

# APPLICABILITY OF THE RENON-PRAUSNITZ (NRTL) EQUATION TO CORRELATION OF STRONGLY NON-IDEAL SYSTEMS\* \*\*

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The analysis of the NRTL equation is carried out in the work with respect to its applicability to the correlation of equilibrium data of systems with large positive deviations from Raoult's law. The influence of parameter  $\alpha$  is discussed in detail and its limiting values are determined. The generalized values of  $\alpha$  can be applied only to weakly non-ideal systems. A new method for their estimation is suggested. In comparison with the Redlich-Kister equation the NRTL equation allows higher values of the logarithms of activity coefficients (by about 0.13) for more symmetric systems ( $\xi < 0.2$ ) and can be used in some cases even for considerably asymmetrical systems where the Redlich-Kister equation fails altogether. But just like the Redlich-Kister equation (for  $\xi > 0.29$ ) it is not able to represent the monotone decreasing course of the ratio of activity coefficients for  $\xi > 0.31$  and simultaneously the convex course of  $\partial^2 \mathcal{G} / \partial x_1^2$ .

In a foregoing paper<sup>1</sup> the concentration dependences of quantities  $Q1 = \partial[\mathcal{G}^E/(2.303RT)]/\partial x_1$  and  $G11 = \partial^2[\mathcal{G}^E/(2.303RT)]/\partial x_1^2$  were investigated in case of the Redlich-Kister equation for different values of  $x_0$  and  $(G11)_{x_0}$  in systems with large positive deviations from Raoult's law.

With regard to the course of  $\mathcal{G}^E$  and/or  $Q1$  the "normal courses" of the following functions were defined:

1) The curve  $Q1$  is a monotone decreasing function in the concentration interval (0; 1),

$$\partial Q1 / \partial x_1 < 0. \quad (1)$$

2) The molar excess Gibbs energy is positive in the concentration interval (0; 1),

$$\mathcal{G}^E > 0. \quad (2)$$

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3) The curve  $G11(x_1)$  is convex in the whole concentration range,

$$\partial^2 G11/\partial x_1^2 = G1111 > 0. \quad (3)$$

4) In case of a non-convex course of  $G11(x_1)$  it is required the curve to show only one extreme in  $x_1 \in (0; 1)$ . This can be expressed by the relation

$$[\partial G11/\partial x_1]_{x_1=x_0} = (G111)_{x_1=x_0} = (G111)_{x_1=x_B} = (G1111)_{x_1=x_B} = 0. \quad (4)$$

If this condition is fulfilled the only extreme is warranted on the curve  $G11(x_1)$  at the point  $x_1 = x_0$  (and a minimum on the assumption that  $(G1111)_{x_1=x_0} > 0$ ) as well as a point of inflexion with the zero line slope at a certain point  $x_1 = x_B$  (on the assumption that  $(\partial^3 G11/\partial x_1^3)_{x_1=x_B} \neq 0$ ). On considering still more extreme conditions, the point of inflexion could turn into a further local minimum which can be a more expressive and deeper one than the minimum at the point  $x_0$ . These extreme cases will not be considered further in detail.

The aim of the calculations undertaken was to judge for the Renon–Prausnitz equation<sup>2</sup> (further NRTL only): How the equation reflects changes in  $x_0$  and  $(G11)_{x_0}$  and how it fulfils the above-mentioned conditions of “normal” behaviour, the rules which are recommended by the authors for the estimation of parameter  $\alpha$ , what possible values of limiting activity coefficients are allowed by the equation, and finally, its advantages and disadvantages in comparison with the equation proposed by Redlich and Kister<sup>3</sup>.

The equation for molar excess Gibbs energy, proposed by Renon and Prausnitz<sup>2</sup>, was used in the form

$$\mathcal{G}^E/(RT) = x_1 x_2 [T_2 G_2 / (x_1 + x_2 G_2) + T_1 G_1 / (x_2 + x_1 G_1)], \quad (5)$$

where

$$G_1 = \exp(-\alpha T_1), \quad G_2 = \exp(-\alpha T_2). \quad (5a)$$

The ratio of activity coefficients and the higher (*i.e.*  $n \geq 2$ ) derivatives of  $\mathcal{G}^E$  are given by the relations

$$\ln(\gamma_1/\gamma_2) = 2.303Q1 = T_1 G_1 (x_2^2 - G_1 x_1^2) / (x_1 G_1 + x_2)^2 + \quad (6)$$

$$+ T_2 G_2 (x_2^2 G_2 - x_1^2) / (x_2 G_2 + x_1)^2,$$

$$\partial^n [\mathcal{G}^E/(RT)] / \partial x_1^n = (-1)^{n+1} n! [T_2 G_2^2 (1 - G_2)^{n-2} / (x_1 + x_2 G_2)^{n+1} + \quad (7)$$

$$+ T_1 G_1^2 (G_1 - 1)^{n-2} / (x_2 + x_1 G_1)^{n+1}].$$

Thus for the second-order derivative of the Gibbs energy with respect to composition we get

$$\partial^2[\mathcal{G}/(RT)]/\partial x_1^2 = 2.303G_{11} = (x_1 x_2)^{-1} + -2[T_2 G_2^2/(x_1 + x_2 G_2)^3 + T_1 G_2^2/(x_2 + x_1 G_1)^3]. \quad (7a)$$

The limiting activity coefficients are given by the relations

$$\lim_{x_1 \rightarrow 0} \log \gamma_1 = \log \gamma_1^0 = L1 = (T_2 + T_1 G_1)/2.303, \quad (8)$$

$$\lim_{x_1 \rightarrow 1} \log \gamma_2 = \log \gamma_2^0 = L2 = (T_1 + T_2 G_2)/2.303. \quad (9)$$

### Calculation Procedure

To find the effect of  $x_0$ ,  $(G_{11})_{x_0}$ , and  $\alpha$  on the course of  $Q1(x_1)$  and  $G_{11}(x_1)$  two calculation procedures were developed. In the first one, by using the Newton method, the system of two non-linear equations was solved:

$$(G_{11})_{x_0} = f(x_0, T_1, T_2, \alpha), \quad (10)$$

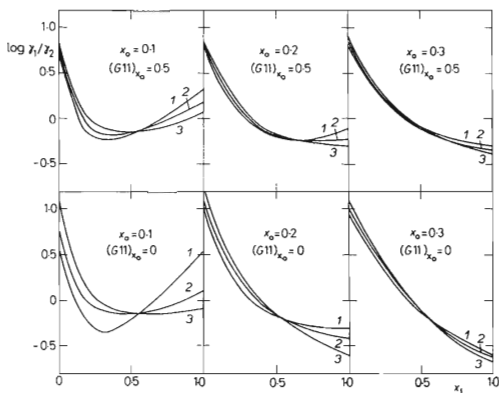


FIG. 1

Concentration Dependence of  $\log \gamma_1/\gamma_2 = Q1$  for Different Values of  $x_0$ ,  $(G_{11})_{x_0}$ , and  $\alpha$   
 1  $\alpha = 0.1$ , 2  $\alpha = 0.3$ , 3  $\alpha = 0.47$ .

$$[\partial G_{11}/\partial x_1]_{x_1=x_0} = (G_{11})_{x_1=x_0} = f_1(x_0, T_1, T_2, \alpha) = 0 \quad (10a)$$

for chosen values  $(G_{11})_{x_0}$ ,  $x_0$ , and  $\alpha$ .

The system of equations (10) did not provide a solution in some cases and it was not possible to decide whether this fact is caused by the non-existence of the solution or by an insufficiently exact starting estimation. For this reason the procedure described below was developed which is based on the solution of one non-linear equation. In this case it is possible to conclude more easily as to the existence of solution. From Eq. (9) we get  $T_1 = 2.303L2 - T_2G_2$ . By substituting this relation into Eq. (10a) we obtain a non-linear equation from which we can calculate  $T_2$  for given values  $x_0$ ,  $\alpha$ ,  $L2$  (the method of halving the interval was used for calculating). By substituting back into Eq. (9), the value  $T_1$  is obtained as well. From the obtained values  $T_1$ ,  $T_2$  and chosen  $\alpha$ ,  $x_0$  we determine the corresponding value  $(G_{11})_{x_0}$  from Eq. (7a), too. The values of  $L2$  were changed and in this way the dependences  $(G_{11})_{x_0} = f(L2)$  were obtained for different  $\alpha$ ,  $x_0$ . A part of calculations is presented in Fig. 3 and more detailed tables will be published elsewhere<sup>4</sup>.

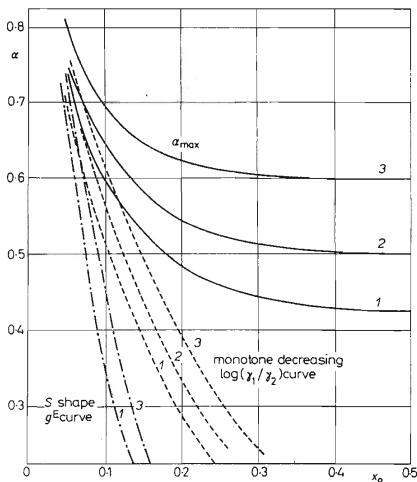


FIG. 2  
Dependence of  $\alpha_{max}$ ,  $\alpha_{mon}$ , and  $\alpha_s$   
on  $x_0$  and  $(G_{11})_{x_0}$   
1  $(G_{11})_{x_0} = 0$ , 2  $(G_{11})_{x_0} = 0.25$ ,  
3  $(G_{11})_{x_0} = 0.5$ .

## RESULTS

The computations carried out on the computer Hewlett-Packard 2116B for the ranges  $(G11)_{x_0} \in \langle -0.1; 0.8 \rangle$ ,  $\alpha \in \langle 0.1; 0.8 \rangle$  and  $\xi \in \langle 0; 0.45 \rangle$  resulted in the following facts:

I. For relatively symmetric systems ( $\xi < 0.2$ ) the values of  $\alpha$  recommended by Renon and Prausnitz warrant the monotone course of  $Q1$ , i.e. fulfilling the condition (1).

II. For more asymmetric systems ( $\xi > 0.2$ ) lower values of  $\alpha$ , especially at higher values of  $(G11)_{x_0}$ , do not ensure the fulfilment of condition (1) and not even the condition (2), which is evident from Fig. 1, too. The minimum values  $\alpha = \alpha_s$  warranting the

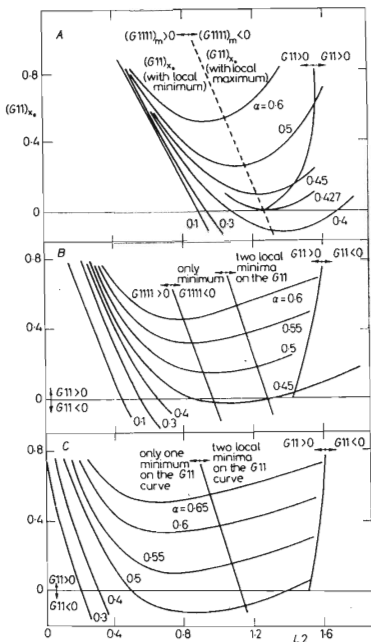


FIG. 3

Dependence of  $(G11)_{x_0}$  on Limiting Activity Coefficient  $L2$  for Different Values  $x_0$  and  $\alpha$

A  $x_0 = 0.5$ , B  $x_0 = 0.25$ , C  $x_0 = 0.15$ .

non-S-shaped course of  $\mathcal{G}^E$  and  $\alpha = \alpha_{\text{mon}}$  warranting the monotone course of  $Q1(x_1)$  are presented in Fig. 2 as a function of  $x_0$  and  $(G11)_{x_0}$ .

III. From Eq. (7) follows that the necessary condition for the extreme on the curve  $Q1(x_1)$  is the difference of signs at  $T_1$  and  $T_2$ . The composition corresponding to the extreme,  $x_1 = x_E$ , is given by the relation

$$x_E = (1 - KG_2)/[1 - G_1 + K(1 - G_2)], \quad (12)$$

where  $K = [-(G_1/G_2)^2 T_1/T_2]^{1/3}$ .

If  $x_E$  is from the interval  $(0; 1)$  the condition (I) will not be fulfilled and an extreme will be on the curve. As it follows from the Gibbs-Duhem equation, the dependences of activity coefficients on composition will have an extreme, too. An important

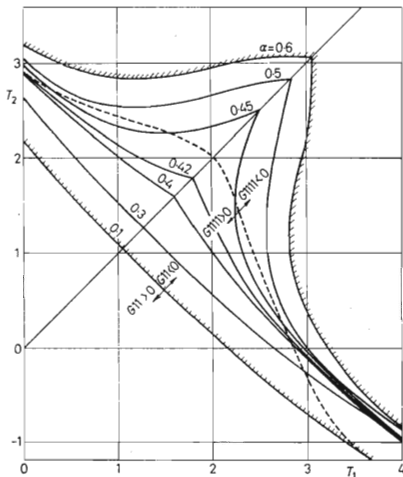


FIG. 4

Limiting Values of  $T_1$  and  $T_2$  Fulfilling the Condition of Thermodynamic Stability for Different Values of  $\alpha$

— — — The curve delimiting parameters  $T_1$  and  $T_2$  which fulfil the conditions  $(G11)_{x_1=x_0} = 0$ ,  $(G111)_{x_1=x_m} = 0$ , where  $x_m$  is composition corresponding to the minimum on the curve  $G111(x_1)$ .

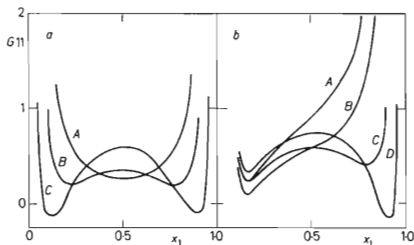


FIG. 5

Courses of  $G_{11}(x_1)$  for  $x_0 = 0.5$  and  $x_0 = 0.15$  and Different Values  $(G_{11})_{x_0}$  or  $L_2$

*a*  $x_0 = 0.5$ ,  $\alpha = 0.5$ : A  $(G_{11})_{x_0} = 0.251$  ( $L_2 = 1.10$ ), B  $(G_{11})_{x_0} = 0.358$  ( $L_2 = 1.35$ ), C  $(G_{11})_{x_0} = 0.603$  ( $L_2 = 1.55$ ); *b*  $x_0 = 0.15$ ,  $\alpha = 0.55$ : A  $(G_{11})_{x_0} = 0.25$  ( $L_2 = 0.45$ ), B  $(G_{11})_{x_0} = 0.109$  ( $L_2 = 0.75$ ), C  $(G_{11})_{x_0} = 0.246$  ( $L_2 = 1.30$ ), D  $(G_{11})_{x_0} = 0.332$  ( $L_2 = 1.60$ ).

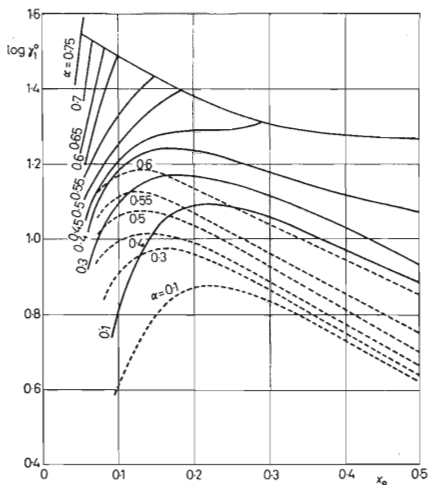


FIG. 6

Dependence of Logarithm of Limiting Activity Coefficient  $L_1$  on  $x_0$ ,  $\alpha$

—  $(G_{11})_{x_0} = 0$ , - - -  $(G_{11})_{x_0} = 0.5$ .

feature of the NRTL equation is the fact that this extreme can be only one, whereas in case of the Redlich-Kister equation with three constants two extremes may occur.

IV. The system of equations (10) is non-linear with respect to the unknowns  $T_1$  and  $T_2$  for chosen  $x_0$ ,  $\alpha$ ,  $(G11)_{x_0}$  and the number of solutions cannot be defined generally. In some cases the solution of the system of equations (10) was not found at all. With a symmetrical system even three different solutions were found. Graphic insight can be obtained from Figs 3a–3c in which several dependences of  $(G11)_{x_0}$  on  $L2$  are plotted for  $x_0 = 0.5, 0.25, 0.15$  and for different  $\alpha$ .

V. It is evident from the course of curves in Fig. 3 that there exists a certain maximum value  $\alpha = \alpha_{\max}$  for a given value  $x_0$  which allows to reach the given value of  $(G11)_{x_0}$  (Fig. 2). With a symmetrical system for  $(G11)_{x_0} = 0$  e.g.  $\alpha_{\max} = 0.427_7$  (this value is somewhat higher than that given by the authors of equation).

VI. The range of applicable values of  $\alpha$  depends considerably on  $\xi$  and on  $(G11)_{x_0}$  and they can be read from Fig. 2. For  $\xi = 0.35$  ( $x_0 = 0.15$  or  $0.85$ ),  $(G11)_{x_0} = 0$  and a monotone course of  $Q1(x_1)$ ,  $\alpha \in \langle 0.36; 0.52 \rangle$  is at our disposal, whereas for  $\xi = 0.4$  only  $\alpha \in \langle 0.62; 0.69 \rangle$ , i.e. the values far higher than those usually recommended.

VII. For the minimum on the curve  $(G11)_{x_0} - L2$  the relation holds

$$D = \begin{vmatrix} \partial G11/\partial T_1 & \partial G11/\partial T_2 \\ \partial G111/\partial T_1 & \partial G111/\partial T_2 \end{vmatrix} = 0. \quad (12)$$

The derivatives in the last relation are considered at the point corresponding to the minimum. The determinant  $D$  has a value  $D = 12$  for the Redlich-Kister equation ( $T_1 = b$ ,  $T_2 = c$ ) and consequently the minimum cannot occur. On using the Newton method to solve the system of equations (10), the determinant of the system of equations just equals the determinant  $D$  and therefore the use of the Newton method in the vicinity of minimum requires multiple precision computation and at the minimum is inapplicable at all.

VIII. When correlating measured data e.g.  $\mathcal{G}^E = \mathcal{G}^E(x_1)$  for strongly non-ideal systems, we can sometimes obtain such  $T_1, T_2$  which, in a certain concentration range, do not fulfil the conditions of thermodynamic stability. It is possible to make sure whether it is so in Fig. 4 in which the region of parameters  $T_1$  and  $T_2$ , corresponding to homogeneous and heterogeneous systems, is delimited for different  $\alpha$ . We emphasize that the use of  $\alpha > \alpha_{\max}$  does not warrant the condition of thermodynamic stability in the entire concentration range but only at  $x_1 = x_0$  and in a certain vicinity of the point.

IX. For a symmetrical system ( $T_1 = T_2$ ,  $x_0 = 0.5$ ) the fulfilment of the condition (3) implicates the occurrence of only one minimum on the curve  $G11(x_1)$ . Let us



consider the curve  $\alpha = 0.5$  in Fig. 3a. With increasing  $L2$  the value of  $(G11)_{x_0}$  decreases first as far as the minimum is attained at  $L2 = 1.1$  and then increases again. With increasing  $L2$   $G1111$  diminishes as well and at  $L2 = 1.15$  takes its zero value. Accordingly at this point holds  $(G11)_{x_0} = 0.26$ ;  $(G111)_{x_1=x_0} = 0 = (G1111)_{x_1=x_0}$ . The NRTL equation also gives the zero value of all odd derivatives of  $\mathcal{G}$  for symmetrical systems and because  $(\partial^6 \mathcal{G} / \partial x_1^6)_{x_1=0.5} < 0$ , the minimum at  $x_1 = 0.5$  changes to the maximum. For higher values of  $L2$  and accordingly also of  $(G11)_{x_0}$  already  $G1111 < 0$  and the maximum at  $x_0$  becomes more expressive and is accompanied with two symmetrically placed minima which with the increasing value of  $L2$  and consequently also  $(G11)_{x_0}$  shift to the concentration ends, become deeper and can reach even negative values (Fig. 5a).

X. As to the systems with  $x_0 = 0.5$ , the curve  $G1111 = 0$  ceases being coincident with the curve delimiting the existence of one minimum on the curve  $G11(x_1)$  (Figs 3a–3c and 4a, 4b). As to the systems with  $\xi > 0.31$ ,  $G1111 < 0$  in a certain interval in all cases and the condition (3) is not therefore fulfilled. The curve delimiting the occurrence of one minimum on the curve  $G11(x_1)$  shifts to lower values of  $L2$  with increasing value of  $\xi$ . (Figs 3a and 3c.)

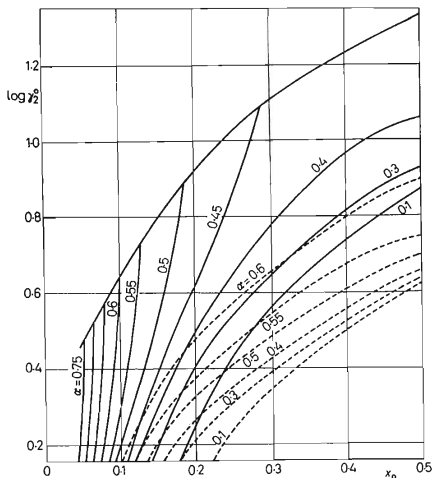


FIG. 7  
Dependence of Logarithm of  
Limiting Activity Coefficient  
 $L2$  on  $x_0$ ,  $\alpha$   
—  $(G11)_{x_0} = 0$ , - - -  
 $(G11)_{x_0} = 0.5$ .

TABLE I  
Dependence of  $L1$  on  $L2$  and  $(G11)_{x_0=0.5}$

$L2$	0.75	1.0	1.3	1.6
$(G11)_{x_0}$	0.109 (minimum)	0.152	0.246	0.332
$L1$	1.40	1.43	1.42	1.38

XI. The values of limiting activity coefficients  $L1$  and  $L2$  or of their logarithms as a function of  $x_0$  and  $\alpha$  for  $(G11)_{x_0} = 0$  and  $0.5$  are given in Figs 6 and 7. More detailed tables are presented elsewhere<sup>4</sup>. When constructing the graphs, only the downward part of curves was considered in Figs 3a–3c to make the unique attachment of values of  $L_1$  and  $(G11)_{x_0}$  possible. It follows from the calculations that in case of asymmetrical systems when overpassing the minimum on the curves  $(G11)_{x_0} \div L2$ , the values  $L1$  change only little as it is seen in Table I ( $x_0 = 0.15$ ,  $\alpha = 0.55$ ; compare with Figs 3c and 5b). Thus the  $L1$  in Fig. 6 calculated for  $\alpha = \alpha_{max}$  can be considered practically to be the maximum values of  $L1$ . The maximum possible values of  $L1$  with a homogeneous system for  $\xi < 0.2$  are approximately 0.13 higher than those allowed by the Redlich–Kister equation with three constants. The greatest advantage of the NRTL equation in comparison with the Redlich–Kister one is the fact that it can be used even at  $\xi > 0.2$  where the Redlich–Kister equation with three constants fails practically wholly.

XII. If we know  $x_0$  and  $(G11)_{x_0}$  for a system (these values can be determined from literature data<sup>5–9</sup>) it is possible to estimate the value of parameter  $\alpha$  (ref.<sup>4</sup>) from the values of  $L1$  and  $L2$  by means of Figs 6 and 7.

XIII. As to the systems which show small deviations from Raoult's law, the effect of parameter  $\alpha$  is relatively small except the immediate proximity of the minimum on the curve  $(G11)_{x_0} \div L2$ .

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#### LIST OF SYMBOLS

- $\mathcal{G}$  molar Gibbs energy  
 $\mathcal{G}^E$  molar excess Gibbs energy  
 $G_1, G_2$  quantities defined in Eq. (5a)  
 $G11$  ( $G111$  etc.) second, (third etc.) derivative of molar Gibbs energy with respect to composition, divided by  $2.303 RT$   
 $L_i = \log \gamma_i^0$  decadic logarithm of the limiting activity coefficient of the component  $i$   
 $(G11)_{x_0}$  ordinate of the minimum on the curve  $G11(x_0)$   
 $Q = \mathcal{G}^E/2.303RT$  dimensionless molar excess Gibbs energy

$Q1$ ( $Q11$ etc.)	first (second) derivative of $Q$ with respect to composition
$R$	universal gas constant
$T$	absolute temperature
$T_1, T_2$	empirical parameters of the NRTL equation
$x_i$	mole fraction of the component $i$
$x_0$	ordinate of the minimum of the curve $G11(x_1)$
$\alpha$	empirical parameter of the NRTL equation
$\alpha_{\text{mon}}, \alpha_{\text{max}}, \alpha_s$	limiting values of parameter $\alpha$ defined in the text
$\gamma_i$	activity coefficient of component $i$
$\gamma_i^0$	limiting values of the activity coefficient of component $i$
$\xi =  0.5 - x_0 $	modified concentration parameter

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