	2621	2339	2022	1671	1291	884	453	0

Chloroform Methanol

TABLE VIII

(*Continued*)

NRTL Parameters

$i-j$	α_{ij}	τ_{ij}	τ_{ji}
1—2	1·3686	0·4565	0·4285
1—3	0·3002	−0·8944	0·2419
2—3	0·0737	−2·5801	5·0230

Acetone

0

− 323 324

− 620 92 603

− 892 −120 450 841

−1137 −310 314 758 1041

−1353 −478 195 687 1019 1206

−1538 −622 94 630 1005 1236 1338

−1693 −740 12 586 1000 1270 1412 1439

−1814 −832 −47 560 1007 1311 1488 1550 1509

−1901 −894 −84 550 1026 1360 1567 1660 1650 1550

−1952 −926 −96 561 1060 1419 1651 1770 1788 1716 1562

−1964 −926 −81 592 1110 1488 1742 1883 1924 1875 1746 1545

−1936 −892 −38 646 1177 1570 1840 2000 2059 2030 1922 1742 1500

−1866 −822 35 725 1264 1667 1949 2121 2196 2182 2090 1929 1705 1426

−1752 −714 141 830 1372 1780 2069 2250 2334 2332 2254 2106 1897 1634 1322

−1592 −566 280 965 1503 1911 2202 2387 2477 2483 2412 2275 2077 1826 1528 1188

−1382 −375 457 1130 1660 2063 2350 2534 2626 2634 2568 2437 2246 2004 1715 1387 1022

−1121 −139 672 1328 1844 2236 2515 2694 2782 2789 2723 2594 2407 2169 1887 1565 1209 823

− 805 145 928 1561 2058 2433 2699 2867 2947 2948 2879 2747 2560 2323 2043 1725 1373 993 588

− 433 479 1229 1832 2304 2657 2905 3057 3123 3114 3036 2898 2706 2467 2185 1867 1517 1138 737 315

0 867 1576 2144 2584 2910 3133 3264 3313 3288 3198 3049 2848 2602 2315 1993 1640 1261 859 437 0

Chloroform Methanol

$$x_1^{(1)}\gamma_1^{(1)} - x_1^{(2)}\gamma_1^{(2)} = 0\,,$$
$$x_2^{(1)}\gamma_2^{(1)} - x_2^{(2)}\gamma_2^{(2)} = 0 \qquad (20)$$

and

$$\left(1 - x_1^{(1)} - x_2^{(1)}\right)\gamma_3^{(1)} - \left(1 - x_1^{(2)} - x_2^{(2)}\right)\gamma_3^{(2)} = 0\,.$$

Index$^{(1)}$ designates the phase relatively rich in component 1. The values of the activity coefficients were calculated by means of the Margules equation and the NRTL equation from the binary constants given in Tables I through III, respectively from the ternary constants (Tables V and VI). The set of equations was solved by the Marquardt method[58]. A starting point of the iterations was the binary solubility in the system 1–2. The values of $x_1^{(1)}$ were gradually decreased in order to obtain the whole solubility line.

The average values of the deviations of the calculated and experimental composition of the conjugated phases in the system ethyl acetate–water–ethanol at 70°C (see note on page 394) for several sets of constants are given in Table IX. The results clearly indicate that the Margules equation enables only a qualitative estimate of the liquid–liquid equilibrium to be made even if the ternary constants evaluated from the ternary vapour–liquid equilibria are used.

TABLE IX

Prediction of Ternary Liquid–Liquid Equilibrium in the System Ethyl Acetate–Ethanol–Water[63]

Type of equation	Mean deviation in liquid phases composition, mol %				Number and origin of parameters[a]			
					binary			ternary
	$\Delta x_2^{(1)}$	$\Delta x_1^{(2)}$	$\Delta x_2^{(2)}$	$\Delta x_3^{(2)}$	1–2	1–3	2–3	
Margules	6·7	10·9	7·8	18·7	2 E	2 E	2 E	0
Eq. (*6*)	6·9	11·0	8·3	19·3	3 E	3 E	3 E	0
	3·7	9·4	3·9	13·3	3 E	3 E	3 E	3 E
	12·6	0·4	5·6	6·0	2 A	2 S	2 A	0
	13·6	0·2	9·9	10·1	2 A	3 AS	2 A	0
	5·7	0·6	1·3	0·9	2 A	2 S	2 A	3 E
NRTL	1·5	12·4	3·2	12·4	2 E	2 E	2 E	0
Eq. (*7*)	3·2	16·1	5·3	10·8	3 E	3 E	3 E	0
	10·9	0·6	3·5	2·9	2 A	2 S	2 A	0
						$(\alpha_{13} = 0{\cdot}2)$		
	2·5	0·6	0·9	1·5	2 A	2 S	2 A	0
						$(\alpha_{13} = 0{\cdot}4)$		
	2·6	0·2	1·1	1·1	2 A	3 AS	2 A	0

[a] Origin of parameters: E vapour–liquid equilibrium data; A azeotropic data; S solubility data; AS azeotropic and solubility data.

The results of the NRTL equation confirm Renon's and Prausnitz's observation[83] that the accuracy of the estimate depends first of all on the method of calculating the constants in the binary system of limited miscibility. Experimental measurements of vapour–liquid equilibrium in systems with components of limited miscibility are usually not sufficiently accurate and the constants evaluated from them inflict a shift of the binodal curve sideways (Fig. 1), while the binary solubility constants fix the curve in two points. The magnitude of the two-liquid area depends then practically on the value of the parameter α_{ij} only: with its increasing value the heterogeneous region diminishes and at $\alpha_{ij} = 0{\cdot}426$ vanishes. $\alpha_{ij} = 0{\cdot}2$ recomended by Renon is probably too low and the calculated region of two liquid phases is larger than in reality. Optimum values of parameters for binary system of limited solubility may be obtained either by calculating several sets of constants (with different values of α_{ij}) from the binary solubility and their subsequent testing on experimental liquid–liquid equilibrium data, or by simultaneous evaluation of the solubility data and one point of vapour–liquid equilibrium from midcomposition range. It is the advantage of the second approach that it requires no ternary data. Predictions resulting from the binary solubility and the azeotrope in the system ethyl acetate–water and from the azeotropic data in the systems ethyl acetate–ethanol and ethanol–water (Fig. 1) are satisfactory at low concentration of the solvent component (ethanol). With its increasing concentration and primarily in the region of plait point the quality of prediction impairs.

CONCLUSION

The Renon–Prausnitz NRTL equation and the IV-suffix Margules equation enable a satisfactory prediction of vapour–liquid equilibrium in ternary system from the binary equilibrium data. Of these the NRTL equation with six binary adjustable parameters provides on average superior characteristics of the behaviour of equilibrium over the IV-suffix Margules equation with nine binary and no ternary constant. The agreement of the calculated and experimental values of composition of the gas phase in 41 tested ternary systems of different type in normal range of the temperature and pressure is for both relations better than 2% molar.

A cautious selection of the binary data used for the calculation of the binary constants enables, with an accuracy sufficient for chemical-engineering calculations, the estimation of equilibrium between two liquid phases in the ternary system with the exception of the plait point region. In contrast, a prediction based on the Margules equation is – even with the use of three ternary constants calculated from the ternary vapour–liquid equilibrium – only semiquantitative.

My sincere thanks are due to Prof. E. Hála for his continued interest and for valuable comments on the results.

LIST OF SYMBOLS

A_{ij}, A_{ji}	Margules constants for the binary mixture *i-j*
B	second virial coefficient of the mixture
B_{ii}	second virial coefficient of the *i*-th component
B_{ij}	second virial cross coefficient for the binary mixture *i-j*
C, C_1, C_2, C_3	ternary constants of the Margules equation
D_{ij}	Margules constant for the binary mixture *i-j*
F, F_{13}, F_{23}	functions defined by the equations (*9*) or (*18*), resp.
f	fugacity
n	number of experimental points
P	pressure
P^o	pure component vapour pressure
Q	error functions defined by the equations (*8*) or (*17*), resp.
R	gas law constant
T	temperature (absolute)
v	molar volume
$\bar{v}$	partial molar volume
W, W_{13}, W_{23}	weight factor defined by the equations (*10*) or (*19*), resp.
x	liquid mole fraction
y	vapour mole fraction
Z	factor defined by the equation (*3*)
α_{ij}	NRTL constant for the binary mixture *i-j*
γ	activity coefficient
ν	fugacity coefficient
τ_{ij}, τ_{ji}	NRTL constants for the binary mixture *i-j*

Subscripts

calc	calculated value
exp	experimental value
i	value for the *i*-th component
m	value for the *m*-th experimental point

Superscripts

g	vapour phase value
l	liquid phase value
o	pure component value
(1), (2)	two liquid phases values

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LIQUID–VAPOUR EQUILIBRIUM. L.

PREDICTION OF MULTICOMPONENT VAPOUR–LIQUID EQUILIBRIA FROM THE BINARY PARAMETERS IN SYSTEMS WITH LIMITED MISCIBILITY

I. MERTL

This Journal *37*, 375 (1972). *1)* Due to a computer error in the preparation of the manuscript some of the parameters A_{21} of the IV suffix Margules equation printed in the Table II (pages 388 to 395) are ten times smaller than the correct values given in the following Table.

Binary system	Data ref.	Temp. °C	IV-Suffix A_{21}
Tetrachloromethane–benzene	30	77–80	0·0325
Tetrachloromethane–2-propanol	119	68–79	0·6190
Chloroform–ethyl acetate	70	64–78	−0·4551
Methanol–benzene	33	57–69	0·9274
Methanol–ethanol	3	66–77	0·0223
Methanol–tetrachloromethane	90	55	0·8609
Methanol–water	62	60	0·0150
Ethanol–benzene	113	68–79	0·6463
Ethanol–1,4-dioxane	45	78–99	0·4892
Ethanol–water	85	77–99	0·3868
Acetone–cyclohexane	56	53–77	0·6933
Acetone–methanol	94	50	0·2973
Acetone–methyl acetate	94	50	0·0689
Acetone–nitromethane	13	45	−0·2303
Acetone–tetrachloromethane	12	45	0·3173
Methyl acetate–methanol	94	50	0·4746
Methyl acetate–water	104	56–58	0·5341
1-Propanol–propyl acetate	77	95–98	0·2569
Methyl ethyl ketone–cyclohexane	22	72–77	0·3929
Methyl ethyl ketone–toluene	99	80–110	0·1996
Ethyl acetate–cyclohexane	17	72–77	0·3574
Ethyl acetate–ethanol	63	40	0·4135
Ethyl acetate–ethanol	63	70	0·4099
Ethyl acetate–water	63	40	0·8750
Ethyl acetate–water	63	70	0·7530
Benzene–acetic acid	36	81–111	−0·0554
Benzene–aniline	53	95–151	−0·1409
Benzene–n-heptane	34	75	0·1591
Benzene–n-heptane	95	80–95	0·1670
Cyclohexane–2-methoxyethanol	105	77–105	0·9569
Cyclohexane–2,2,3-trimethylbutane	40	79–80	0·1207
1-Hexene–2-ethoxyethanol	101	65–111	0·7069
n-Hexane–benzene	102	70	0·2288
n-Hexane–ethanol	44	55	1·0719
n-Hexane–methylcyclopentane	69	69–72	0·0256
n-Hexane–1,2,3-trichloropropane	101	70–113	0·4173
Toluene–furfural	105	111–153	0·7178
2,2,4-Trimethylbutane–toluene	105	100–110	0·1154

2) The equation (*7*) on the page 378 for ln γ_1 (the first equation) is incorrect: the figure "2" behind the second fraction must be removed.