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PHASE DIAGRAMS IN THE BINARY SYSTEMS OF 2,4,7-TRINITROFLUOREN-9-ONE WITH AROMATIC AND HETEROAROMATIC COMPOUNDS. II. THERMODYNAMIC ANALYSIS

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ABSTRACT

The shape of the liquidus lines in phase diagrams of binary systems with CT interaction formed by 2,4,7-trinitrofluoren-9-one (TNF) with six aromatic and heteroaromatic compounds has been calculated by a procedure based on the Van Laar equation. To fit the simulated curve to experimental results two alternative models of the melt have been employed, viz., that of a regular solution of components of a completely dissociated CT complex, and that of a perfect solution of a partially dissociated CT complex in equilibrium with its components, the values of heat of mixing (ΔH^{M}) or dissociation constant (K), respectively, being used as adjustable parameters. Both procedures are proved to be nearly equally adequate to represent the experimental liquidus lines, the values of the parameters ΔH^{M} and K being -0.5 to -6 kJ mole^{-1} and 0.2 to 1, respectively.

INTRODUCTION

In Part I of this work [1] phase diagrams of six binary systems with CT interaction formed by 2,4,7-trinitrofluoren-9-one with naphthalene (N), anthracene (AN), pyrene (P), fluorene (F), dibenzothiophene (BDT), and carbazole (C) were determined by differential scanning calorimetry and hot-stage microscopy. Apart from congruently melting 1:1 CT complexes existing in each system, the formation of incongruently melting AN(TNF)$_2$, P(TNF)$_2$, and C(TNF)$_2$ complexes has been established. There is no miscibility within solid phases; appropriate components form simple eutectics with 1:1 or 1:2 complexes, respectively. In the present work a thermodynamic discussion of solid–liquid equilibria in the systems is given.

EQUILIBRIUM BETWEEN THE PURE SOLID COMPONENT AND THE BINARY MELT

From the general phase-equilibrium condition

$$\mu_i^{0l} + RT\ln(x_i^l\gamma_i^l) = \mu_i^{0s} + RT\ln(x_i^s\gamma_i^s) \tag{1}$$

and by simple thermodynamic relations, one gets

$$\mathrm{d}\ln\frac{x_i^l\gamma_i^l}{x_i^s\gamma_i^s} = \frac{\Delta H_{f,i}^0}{RT^2}\,\mathrm{d}T \tag{2}$$

where x_i^s and x_i^l are the mole fractions of a given component at temperature T in equilibriated solid and liquid phases, respectively; γ_i^s and γ_i^l are the appropriate activity coefficients; and $\Delta H_{f,i}^0$ is the molar heat of fusion of pure component i. Assuming that $\Delta H_{f,i}^0$ is independent of temperature and the solid phase contains only one component ($x_i^s\gamma_i^s \equiv 1$), and integrating between the melting temperature of the pure component ($T_{0,i}$) and that of a sample of a given composition (T), the well-known Van Laar relation is obtained

$$\ln(x_i^l\gamma_i^l) = -\frac{\Delta H_{f,i}^0}{R}\left(T^{-1} - T_{0,i}^{-1}\right) \tag{3}$$

This relation is used for the evaluation of activity coefficients, γ_i^l, by cryoscopic method. For binary systems where components (1) and (2) form a solid addition compound (12), however, the problem of the actual composition of the melt should be considered.

(i) n_{01} and n_{02} denote the mole numbers of the components used in the preparation of the sample, and n_1, n_2, and n_{12} are the mole numbers of the components and of the 1:1 addition compound in the melted sample. For simplicity, let us assume $n_{01} + n_{02} \equiv 1$. Then

$$n_1 = n_{01} - n_{12}, \quad n_2 = n_{02} - n_{12} \tag{4}$$

$$x_1^l = \frac{n_{01} - n_{12}}{1 - n_{12}}, \quad x_2^l = \frac{n_{02} - n_{12}}{1 - n_{12}}, \quad x_{12}^l = \frac{n_{12}}{1 - n_{12}} \tag{5}$$

On the other hand, by the law of mass action, the mole number of undissociated compound in a perfect solution is

$$n_{12} = \frac{(K+1) - \sqrt{(K+1)^2 - 4(K+1)n_{01}n_{02}}}{2(K+1)} \tag{6}$$

where K is the dissociation constant of the addition compound in the (perfect) melt at a given temperature

$$K = \frac{x_1^l x_2^l}{x_{12}^l} \tag{7}$$

Estimating experimentally the values of $\Delta H^0_{f,i}$ and the melting temperature of the sample of a given composition (n_{01}, n_{02}), i.e., knowing $\Delta H^0_{f,i}$ and the position of the liquidus line in the phase diagram, and assuming the melt to be a perfect solution $(\gamma^l_i \equiv 1)$, the dissociation constant of the addition compound at a given temperature is evaluated by using relations (3), (5), and (6). However, this is a rather arduous and not very successful procedure due to the large scatter of K values caused by experimental errors. Thus it is more convenient to draw a pencil of lines $T(n_{0i})$ for different K values and to fit one of them to the experimental points *.

(ii) If it is assumed that the addition compound dissociates completely in the melted state (thus if $x^l_i \equiv n_{0i}$), it is possible to evaluate the activity coefficient of the component in the melt of a given composition and at a given temperature (melting temperature of the sample) using eqn. (3). Here it is also more convenient to introduce a suitable general relation $\gamma^l_i = f(x^l_i, T)$ and to draw a set of "theoretical" $T(x^l_i)$ lines. It seems reasonable to assume the melt to be regular solution for which [2]

$$\gamma^l_i = \exp\left[\frac{4\,\Delta H^M}{RT}\left(1 - x^l_i\right)^2\right] \tag{8}$$

Then, as in case (i), we have a pencil of lines (with the value of molar heat of mixing ΔH^M as a parameter) which could be fitted to the experimental results **.

EQUILIBRIUM BETWEEN THE SOLID ADDITION COMPOUND AND THE BINARY MELT

Applying eqn. (2) and noting that $x^s_{12}\gamma^s_{12} \equiv 1$, for the case studied here

$$\mathrm{d}\ln\left(x^l_{12}\gamma^l_{12}\right) = -\frac{\Delta H^0_{f,12}}{RT^2}\,\mathrm{d}T \tag{2a}$$

The mole fraction of the addition compound in the melt is related to the mole fractions of the components by the law of mass action

$$K_a = \frac{x^l_1\gamma^l_1 \cdot x^l_2\gamma^l_2}{x^l_{12}\gamma^l_{12}} \tag{7a}$$

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* The limited accuracy of measurements did not allow us to ascertain the temperature dependence of the dissociation constant.

** To evaluate γ^l_i for a given x^l_i by eqn. (8) the melting temperature of the sample must be known—a quantity being determined. The problem can be solved by combining (8) with (3) which gives a simple relation $x^l_i = f(T)$ with ΔH^M, $\Delta H^0_{f,i}$ and $T_{0,i}$ as known parameters.

thus eqn. (2a) is equivalent to

$$\mathrm{d}\ln\left(x_1^1\gamma_1^1 \cdot x_2^1\gamma_2^1\right) - \mathrm{d}\ln K_a = -\frac{\Delta H^0_{f,12}}{RT^2}\,\mathrm{d}T \tag{9}$$

Integrating between the melting temperature of the pure addition compound (where $n_{01} = n_{02} = 0.5$) and that of the sample of a given composition (n_{01}, n_{02}) and taking into account the van't Hoff isobar

$$\ln\frac{K_a(T)}{K_a(T_{0,12})} = -\frac{\Delta H^0_{\mathrm{diss}}}{R}\left(T^{-1} - T^{-1}_{0,12}\right) \tag{10}$$

gives

$$\ln\frac{\left(x_1^1\gamma_1^1 \cdot x_2^1\gamma_2^1\right)_{n_{01}\neq n_{02}}}{\left(x_1^1\gamma_1^1 \cdot x_2^1\gamma_2^1\right)_{n_{01}=n_{02}=0.5}} = -\frac{\Delta H^0_{\mathrm{eff}}}{R}\left(T^{-1} - T^{-1}_{0,12}\right) \tag{11}$$

where

$$\Delta H^0_{\mathrm{eff}} = \Delta H^0_{f,12} + \Delta H^0_{\mathrm{diss}} \tag{12}$$

is the effective heat of fusion of the addition compound *.

As in the preceding paragraph two limiting cases will be considered.

(iii) Partially dissociated addition compound forming a perfect solution with the components.

Since $\gamma_i^1 \equiv 1$ here, we get

$$\ln\frac{\left(x_1^1 x_2^1\right)_{n_{01}\neq n_{02}}}{\left(x_1^1 x_2^1\right)_{n_{01}=n_{02}=0.5}} = -\frac{\Delta H^0_{\mathrm{eff}}}{R}\left(T^{-1} - T^{-1}_{0,12}\right) \tag{13}$$

Similarly as in case (i), the mole fractions of the components are related to the (known) values of n_{0i} by relations (5) and (6); nevertheless eqn. (13) cannot be solved for K unless additional assumptions are made. With $\Delta H^0_{\mathrm{eff}}$, $T_{0,12}$, and T known, there is only one equation and two unknowns: the values of K corresponding to $T_{0,12}$ and T. Thus it was decided to neglect the temperature dependence of the dissociation constant and adopt the same procedure used previously: to fit one of the $T(n_{0i})$ lines calculated from (13), (5), and (6) for different K values to experimental results.

(iv) Addition compound dissociates completely, molten components form a regular solution.

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* If the addition compound dissociates completely upon melting, $\Delta H^0_{\mathrm{eff}}$ is equal to the experimentally measured molar heat of fusion $\Delta H^0_{\mathrm{exp}}$. If the degree of dissociation (at $n_{0i} = 0.5$) is α $\Delta H^0_{\mathrm{eff}} = \Delta H^0_{\mathrm{exp}} + (1-\alpha)\ \Delta H^0_{\mathrm{diss}}$. The difference is neglected as a more crude approximation, $K \neq f(T)$ has to be made (see below).

Now $x_i = n_{0i}$ and (11) reduces to

$$\ln \frac{\left(n_{01} n_{02} \gamma_1^1 \gamma_2^1\right)_{n_{01} \neq n_{02}}}{\left(0.25 \cdot \gamma_1^1 \gamma_2^1\right)_{n_{01} = n_{02} = 0.5}} = -\frac{\Delta H^0_{\mathrm{eff}}}{R}\left(T^{-1} - T^{-1}_{0,12}\right) \tag{13a}$$

Assuming as in (ii) a suitable general expression for γ_i as a function of n_{0i} and T, the procedure described there can be followed, and the theoretical plot $n_{0i}(T)$ can be compared with the actual one. For regular solutions $\gamma_i(x_i, T)$ is given by (8). One should bear in mind, however, that in (8) the ideal state of reference is the pure liquid component i ($\gamma_i \to 1$ when $x_i \to 1$), whereas in (7a) and thus in (13a) it is an infinitely diluted solution ($K_a \to K$ when $x_i \to 0$). The problem of an analytical expression for γ_i of the solute in a regular solution is dealt with in the Appendix where instead of eqn. (8) we have found the relation

$$\gamma_i = \exp\left[-\frac{4\,\Delta H^{\mathrm{M}}}{RT} x_i (2 - x_i)\right] \tag{14}$$

Applying (14) to (13a) and taking $\Delta H^0_{\mathrm{eff}} = \Delta H^0_{\mathrm{exp}}$ and $T_{0,12}$ from experimental results, we have simulated $T(n_{0i})$ lines for different ΔH^{M} values as a parameter and compared them to the liquidus line found experimentally.

RESULTS

Detailed results of the TNF–naphthalene system are given as an example. Figure 1 shows the plot of calculated $T(n_{0,\mathrm{TNF}})$ lines together with experimental points. An equally good fit was attained in both procedures (i) and (ii), the values of the parameters being $K = 1$ and $\Delta H^{\mathrm{M}} = -0.55$ kJ mole^{-1}, respectively. For the sake of comparison, liquidus lines calculated for $\Delta H^{\mathrm{M}} = 0$ (i.e. for a perfect binary solution) and for $\Delta H^{\mathrm{M}} = -1$ kJ mole^{-1} are also shown. In Fig. 2, the equilibrium between the solid TNF–N complex and the molten phase is reviewed. Melting temperatures of both naphthalene-rich and TNF-rich samples fit the same liquidus line (i.e. the liquidus line is symmetrical with respect to $n_{0i} = 0.5$). Here again the melting curve can be equally well reproduced by schemes (iii) or (iv); in the latter case, however, a value of $\Delta H^{\mathrm{M}} = -1$ kJ mole^{-1}, different from that found previously, has to be used. The discrepancy is beyond experimental error (note the line for $\Delta H^{\mathrm{M}} = -1$ kJ mole^{-1} in Fig. 1 and that for $\Delta H^{\mathrm{M}} = -0.55$ kJ mole^{-1} in Fig. 2), thus we are inclined to regard the model of incomplete dissociation of the CT complex in the molten state as more adequate.

In Fig. 3 the complete phase diagram of the TNF–naphthalene system as

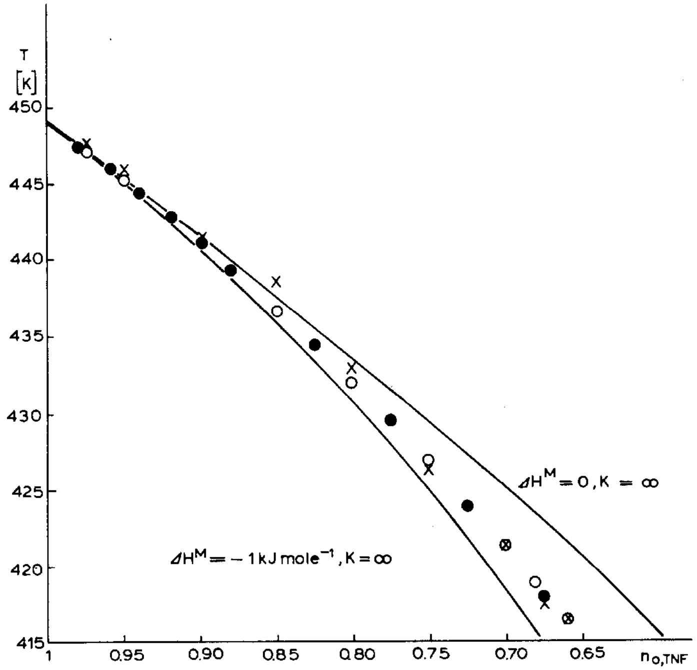

Fig. 1. Equilibrium temperature in the system solid TNF–liquid TNF + naphthalene. x, Experimental values; ○, calculated for $\Delta H^M = -0.55$ kJ mole^{-1}, $K = \infty$; ●, calculated for $\Delta H^M = 0$, $K = 1$.

calculated within the latter model with $K = 1$ is shown together with experimental results. Liquidus lines calculated for the limiting case $\Delta H^M = 0$, $K = \infty$ are also drawn. Similar results have been found for TNF–dibenzo-

TABLE 1

Parameters of two alternative thermodynamic descriptions of the systems

System	Perfect solution incomplete dissociation	Regular solution, complete dissociation ΔH^M (kJ mole^{-1})
TNF–N	1	(−0.5 to −1)
TNF–AN	0.25	(−2.5 to −3.5)
TNF–P	(0.2–0.3)	−4.25
TNF–F	(>1)	−0.75
TNF–DBT	0.3 to 0.4	−2.25
TNF–C	(0.2)	(−6.25)

The values in parentheses are regarded as less reliable.

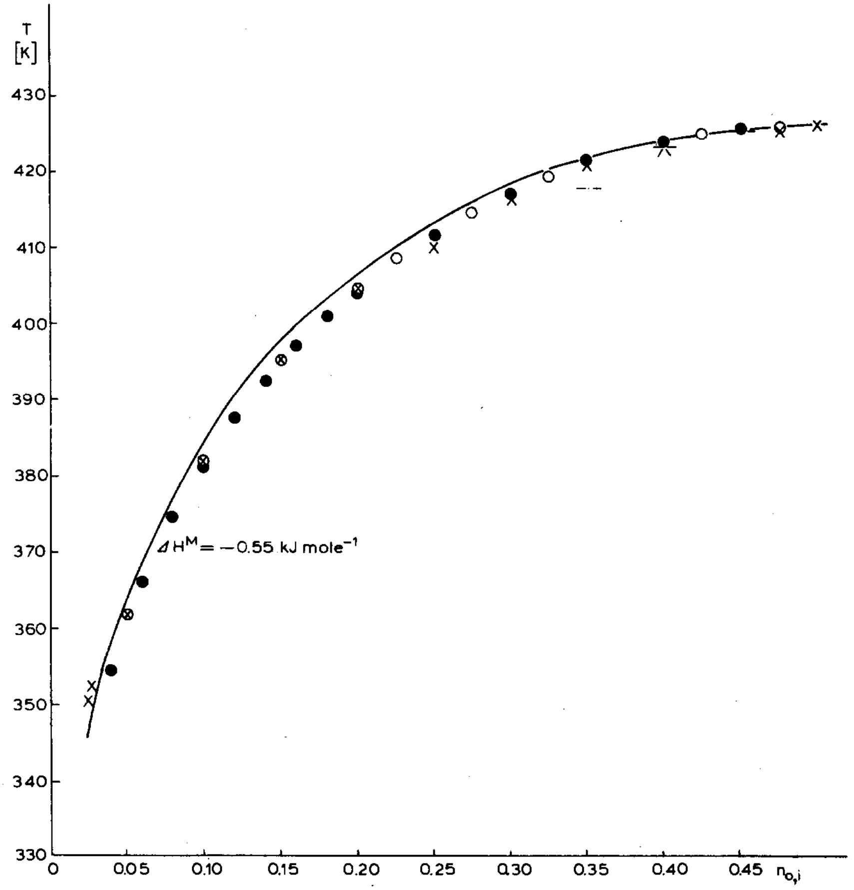

Fig. 2. Equilibrium temperature in the system solid TNF–N complex—binary melt. —·—, Experimental values for TNF-rich melts; x, experimental values for naphthalene-rich melts; ○, calculated for $\Delta H^M = -1$ kJ mole^{-1}, $K = \infty$; ●, calculated for $\Delta H^M = 0$, $K = 1$.

thiophene and TNF–anthracene systems (beyond the existence region of $AN(TNF)_2$ complex).

In the TNF–carbazole system the melting curve of the 1 : 1 complex can be satisfactorily reproduced by the model of incomplete dissociation; the melting curve of carbazole, however, cannot be described by any of the two models.

For the TNF–fluorene and TNF–pyrene systems a better fit was attained in the framework of the regular solution model. However, it is possible that it is the oversimplified assumption of the temperature-independent dissociation constant which accounts for the inadequacy of the alternative model in this case. The results of calculations are briefly summarized in Table 1.

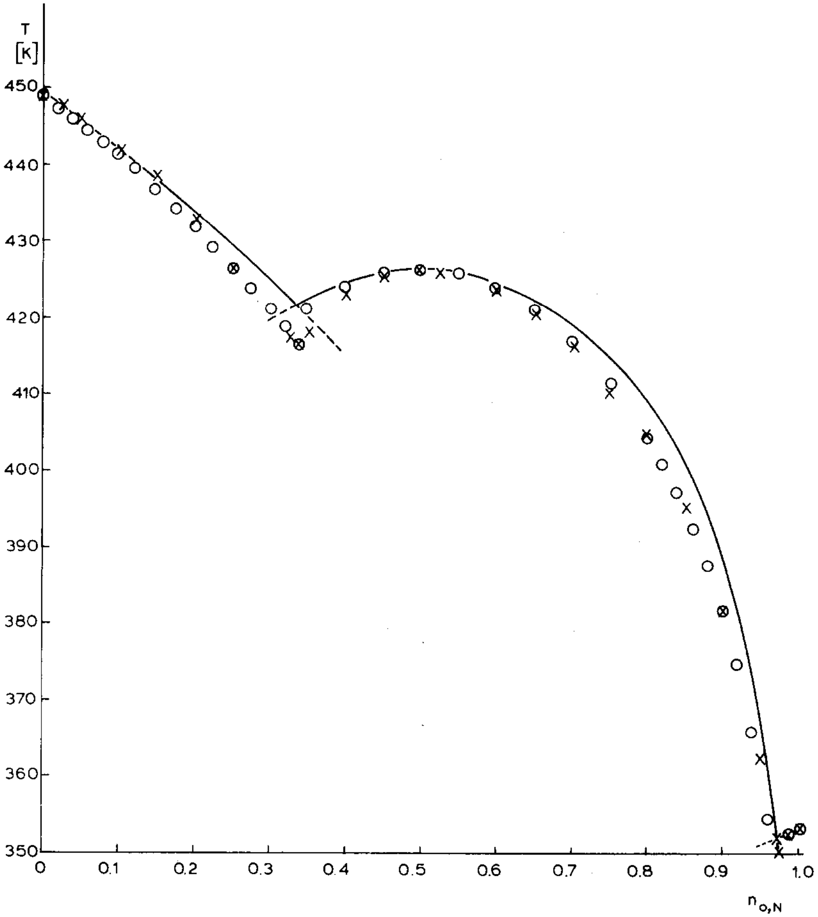

Fig. 3. Liquidus lines in the TNF–naphthalene system. x, Experimental results; O, calculated for $\Delta H^{M}=0$, $K=1$; ———, calculated for $\Delta H^{M}=0$, $K=\infty$.

DISCUSSION

Two alternative treatments proposed in the present work for solid–liquid equilibria in binary systems with CT interactions are proved to be of similar usefulnes. As a matter of fact, in spite of the different formalism used in each of the methods, they account for the same chemical .reality: the occurrence of attractive interactions between donor and acceptor molecules in the melt expressed by the negative value of the enthalpy of mixing or by the existence of the undissociated CT complex in the molten state. Thus the clear distinction between the two models proposed here seems neither necessary nor possible. Nevertheless, the concept presented allows some qualitative conclusions to be drawn. The low dissociation constant values found here ($K = 0.2$–1) suggest that even for rather weak CT complexes (as those of TNF with aromatic donors) about 50% of complex molecules still do not decompose into their components after melting. It would be interesting to check this estimation by an independent experiment, e.g. spectroscopically.

A paper has recently been published by M. Radomska and R. Radomski [3] concerning this problem. The authors discussed phase equilibria of CT complexes of trinitrobenzene with aromatic compounds along similar lines based on the Van Laar equation. Although we agree with the general conclusions of the authors concerning incomplete dissociation of the complex in the molten state and even with the concept of a positive contribution to the heat of mixing, we differ in the discussion of the thermodynamic condition of equilibrium between the solid 1 : 1 complex and the melt [eqns. (2) and (4) in ref. 3 or eqns. (11), (13), and (13a) in the present work]. A comparison of these equations shows that the authors have tacitly assumed complete dissociation of the complex in the stoichiometric melt, which is inconsistent with their results.

APPENDIX

Activity coefficient of the solute in a regular binary solution

By definition of activity coefficient [4]

$$RT \ln \gamma_i = \mu_i^{\mathrm{real}} - \mu_i^{\mathrm{id}} \tag{15}$$

where μ_i^{real} is the chemical potential of component i in the real solution, and μ_i^{id} is that in the ideal reference state, for a regular solution with

$$\ln \gamma_i = \frac{4\,\Delta H^{\mathrm{M}}}{RT}(1 - x_i)^2 \tag{8}$$

$$\mu_i^{\mathrm{reg}} - \mu_i^0 = RT\left[\ln x_i + \frac{4\,\Delta H^{\mathrm{M}}}{RT}(1 - x_i)^2\right] \tag{16}$$

where μ_i^0 is the standard chemical potential which is identical for both the real solution and the ideal reference state.

Figure 4 shows a schematic plot of $(\mu_i^{\mathrm{reg}} - \mu_i^0)$ vs. $\ln x_i$ together with two straight lines representing $(\mu_i^{\mathrm{id}} - \mu_i^0)$ vs. $\ln x_i$ plots for two ideal reference states, viz., that of pure liquid i (which is the state of reference assumed in (8)—upper line) and that of an infinitely diluted solution (lower line). The vertical distance between the actual $\mu_i^{\mathrm{reg}} - \mu_i^0$ line and a given straight line $(\mu_i^{\mathrm{reg}} - \mu_i^0) - (\mu_i^{\mathrm{id}} - \mu_i^0) = \mu_i^{\mathrm{reg}} - \mu_i^{\mathrm{id}}$ is, according to eqn. (15) equal to $RT \ln \gamma_i$

for a given choice of the reference state; the vertical distance between two straight lines is equal to $-4\,\Delta H^{\mathrm{M}}$.

For clarity we shall denote the activity coefficient for the "pure liquid",

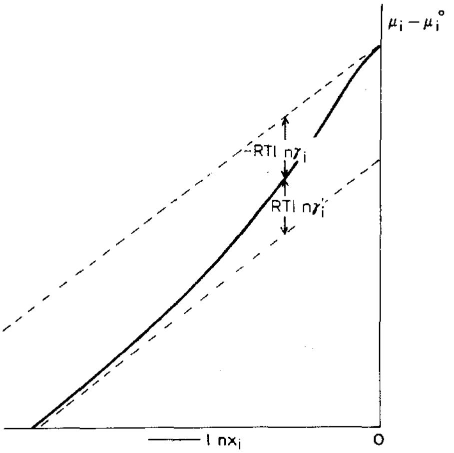

Fig. 4. The relationship between the activity coefficients of a component of a binary regular solution for two different ideal reference states.

and that for the "infinitely diluted solution" state of reference by γ_i and γ_i', respectively. From Fig. 4

$$RT(\ln\gamma_i' - \ln\gamma_i) = -4\,\Delta H^{\mathrm{M}}$$

and introducing (8)

$$RT\ln\gamma_i' = -4\,\Delta H^{\mathrm{M}} + 4\,\Delta H^{\mathrm{M}}(1-x_i)^2 = -4\,\Delta H^{\mathrm{M}} x_i(2-x_i)$$

Thus

$$\gamma_i' = \exp\left[-\frac{4\,\Delta H^{\mathrm{M}}}{RT}x_i(2-x_i)\right] \tag{14}$$

It is to be noted that for $\Delta H^{\mathrm{M}} < 0$, $\gamma_i < 1$ and $\gamma_i' > 1$, whereas for $\Delta H^{\mathrm{M}} > 0$, $\gamma_i > 1$ and $\gamma_i' < 1$.

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