LIQUID–LIQUID EQUILIBRIUM. APPLICABILITY OF THE REDLICH–KISTER, NRTL AND LEMF EQUATIONS TO HETEROGENEOUS SYSTEMS

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The limits of applicability of the Redlich–Kister, NRTL and LEMF equations when applied to heterogeneous systems are specified. These limits follow from the requirement of solvability of relations of the equality of activities in coexisting phases on the one hand and of the monotonous dependence of activity coefficients on the other hand.

In a number of works, the applicability of the Redlich–Kister[1], NRTL (ref.[2,3]) and other equations[4,5] have been investigated systematically for the thermodynamic description of homogeneous systems, whether from the point of view of the concentration[6-16] or temperature dependence[17-19]. However, comparatively little attention has been paid hitherto to the examination of the applicability of those equations to heterogeneous systems[7,11,20,21], though it is well-known that in some cases, use of the Redlich–Kister or NRTL equations results in a qualitatively false description of the respective heterogeneous system. Probably the first ones who stated these facts in connection with the NRTL equation were Guffey and Wehe[7].

Considering that the constants of empirical relations for G^E for heterogeneous systems are usually determined on the basis of mutual solubility of components (the compositions of coexisting phases are denoted by $\bar{x}_1$ and $\bar{\bar{x}}_1$) from the relations

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

it is possible to determine in this way only two parameters at one temperature. In case of three-parameter equations, the third parameter must be chosen, and its value may considerably influence the dependence obtained. The parameters calculated on the basis of Eq. (1) give a certain $G^E = f(x_1)$ dependence and so the course of activity coefficients which are dependent on the equation employed.

If we do not want to limit our investigation of the applicability of the equations to an actual system, it is necessary to define in advance the courses of G^E or activity coefficients which will be considered as "normal". Three types of the courses of activity coeficients or G^E on composition were considered in works[16,21,22] — see Fig. 1:

a) There exists an only extreme (a maximum in case of positive deviations from Raoult's law) and no inflex point on the curve $G^E(x_1)$. The courses of activity coefficients as well as of their ratio are monotonous functions of composition (Fig. 1, first column).

b) There exists one extreme and one inflex point on the curve $G^E(x_1)$. The curve of activity coefficients and of their ratio exhibits an extreme at the composition which corresponds to the inflex point $G^E(x_1)$ (Fig. 1, second column).

c) There are two extremes and one inflex point on the curve $G^E(x_1)$ (so-called an S-shaped course; Fig. 1, third column). The activity coefficients exhibit an extreme on dependence on compositions, and besides, the logarithms of limiting activity coefficients $L_i = \ln \gamma_i^\infty$ have oposite signs.

With strongly nonideal systems (with positive deviations from Raoult's law) and above all with heterogeneous systems, the only case of a system[23] is known to the
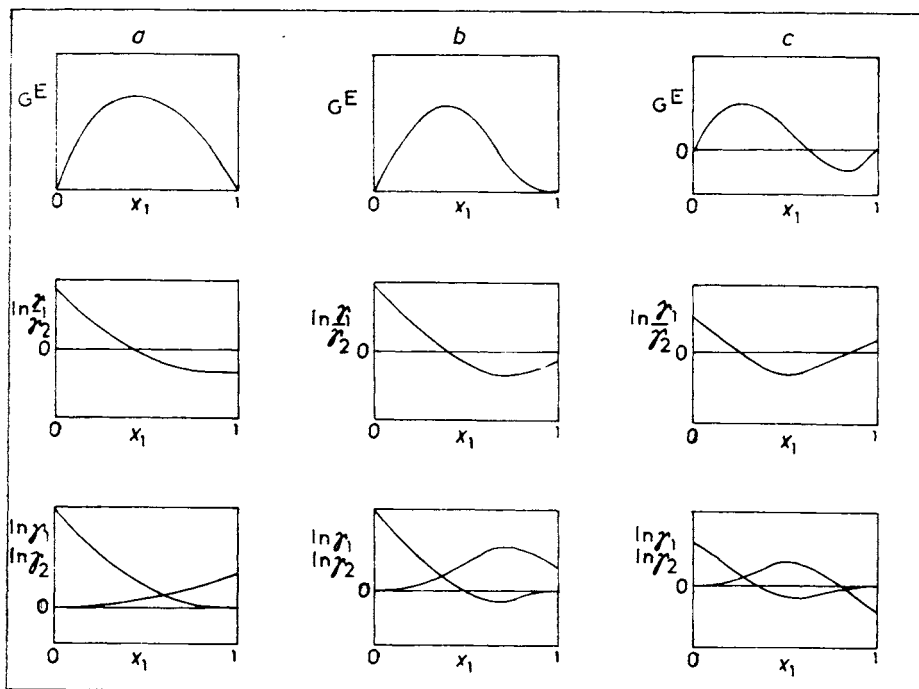

FIG. 1

The basic types of the course of $G^E/(RT)$, activity coefficients and their ratio in dependence on composition

authors which does not pertain to the first group. For this reason, the course appertaining to the first group was required when verifying the applicability of equations to the description of heterogeneous systems whereas the other variants were not considered "normal".

Here it is necessary to emphasize that the behaviour of real systems may naturally fall under the groups *b*) and *c*) even if probably seldom. However, some equations with the parameters determined by solving Eqs (*1*) give the courses belonging to *b*) or *c*), which is then at variance with the experimental reality. The limit of applicability resulting from the fact that the solution of equations for the equality of activities (*1*) does not exist at all, is, of course, of another kind.

Determination of the Limit of Applicability of the Redlich–Kister and NRTL Equations

The limits of applicability have been determined for the three-constant Redlich–Kister equation[1]

$$G^E/(RT) = x_1 x_2 [b + c(x_1 - x_2) + \mathrm{d}(x_1 - x_2)^2] \qquad (2)$$

and for the NRTL equation[2]

$$G^E/(RT) = x_1 x_2 [T_{21} G_{21}/(x_1 + x_2 G_{21}) + T_{12} G_{12}/(x_2 + x_1 G_{12})], \qquad (3)$$

$$G_{12} = \exp(-\alpha T_{12}), \quad G_{21} = \exp(-\alpha T_{21}),$$

where G^E is the molar excess Gibbs energy, R the gas constant, T the absolute temperature, $x_1 (x_2 = 1 - x_1)$ the mole fraction of the first component, b, c, d and T_{12}, T_{21}, α the parameters of the Redlich–Kister and NRTL equation, respectively.

When determining the limit of applicability, we proceeded tentatively. The values of $\bar{x}_1$ (composition of the conjugate phase) were chosen to a fixed value of $\bar{x}_1$ (composition of the first phase), and for the given pair $\bar{x}_1, \bar{x}_1$ the parameters b, c of the Redlich–Kister equation $(d = 0$, or $d = 1/3)$ and T_{12}, T_{21} of the NRTL equation (for a given value of α) were calculated. On the basis of the parameters calculated, the limiting activity coefficients were determined

$$L1 = \ln \gamma_1^\infty = b - c + d, \quad L2 = \ln \gamma_2^\infty = b + c + d \qquad (3a)$$

for the Redlich–Kister or

$$L1 = T_{21} + T_{12} G_{12}, \quad L2 = T_{12} + T_{21} G_{21} \qquad (3b)$$

for the NRTL equation, as well as the coefficients

$$\lim_{x_1 \to 0} \partial \ln \gamma_i / \partial x_i \, . \tag{4}$$

These coefficients represent the slope of the dependence $\ln \gamma_i = f(x_i)$ at the concentration ends. The necessary but not sufficient condition for the course obtained to belong to the first group specified at the beginning of this work is identical sign of coefficient (4) for both components. These coefficients for the Redlich–Kister and NRTL equations are expressed by the relations

$$\lim_{x_1 \to 0} \partial \ln \gamma_1 / \partial x_1 = -2b + 6c - 10d \, , \tag{5a}$$

$$\lim_{x_1 \to 0} \partial \ln \gamma_2 / \partial x_2 = -2b - 6c - 10d \, , \tag{5b}$$

$$\lim_{x_1 \to 0} \partial \ln \gamma_1 / \partial x_1 = -2T_{21}/G_{21} - 2T_{12}G_{12}^2 \, , \tag{6a}$$

$$\lim_{x_1 \to 0} \partial \ln \gamma_2 / \partial x_2 = -2T_{12}/G_{12} - 2T_{21}G_{21}^2 \, . \tag{6b}$$

Results of the calculations are given for the Redlich–Kister equation in Fig. 2 and for the NRTL equation in Figs 3 and 4.

With the Redlich–Kister two-constant equation $(d = 0)$, a narrow concentration range of applicability is surprising at the first glance which can be considerably extended on using the value $d = 1/3$. The value $d = 1/3$ is the maximum one which still ensures a single two-phase region in binary systems and invariably convex course of the second derivative with respect to composition[12]. It is possible to use even higher values of d than $1/3$ but in such a case it is always necessary to investigate carefully the obtained course of activity coefficients, the second order derivative of the Gibbs energy, *etc.*

The results obtained prove the analysis performed formerly[12]. The points *A*, *B* in Fig. 2 correspond to the point of intersection of the curve delimiting the applicability of the Redlich–Kister equation with $d = 0$ and the line $\bar{x}_1 = \bar{\bar{x}}_1$, which means that the points *A*, *B* correspond to the maximum and minimum values of $\bar{x}_1$ (or $\bar{\bar{x}}_1$) for which the compositions of both phases merge, *i.e.* to the critical point x_1^c. From the analysis of the Redlich–Kister equation followed[12] that when retaining the monotonous course of activity ciefficients, the Redlich–Kister equation may be used for $x_1^c \in \langle 1/3, 2/3 \rangle$ with $d = 0$ and for $x_1^c \in \langle 0\cdot215, 0\cdot795 \rangle$ with $d = 1/3$.

For the NRTL equation (Figs 3 and 4), the applicability depends on the parameter α as well. For usual values of α, the limits of applicability are given in Fig. 3; for $\alpha > 0\cdot426$ the limits are given with more precision in Fig. 4. It is evident that

higher values of α (for $\alpha > 0$) extend the concentration range of applicability of the NRTL equation. It is apparent from the comparison of Figs 2 and 3 that the NRTL equation with $\alpha = 0.2$ covers the concentration region only slightly larger than the
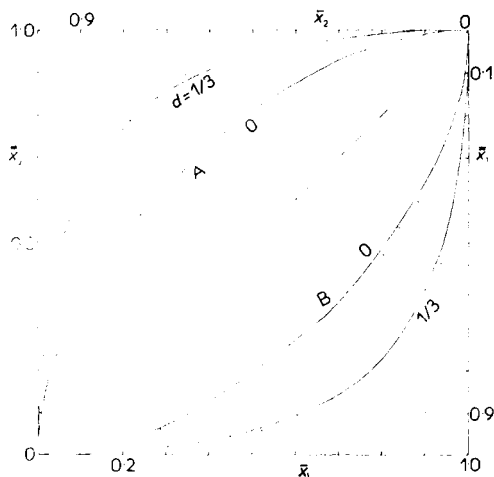

FIG. 2

The limits of applicability of the Redlich– –Kister equation with $d = 0$ and $d = 1/3$ in dependence on $\bar{x}_1$ and $\bar{\bar{x}}_1$. The equation is applicable for the values of $\bar{x}_1$, x_1 from lenticular region
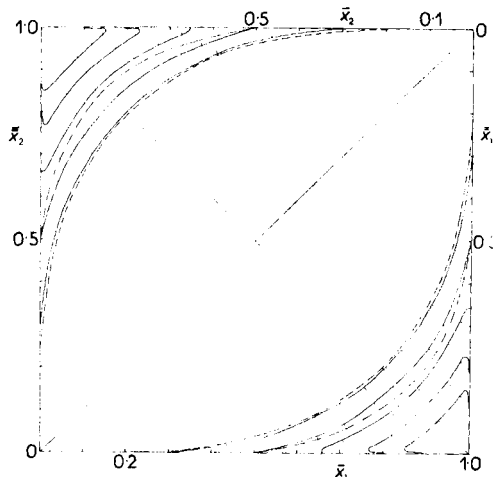

FIG. 3

Upper limits of applicability of the NRTL equation in dependence on the parameter α. ——— (from above down) $\alpha = 0.6; 0.5; 0.4;$ $0.3; 0.2.$ – – – – – $\alpha = -0.5, -\cdot-\cdot- \alpha = -1$
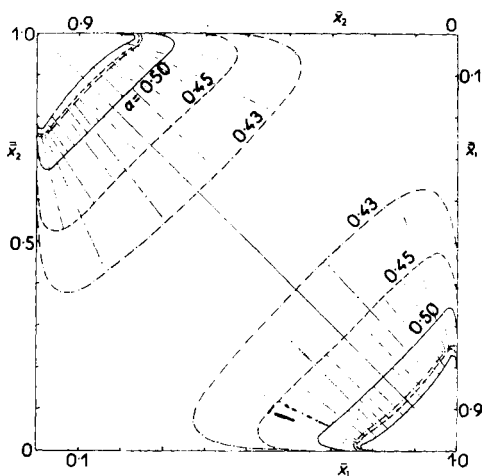

FIG. 4

Upper and lower limits of applicability of the NRTL equation for $\alpha > 0.426$

Redlich–Kister equation with $d = 1/3$. It is possible to read from Fig. 3 the limits of composition of the critical point which are $x_1^c \in \langle 0.20, 0.80 \rangle$ for $\alpha = 0.20$ whereas for $\alpha = 0.40$ they are extended to $x_1^c \in \langle 0.135, 0.865 \rangle$ on satisfying the requirement of monotonous course of activity coefficients.

The applicability of the NRTL equation with $\alpha = -0.50$ and $\alpha = -1$ (LEMF equation[3]) was also verified. A monotonous course of activity coefficients was found in each case. The limits of applicability given in Fig. 3 correspond to the limits of solvability of system of equations (1). For instance, for $\bar{x}_1 = 0.05$ and $\bar{x}_1 = 0.25$ the solution of the system was not found for $\alpha = -1$ whereas for $\bar{x}_1 = 0.05$ and $\bar{x}_1 = 0.32$ it was, and condition (4) were fulfilled.

When using $\alpha > 0.426$ in the NRTL equation, the boundary curves in Fig. 3 for $\alpha = 0.50$ and $\alpha = 0.60$ correspond only to the upper limit. Use of these values is, on the other hand, limited moreover from below (Fig. 4), *viz.* by the solvability of system of equations (1). Only the hatched areas correspond to the regions where system (1) has "acceptable" physical solution.

It is well-known[9–11] that the NRTL equation is formally very flexible and can yield more solutions but only one of them has the lowest values of the Gibbs energy (neglecting the existence of isolated points). During the computations carried out in this work, a continuous series of concentrations was always calculated, the solution found at a concentration being used as the first approximation for the next concentration of coexisting phases. At the beginning we started for $\alpha < 0.426$ from the symmetric system $\bar{x}_1 = \bar{x}_2$. On the contrary, for $\alpha > 0.426$ from the point $\bar{x}_1 = \bar{x}_1 + 0.01$, the parameters T_{12}, T_{21} corresponding to the critical point $\bar{x}_1 = \bar{\bar{x}}_1$ given in the literature[11] being used as the first approximation.

It is evident that the NRTL equation with $\alpha > 0.40$ allows to describe systems with critical points outside the range $x_1^c \in \langle 0.135, 0.865 \rangle$ retaining the monotonous course of activity coefficients. When choosing α, we are, especially for aqueous systems, on the other hand limited by the second limit which correspond to the solvability of system of equations (1).

DISCUSSION

The limits of applicability of the Redlich–Kister equation with $d = 0$ and $d = 1/3$ and of the NRTL equation with different values of α for thermodynamic description of heterogeneous systems are presented in Figs 2 − 4. These limits followed partly from the requirement of monotonous course of activity coefficients and partly from the requirement of solvability of system (1). With the LEMF equation it was further found out that for heterogeneous systems, the monotonous course of activity coefficients was obtained in all cases.

From this point of view the judgement of other equations (van Laar, UNIQUAC (ref.[4]), modified Wilson equation[5]) was also performed. The van Laar two-constant equation, with respect to the fact that it is unable to describe an extreme on the

dependence of activity coefficients, is with regard to the above-mentioned criteria, applicable within the entire range of $\bar{x}_1$ and $\bar{\bar{x}}_1$.

The modified Wilson equation and the UNIQUAC equation allow, under usual conditions, to describe an extreme in activity coefficients only in a system with low or medium deviations from ideality (for the UNIQUAC equation this case can occur more easily in systems with the values of $q_i \gg 1$), and therefore they are from this point of view as well more acceptable than the NRTL or Redlich–Kister three-constant equations.

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