DETERMINATION OF THE CONCENTRATION DEPENDENCE OF THE SECOND DERIVATIVE OF GIBBS' ENERGY WITH RESPECT TO COMPOSITION ON THE BASIS OF VAPOUR-LIQUID EQUILIBRIUM DATA*

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The course of the second derivative of Gibbs' energy with respect to composition for binary systems is evaluated. The representation of this quantity in terms of different correlation relations (the Wilson, NRTL and UNIQUAC equations and the ASOG and UNIFAC methods) is also discussed.

The second derivative of Gibbs' energy with respect to composition, $G11$,

$$G11 = [\partial^2(G^M/RT)/\partial x_1^2]_{T,P} \qquad (1)$$

is an important quantity which characterizes the thermodynamic stability of a system. The condition

$$G11 < 0 \qquad (2)$$

is satisfied for the system which occurs in the homogeneous and metastable regions. The characteristic course of $G11(x_1)$ is illustrated in Fig. 1. The important characteristic of a binary system is the position of minimum of $G11(x_1)$ and/or its coordinates, *i.e.* x_0 and $(G11)_{x0}$. For the system which is at the critical temperature, it is $(G11)_{x0} = 0$ and $x_0 = x_{crit}$.

The importance of the $G11(x_1)$ course has been shown formerly when correlating the vapour-liquid equilibrium data[1], the liquid-liquid equilibrium data[2] and in discussing the applicability of correlation relations to describe the concentration dependence of activity coefficients[3-5].

Relations for Determining G11 *on the Basis of Vapour-Liquid Equilibrium Data*

From thermodynamic relations we get the following expressions[6-9] for $G11$ in a binary system:

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Isothermal data:

$$G11 = (\partial P/\partial x_1)_T[RT(y_1 - x_1)]^{-1} \sum_{i=1}^{2} y_i(\bar{V}_i^g - \bar{V}_i^l)\,, \tag{3}$$

$$G11 = (\partial y_1/\partial x_1)_T\,(G11)^g \sum_{i=1}^{2} y_i(\bar{V}_i^g - \bar{V}_i^l)/\sum_{i=1}^{2} x_i(\bar{V}_i^g - \bar{V}_i^l)\,; \tag{4}$$

Isobaric data:

$$G11 = -(\partial T/\partial x_1)_P\,[RT^2(y_1 - x_1)]^{-1} \sum_{i=1}^{2} y_i(\bar{H}_i^g - \bar{H}_i^l)\,, \tag{5}$$

$$G11 = (\partial y_1/\partial x_1)_P\,(G11)^g \sum_{i=1}^{2} y_i(\bar{H}_i^g - \bar{H}_i^l)/\sum_{i=1}^{2} x_i(\bar{H}_i^g - \bar{H}_i^l)\,. \tag{6}$$

If we limit the description to the pressure range where it is possible to express the P-V-T behaviour of the vapour phase by the second virial coefficient, then

$$\begin{aligned} V^g = z^g RT/P = RT/P + B_{11}y_1^2 + 2B_{12}y_1y_2 + B_{22}y_2^2 = \\ = RT/P + B_{11}y_1 + B_{22}y_2 + y_1y_2\delta_{12}\,. \end{aligned} \tag{7}$$

If we further justifiably assume that $V^l \ll V^g$ and neglect the effect of pressure on the enthalpy of liquids, then the differential molar volumes of vaporization, the enthalpy and the second derivative of Gibbs' energy in the vapour phase, $(G11)^g$, will be given by the expressions[10]:

$$\sum_{i=1}^{2} y_i(\bar{V}_i^g - \bar{V}_i^l) = V^g = RT/P + B_{11}y_1 + B_{22}y_2 + y_1y_2\delta_{12}\,, \tag{8}$$

$$\sum_{i=1}^{2} x_i(\bar{V}_i^g - \bar{V}_i^l) = V^g - (y_1 - x_1)\,[B_{11} - B_{22} + \delta_{12}(y_2 - y_1)]\,, \tag{9}$$

$$\begin{aligned} \sum_{i=1}^{2} y_i(\bar{H}_i^g - \bar{H}_i^l) = \sum_{i=1}^{2} y_i[\Delta H_{vi}^0 + (P - P_i^0)\,(B_{ii} - T\,\partial B_{ii}/\partial T)] + \\ + y_1y_2P(\delta_{12} - T\,\partial\delta_{12}/\partial T) - (H^E)^l - (y_1 - x_1)\,(\partial H^E/\partial x_1)^l\,, \end{aligned} \tag{10}$$

$$\begin{aligned} \sum_{i=1}^{2} x_i(\bar{H}_i^g - \bar{H}_i^l) = \sum_{i=1}^{2} x_i[\Delta H_{vi}^0 + (P - P_i^0)\,(B_{ii} - T\,\partial B_{ii}/\partial T)] + \\ + (y_1 - x_1)\,(y_1 - y_2)\,(\delta_{12} - T\,\partial\delta_{12}/\partial T)\,P - (H^E)^l\,, \end{aligned} \tag{11}$$

$$(G11)^g = 1/(y_1y_2) - 2P\delta_{12}/(RT)\,, \tag{12}$$

where

$$\delta_{12} = 2B_{12} - B_{11} - B_{22}\,. \tag{13}$$

In case of an ideal behaviour of the vapour phase and on neglecting the heat of mixing in the liquid phase the following relatively simple relations result

$$G11 = (\partial P/\partial x_1)_T/[P(y_1 - x_1)]\,, \tag{14}$$

$$G11 = (\partial y_1/\partial x_1)_T/(y_1 y_2)\,, \tag{15}$$

$$G11 = -(\partial T/\partial x_1)_P\,(\sum_{i=1}^{2} y_i\,\Delta H^0_{vi})/[RT^2(y_1 - x_1)]\,, \tag{16}$$

$$G11 = (\partial y_1/\partial x_1)_P\,(y_1 y_2)^{-1}\,(\sum_{i=1}^{2} y_i\,\Delta H^0_{vi})/(\sum_{i=1}^{2} x_i\,\Delta H^0_{vi})\,. \tag{17}$$

That this extreme simplification is acceptable, it follows from the comparison of Eq. (*14*) with (*18*) which results from the combination of Eqs (*3*) and (*8*), *i.e.*

$$G11 = (\partial P/\partial x_1)_T\, z^g/[P(y_1 - x_1)]\,. \tag{18}$$

Considering that for usual systems at temperatures around boiling point it is $z^g \approx \approx 0{\cdot}95$, we get $G11$ from Eq. (*14*) about 5% higher compared to the exact relation (*18*). This error is, however, much lower than that one which results from an inaccurate determination of the derivative $\partial P/\partial x_1$.

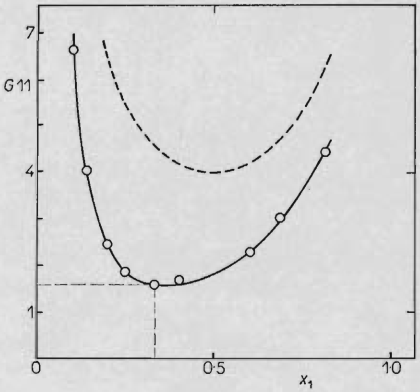

FIG. 1

Course of $G11(x_1)$ in the ethanol(1)–water(2) system at 70°C[11], — — — course of $G11(x_1)$ in an ideal system

The requirement of the accuracy of vapour–liquid equilibrium data of strongly non-ideal systems can be demonstrated by the following example: Let us consider a system with normal boiling point of 80°C for which further holds: $x_1 = 0\cdot4$, $y_1 = 0\cdot6$, $(G11)_{x_1=0.4} = 0\cdot2$, $\Delta H^0_{v1} = \Delta H^0_{v2} = 33$ kJ/mol. By inserting into Eqs (*14*)–(*17*) we get $\partial P/\partial x_1 = 4\cdot05$ kPa, $\partial y_1/\partial x_1 = 0\cdot48$, $\partial T/\partial x_1 = -12\cdot5$ K. Thus, it is evident that two experimental points differing by $\Delta x_1 = 0\cdot05$ will exhibit the pressure difference $\Delta P = 0\cdot2$ kPa (1·5 Torr), $\Delta y_1 = 0\cdot0024$, $\Delta T = -0\cdot062$ K. These differences are often comparable to the experimental errors in these quantities and so the error in the determined derivatives $\partial P/\partial x$, $\partial y/\partial x$, $\partial T/\partial x$ for strongly non-ideal systems can be subjected to an error even 100% and plays a decisive role in the resulting error of $G11$.

Further it is necessary to draw attention to the fact that Eqs (*3*) and (*5*) or (*14*) and (*16*) cannot be practically used in the vicinity of the azeotropic point for they require extremely accurate data.

In case of isothermal or isobaric data, we should obtain, according to Eqs (*3*) and (*4*) or (*5*) and (*6*), the same values of $G11$ in the limits of the estimated maximum error $\delta(G11)$. It will be so just only in case of the thermodynamically consistent data. The difference in the values of $G11$ can be considered as a measure of thermodynamic consistence of experimental data and of correctness of the error estimates of δx, δy, δT and δP.

TABLE I

Calculated values of $G11$ for the ethanol(1)–water(2) system at 70°C. To calculate the errors, the values $\delta x = \delta y = 0\cdot001$, $\delta T = 0\cdot02$ K, $\delta P = 0\cdot1$ kPa were used

x_1	y_1	P kPa	$G11$ Eq. (*14*)	$G11$ Eq. (*15*)
0·062	0·374	48·33		
0·095	0·439	53·20	6·62 ± 0·05	6·49 ± 0·18
0·131	0·482	56·53	4·01 ± 0·03	4·01 ± 0·17
0·194	0·524	60·11	2·41 ± 0·02	2·29 ± 0·08
0·252	0·552	62·40	1·86 ± 0·01	1·77 ± 0·10
0·334	0·583	64·77	1·61 ± 0·02	1·64 ± 0·08
0·401	0·611	66·34	1·64 ± 0·01	1·75 ± 0·10
0·593	0·691	70·12	2·18 ± 0·04	2·38 ± 0·09
0·680	0·739	71·24	2·75 ± 0·06	3·15 ± 0·10
0·810	0·826	72·41	2·53 ± 0·4	4·31 ± 0·8
0·943	0·941	72·60	—0·2 ± 5	17·9 ± 9
0·947	0·945	72·60		

Determination of Derivatives $\partial P/\partial x$, $\partial y/\partial x$ and $\partial T/\partial x$. The employment of the relatively simple relations (*14*)–(*17*) is complicated by the need of derivatives $\partial P/\partial x$, $\partial y/\partial x$ and $\partial T/\partial x$. To determine them, a graphic differentiation[1] was used which is tedious and rather subjective. To be able to carry out the computations on a computer the following two numerical methods were used: *a*) the arithmetic average of two proportional differences, *e.g.*

$$(\partial P/\partial x)_{x=x_i} = F \approx (1/2)\left[(P_{i+1} - P_i)/(x_{i+1} - x_i) + \right.$$
$$\left. + (P_i - P_{i-1})/(x_i - x_{i-1})\right] ; \qquad (19)$$

b) the Lagrange second-order polynomial. The respective relation is given in Appendix.

It was found that both methods give in case of "good" data practically the same results. In the opposite case (when there exist faulty points), however, the obtained values can differ considerably.

On the basis of the experimental errors δx, δy, δP, δT it is also possible to estimate the maximum error in corresponding derivatives and consequently also the error in $G11$. For instance, on the basis of Eq. (*19*) we get

$$\delta F = (\partial P/\partial x) = (\delta P) \sum_{j=i-1}^{i+1} |\partial F/\partial P_j| + (\delta x) \sum_{j=i-1}^{i+1} |\partial F/\partial x_j| , \qquad (20)$$

where $\partial F/\partial P_j$ are determined from Eq. (*19*). For the error in $G11$ we get from Eq. (*14*)

$$\delta(G11) = (G11)\left\{|\delta(\partial P/\partial x)/(\partial P/\partial x)| + |\delta P/P| + |\delta x/(y_1 - x_1)| + \right.$$
$$\left. + |\delta y/(y_1 - x_1)|\right\} . \qquad (21)$$

We give in Table I the values of $G11$ and $\delta(G11)$ for the ethanol(1)–water(2) system determined on the basis of data by Mertl[11] at a temperature of 70°C. Except for several values whose $x_1 > 0{\cdot}8$ and consequently are already in the vicinity of the azeotropic point, the agreement of calculated data is very good. The parameters of the $G11$ minimum determined graphically are: $(G11)_{x0} = 1{\cdot}60 \pm 0{\cdot}02$ and $x_0 = 0{\cdot}36 \pm \pm 0{\cdot}02$.

In Table II we present the minimum values of $(G11)_{x0}$ for the ethanol(1)–benzene(2) system determined on the basis of data of different authors. It is evident that the scatter of the obtained values of $(G11)_{x0}$ is greater than the error calculated on the basis of the assumed errors in x, y, T, P. This fact can be explained by systematic errors in individual measurements and by large sensitivity of $G11$ to the experimental errors. In Fig. 2, $(G11)_{x0}$ are plotted at different temperatures and through the points obtained, the straight line is drawn. The line slope is in good agreement with the calorimetric data by Mrazek and Van Ness[27] at 25°C. According to their correlation it

TABLE II

Values of x_0 and $(G11)_{x0}$ for the ethanol(1)–benzene(2) system

t, °C	Experimental		UNIQUAC		NRTL		Wilson		Ref.
	x_0	$(G11)_{x0}$	x_0	$(G11)_{x0}$	x_0	$(G11)_{x0}$	x_0	$(G11)_{x0}$	
20	0·37 ± 0·03	0·77 ± 0·05							12
20	0·42 ± 0·03	0·95 ± 0·15(?)	0·45	0·74	0·45	0·63	0·47	0·99	13
25	0·34 ± 0·02	0·62 ± 0·05	0·34	0·38	0·35	0·30	0·34	0·70	14
32	0·34 ± 0·03	0·77 ± 0·05	0·35	0·43	0·36	0·76	0·35	0·74	15
40	0·43 ± 0·02	0·76 ± 0·05	0·34	0·26	0·27	0·74	0·35	0·72	16
45	0·42 ± 0·02	0·90 ± 0·05	0·35	0·48	0·35	0·29	0·35	0·84	17
50	0·40 ± 0·03	1·10 ± 0·1	0·40	0·52	0·38	0·47	0·40	0·80	18
50	0·50 ± 0·04	0·44 ± 0·05(?)	0·52	0·45	0·51	0·47	0·52	0·75	19
50	0·40 ± 0·02	076 ± 0·1	0·35	0·36	0·36	0·26	0·38	0·78	16
50	0·39 ± 0·02	1·05 ± 0·05	0·34	0·57	0·32	0·84	0·38	0·89	20
51	0·36 ± 0·02	0·95 ± 0·05	0·38	0·60	0·38	0·55	0·39	0·84	15
55	0·42 ± 0·02	1·05 ± 0·1	0·32	0·63	0·32	0·79	0·35	0·92	21
60	0·40 ± 0·03	0·70 ± 0·1	0·35	0·49	0·36	0·77	0·39	0·84	16
68	0·43 ± 0·03	0·9 ± 0·1			0·43	0·72	0·44	1·00	22
68	0·45 ± 0·05	1·10 ± 0·2	0·40	0·60	0·40	1·27	0·42	0·90	23
68	0·42 ± 0·02	1·20 ± 0·05	0·40	0·95	0·40	0·83	0·47	1·17	24
68	0·41 ± 0·02	1·25 ± 0·05	0·42	0·94	0·43	0·89	0·43	1·09	25
68	0·38 ± 0·04	1·15 ± 0·15	0·32	0·67	0·32	0·85	0·38	1·03	26
115	0·55 ± 0·05	1·70 ± 0·15	0·55	1·51	0·55	1·50	0·55	1·61	22

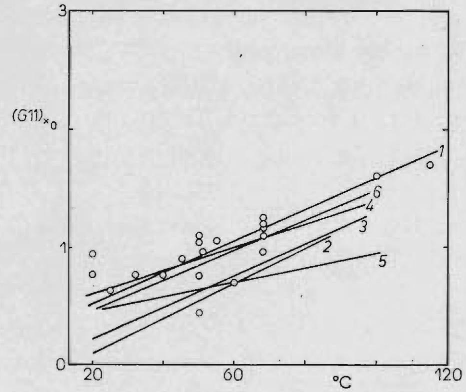

FIG. 2

Dependence of $(G11)_{x0}$ on temperature in the ethanol(1)–benzene(2) system. *1* straight line drawn through the points determined directly from experimental data (Table II), *2* UNIQUAC, *3* NRTL, *4* Wilson, *5* UNIFAC, *6* ASOG should hold for this system at $x_1 = 0{\cdot}35 \sim x_0$

$$\partial G11/\partial T = -\partial^2[H^E/(RT^2)]/\partial x_1^2 = 0{\cdot}010_6$$

which is in very good agreement with the slope of the straight line drawn.

The minimum of the second-order derivative of Gibbs' energy $(G11)_{x0}$ was determined for the ethanol(1)–benzene(2) system also on the basis of the NRTL[28], UNIQUAC[29] and Wilson[30] equations. The parameters of these equations were taken from the Gmehling and Onken monograph[31]. The obtained dependences are given in Fig. 2 as well. Except for the Wilson equation, the determined values of $(G11)_{x0}$ are significantly lower, which is in agreement with the findings obtained previously[1,32]. Further the applicability of the group-contribution methods UNIFAC[33] and ASOG[34] was verified as well and it was found that in this concrete case the ASOG method yielded better results.

The coordinates of the $G11$ minimum found for the aqueous solutions and mixtures of alcohols with benzene are given in Table III. The table presents also the values determined on the basis of light scattering which were taken from the Vuks monograph[12].

The dependence of $(G11)_{x0}$ on the number of carbon atoms in n-alcohols in systems water–n-alcohols[35] and benzene–n-alcohols is illustrated in Figs 3 and 4. The numbers at the points correspond to temperature in °C which they refer to. The dependence

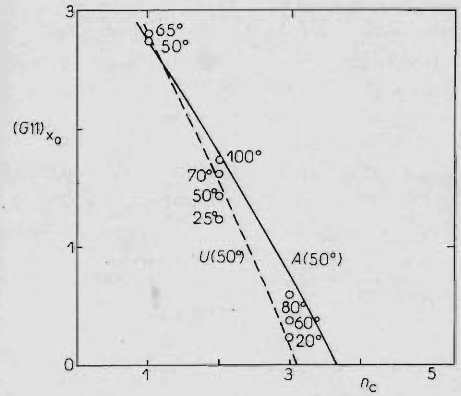

FIG. 3

Dependence of $(G11)_{x0}$ on the number of carbon atoms in n-alcohols, n_C, in the water–n-alcohol systems ($A \equiv$ ASOG, $U \equiv$ UNIFAC)

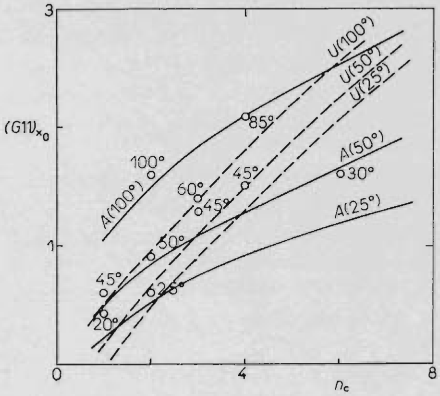

FIG. 4

Dependence of $(G11)_{x0}$ on the number of carbon atoms in n-alcohols, n_C, in the benzene–n-alcohol systems ($A \equiv$ ASOG, $U \equiv$ UNIFAC)

TABLE III

Coordinates of the $G11(x_1)$ minimum ($x_0 = (x_1)_{\mathrm{min}}$)

	t, °C	$x_0{}^a$	$(G11)_{x0}{}^a$	Ref.
Methanol(1)–water(2)	50	0·46 +	2·75 +	36
Methanol(1)–water(2)	65	0·47 +	2·80 +	36
Ethanol(1)–water(2)	25	0·41	1·52	12
Ethanol(1)–water(2)	25	0·35 +	1·23 +	37
Ethanol(1)–water(2)	50	0·35 +	1·42 +	37
Ethanol(1)–water(2)	70	0·36 +	1·60 +	11
Ethanol(1)–water(2)	115	0·40	1·75	38
1-Propanol(1)–water(2)	20	0·24	0·23	12
1-Propanol(1)–water(2)	60	0·26	0·35	39
1-Propanol(1)–water(2)	60	0·30	0·40	40
1-Propanol(1)–water(2)	88	0·27	0·60	41
2-Propanol(1)–water(2)	20	0·29	0·67	12
2-Propanol(1)–water(2)	80	0·32	1·0 —	42
2-Propanol(1)–water(2)	200	0·30	1·30	43
Allyl alcohol(1)–water(2)	90	0·29	1·0	44
1-Butanol(1)–water(2)	127	0·10 +	0 +	45, 46
Sec-butyl alcohol(1)–water(2)	110		0 +	45, 46
Isobutyl alcohol(1)–water(2)	129	0·12 +	0 +	45, 46
Tert-butyl alcohol(1)–water(2)	20	0·24	0·38	12
Tert-butyl alcohol (1)–water (2)	58	0·18	0·50	47
2-Chloroethanol(1)–water(2)	65	0·30	1·70	48
Acetone(1)–water(2)	20	0·41	0·70	12
Acetone(1)–water(2)	60	0·45	0·70	49
Acetone(1)–water(2)	60	0·42	0·75	50
Methyl vinyl ketone(1)–water(2)	77	0·35	0·40	51
1,4-Dioxane(1)–water(2)	20	0·55	0·70	12
1,4-Dioxane(1)–water(2)	70	0·45 +	0·40 +	52
1,4-Dioxane(1)–water(2)	87	0·48	0·42	53
Tetrahydrofuran(1)–water(2)	65	0·24	0·01	54
Tetrahydrofuran(1)–water(2)	70	0·23 +	0·01 +	55
Tetrahydrofuran(1)–water(2)	71·8	0·23 +	0 +	56
1,3-Dioxolane(1)–water(2)	50	0·45 +	0·25 +	57
1,3-Dioxolane(1)–water(2)	70	0·45 +	0·35 +	57
N-Ethyl-sec-butylamine(1)–water(2)	20	0·10	0·20	58
Pyridine(1)–water(2)	20	0·10	1·50	12
3-Methylpyridine(1)–water(2)	75	0·07 +	0·002 +	12
3-Methylpyridine(1)–water(2)	70	0·08 +	0·05 +	59
4-Methylpyridine(1)–water(2)	70	0·10	0·30	59
Acetonitrile(1)–water(2)	77	0·40	0·90	60
Methanol(1)–benzene(2)	20	0·38	0·43	12
Methanol(1)–benzene(2)	45	0·45 +	0·60 +	61
Ethanol(1)–benzene(2) see Table II				

TABLE III
(*Continued*)

	t, °C	x_0 [a]	$(G11)_{x0}$ [a]	Ref.
1-Propanol(1)–benzene(2)	45	0·40 +	1·30 +	62
1-Propanol(1)–benzene(2)	60	0·42	1·4 —	63
2-Propanol(1)–benzene(2)	45	0·42 +	1·20 +	64
2-Propanol(1)–benzene(2)	50	0·44	1·3 —	65
1-Butanol(1)–benzene(2)	45	0·38 +	1·50 +	62
1-Butanol(1)–benzene(2)	85	0·40	2·1 —	66
2-Butanol(1)–benzene(2)	45	0·42 +	1·70 +	67
2-Butanol(1)–benzene(2)	70	0·40	2·3 —	68
Tert-butyl alcohol(1)–benzene(2)	45	0·42 +	1·80	67
Isobutyl alcohol(1)–benzene(2)	45	0·42 +	1·45	67
Isobutyl alcohol(1)–benzene(2)	60	0·35	1·75	68
Tert-pentyl alcohol(1)–benzene(2)	30	0·40	1·50 —	69
1-Hexyl alcohol(1)–benzene(2)	30	0·45	1·60 —	69

[a] The values x_0 and $(G11)_{x0}$ are determined with an accuracy of ±0·05. If better accuracy is attained, the sign + is attached; in the opposite case —.

is also given in the figures predicted by the group-contribution methods UNIFAC and ASOG. In case of methanol and ethanol with water, the predictions of both methods are good but they differ more substantially for n-propanol (and for 2-propanol and tert-butyl alcohol) where UNIFAC yields lower values. In mixtures of alcohols with benzene, the agreement of both methods with the experimental data for methanol and ethanol is very good, especially at lower temperatures.

DISCUSSION

The procedure proposed allows to determine the values $G11(x_1)$ directly from the experimental vapour–liquid equilibrium data. This, however, fortunately, is not the only source of these data. For strongly non-ideal systems the error in $G11$, which results from the experimental data on vapour–liquid equilibrium, is too large and so it is more convenient to start from the data on light scattering. For more ideal systems (the boundary will depend on the accuracy reached in measurement and on relative volatility of substances) the vapour–liquid equilibrium will be on the contrary more suitable for obtaining accurate $G11$ data.

We would like yet to emphasize that the determination of $G11$ on the basis of a correlation equation only will be successful only exceptionally, *viz.* most probably with those systems which exhibit small deviations from ideality. As it has been demonstrated by the ethanol–benzene system, the $G11(x_1)$ course is not represented well not even by the modern correlation equations (in this particular case, with the exception of the Wilson equation). The $G11$ minimum is usually, in correlations, shifted lower than it corresponds to the experimental data and the resulting description corresponds to a system which is more non-ideal in comparison with reality.

Reasons of this shift are in our opinion as follows: The more non-ideal (*i.e.* having lower $G11$ value) and less symmetric ($x_0 \neq 0·5$) the system is the higher activity coefficients it shows (we consider systems with positive deviations from the Raoult law here). The correlation relation used does not often allow (if it is to reproduce the $G11$ (x_1) minimum) to reach so high values of activity coefficients which the given system has. Then a shift of the $G11(x_1)$ minimum occurs in the direction (to lower $G11$ values if the true activity coefficients are higher) to reach the true activity coefficients.

This fact is also apparent in Table IV where the values of limiting activity coefficients are presented as they follow from the requirement of reproducing the $G11$ minimum with coordinates $x_0 = 0·4$ and $(G11)_{x0} = 0·90$. By none of the mentioned equations, the value $\gamma_i^\infty > 10$ was obtained. In the second part of the table, the values of limiting activity coefficients are given for the ethanol–benzene system which the above mentioned coordinates of minimum at 50°C approximately correspond

TABLE IV

Limiting activity coefficients for a system with $x_0 = 0·4$ and $(G11)_{x0} = 0·90$ (upper part) and for the ethanol(1)–benzene(2) system at 50°C (lower part of the table)

	γ_1^∞	γ_2^∞
Redlich-Kister ($d = 0$)	5·75	3·22
Redlich-Kister ($d = 1/3$)	9·00	8·88
van Laar ($D = 0$)	6·23	3·65
van Laar ($D = 4/3$)	9·45	7·21
Wilson	9·53	4·86
NRTL ($\alpha = 0·30$)	6·49	3·96
NRTL ($\alpha = 0·50$)	8·61	5·64
UNIQUAC	8·58	3·88
UNIFAC (ref.[70]) (50°C), ($x_0 = 0·40$, $(G11)_{x0} = 0·65$)	8·68	4·65
ASOG (50°C), ($x_0 = 0·40$, $(G11)_{x0} = 0·84$)	9·52	5·18
Ninni (20°C) (ref.[71])	15·2	5·15
Udovenko (40°C) (ref.[16])	12·2	5·90
Brown, Smith (45°C) (ref.[17,72])	10·6	4·45
Zharov, Morachevskii (50°C) (ref.[20])	12·3	4·26

to. In all four cases we have $\gamma_i^\infty > 10$. It is evident from it that on applying the given equations to these data, then, considering that the minimized quantity is more or less proportional to the activity coefficients, a shift of the $G11$ minimum will take place towards lower values. In case of systems yet more non-ideal and asymmetric, the agreement would be still worse.

The fact is also in agreement with the finding of Brandani[73] who intended to predict the limited miscibility of systems by means of experimental activity coefficients and the van Laar equation (this effect is, however, common also to the other correlations). In some cases, as γ_i^∞ were too high, Brandani obtained such parameters for homogeneous systems which even predicted the heterogeneous systems, *i.e.* he obtained $G11 < 0$. The decisive importance of $G11(x_1)$ in binary systems for the correlation of liquid–liquid equilibrium data in the ternary system will be shown in a next work.

APPENDIX

The Lagrange interpolation polynomial of the second order has for our case the form

$$P(x) = \sum_{j=i-1}^{i+1} \prod_{\substack{k=i-1\\k\neq j}}^{i+1} P_j(x - x_k)/(x_j - x_k)\,. \tag{A1}$$

For the derivative at a point x_i we get from Eq. (*A1*)

$$\begin{aligned}(\partial P/\partial x)_{x=x_i} = F = {} & P_{i-1}\,.\,(x_i - x_{i+1})/[(x_{i-1} - x_i)(x_{i-1} - x_{i+1})] + \\ & + P_i[(x_i - x_{i+1}) + (x_i - x_{i-1})]/[(x_i - x_{i-1})(x_i - x_{i+1})] + \\ & + P_{i+1}\,.\,(x_i - x_{i-1})/[(x_{i+1} - x_{i-1})(x_{i+1} - x_i)]\,.\end{aligned} \tag{A2}$$

The derivatives needed for estimating the errors in Eq. (*20*) are given by the expressions

$$\begin{aligned}\partial F/\partial P_{i-1} &= (x_i - x_{i+1})/[(x_{i-1} - x_i)(x_{i-1} - x_{i+1})]\,,\\ \partial F/\partial P_i &= [(x_i - x_{i+1}) + (x_i - x_{i-1})]/[(x_i - x_{i-1})(x_i - x_{i+1})]\,,\\ \partial F/\partial P_{i+1} &= (x_i - x_{i-1})/[(x_{i+1} - x_{i-1})(x_{i+1} - x_i)]\,,\\ \partial F/\partial x_{i-1} &= -P_{i-1}\,.\,(x_i - x_{i+1})\,[(x_{i-1} - x_{i+1}) + (x_{i-1} - x_i)]\,.\\ &\quad .\,[(x_{i-1} - x_i)(x_{i-1} - x_{i+1})]^{-2} + \\ &\quad + P_i/(x_i - x_{i-1})^2 + P_{i+1}/(x_{i+1} - x_{i-1})^2\,,\\ \partial F/\partial x_i &= P_{i-1}/(x_{i-1} - x_i)^2 + P_{i+1}/(x_{i+1} - x_i)^2 - \\ &\quad - P_i[(x_i - x_{i+1})^2 + (x_i - x_{i-1})^2]/[(x_i - x_{i-1})(x_i - x_{i+1})]^2\,,\end{aligned}$$

$$\begin{aligned}\partial F/\partial x_{i+1} &= -P_{i-1}/(x_{i-1} - x_{i+1})^2 + P_i/(x_i - x_{i+1})^2 - \\ &- P_{i+1}(x_i - x_{i-1})\left[(x_{i+1} - x_i) + (x_{i+1} - x_{i-1})\right] . \\ &. \left[(x_{i+1} - x_{i-1})(x_{i+1} - x_i)\right]^{-2} . \qquad (A3)\end{aligned}$$

LIST OF SYMBOLS

B_{ij}	second virial coefficient
G	molar Gibbs' energy
$G11$	second-order derivative of Gibbs' energy with respect to composition in the liquid phase
$(G11)_{x0}$	ordinate of $G11(x_1)$ minimum
H	molar enthalpy
H^E	enthalpy of mixing in the liquid phase
ΔH_{vi}^0	heat of vaporization of pure substance at temperature T and pressure P_i^0
P	pressure
P_i^0	saturated vapour pressure of substance at temperature T
R	gas constant
T	temperature
x	mole fraction in the liquid phase
x_0	coordinate of $G11(x_1)$ minimum
y	mole fraction in the vapour phase
$z = PV/RT$	compressibility factor
V	volume
γ^{∞}	activity coefficient at infinite dilution
δ_{12}	quantity defined by Eq. *(13)*
δ	error operator

Superscripts

E	excess quantity
g	gas phase
l	liquid phase
M	mixing quantity
—	(bar) partial molar quantity

Subscripts

i	component, summation index
j	component, summation index

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