

PERTURBATION OF CRITICAL SOLUTION TEMPERATURES BY IMPURITY DOPING

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An expression is developed for the variation of the critical solution temperature of a binary liquid system when a third component (dopant) is added, using an extension of the regular solution theory. The model can be used for UCST, LCST and for closed loop systems and has the correct features in the limiting cases.

Introduction

It is well known in thermal studies of partially miscible solutions that critical solution temperatures are sensitive to the presence of impurities in the system. In the case of binary liquid systems, an impurity which dissolves in both the liquids generally lowers the UCST while an impurity which is soluble in one of the liquids raises the UCST [1-4]. A general theoretical framework which provides qualitative, and in some cases semi-quantitative, description of the phenomena is the regular solution theory [5-7]. Several authors have studied the impurity effect as a quasi-binary or as a ternary system phenomenon [3, 8, 9]. The theoretical expressions turn out to be somewhat complicated, involving many parameters and have therefore not been widely used. In recent years, experimental studies have extended the phenomena in many directions [10]. Impurity effects in LCST systems have been studied; closed loop phase diagrams which shrink as a result of doping have also been studied. These extensions add to the complications which have to be handled by the theory which must nevertheless be amenable to simple interpretations and applications.

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Recently Raz and Wisniak [11] have suggested a version of the simple regular solution theory which has some interesting features. In the simple model, the excess molar Gibbs energy of G is written for binary system as

$$g^E = An(1 - n) \quad (1)$$

in terms of the mole fraction of one of the compounds. Phase separation occurs when

$$A/RT > 2 \quad (2)$$

Thus the (upper) critical solution temperatures is determined in terms of the A - constant as

$$T_c = A/2R \quad (3)$$

and at lower temperatures the two phase separate out. Earlier authors had pointed out that a temperature dependent A can explain LCST and closed loop phenomena, but the logarithmic dependences introduced in analogy with other situations have greatly added to the complexity of the expressions. Raz and Wisniak showed that instead of a constant value of A , a quadratic form

$$A(T) = a + bT + CT^2 \quad (4)$$

is able to explain a variety of phenomena, including the presence of UCST, LCST and closed loop phase diagrams. The extension of the regular solution theory does not appear to be widely known and utilized.

Model Theory

The calculation of the effect of an impurity on the critical temperature can be conveniently performed in the frame work of the regular solution theory [5-7]. In a three component system, one writes

$$g^E = A_{12}n_1n_2 + A_{13}n_1n_3 + A_{23}n_2n_3. \quad (5)$$

In the strictly regular solution theory of binary systems

$$(n_1)_C = (n_2)_C = 0.5 \quad \text{and} \quad T_C = A_{12}/2R. \quad (6)$$

Following Raz and Wisniak [11] one takes the A 's to be quadratic in temperatures in Eq. (4). In view of the many approximations in the model one retains only the first temperature derivative of A in the calculations. Further one assumes the third component mole fraction n_3 to be small. The coexistence curve is described by the boundary P , which separate the stable and unstable phases and in terms of its variation with n_3 and T one can write,

$$\frac{\partial T_C}{\partial n_3} = - \frac{\frac{\partial P}{\partial n_3}}{\frac{\partial P}{\partial T}} \quad (7)$$

for the change of T_C with n_3 . For a three component system, in the regular solution theory the change of P with n_3 is obtained as [5-7],

$$\frac{\partial P}{\partial n_3} = - \frac{1}{4n^2} \cdot [A_{12} - A_{13} + A_{23}] \cdot [A_{12} + A_{13} - A_{23}] \quad (8)$$

Extra terms arise in the derivative of the temperature because of the additional terms in Eq. (4). One starts with the expression for the chemical potential,

$$\mu_i = \mu_i^\circ(T, P) + RT \ln(n_i) + RT \ln(\gamma_i), \quad (9)$$

where the last term arises from the non-ideality of the system,

$$\left. \frac{\partial g^E}{\partial n_i} \right|_T, P = RT \ln(\gamma_i). \quad (10)$$

The phase boundary P is given by

$$P = n_1 \cdot \frac{\partial \mu_1}{\partial n_2} \cdot \frac{\partial \mu_1}{\partial n_3} + n_2 \cdot \frac{\partial \mu_2}{\partial n_1} \cdot \frac{\partial \mu_2}{\partial n_3} + n_3 \cdot \frac{\partial \mu_3}{\partial n_1} \cdot \frac{\partial \mu_3}{\partial n_2}. \quad (11)$$

Using the above values of μ_i one gets,

$$\begin{aligned} \frac{\partial \mu_1}{\partial n_2} = \frac{1}{n} \cdot [& -RT + 2n_2 A_{12} - 2n_2^2 A_{12} - 2n_3^2 A_{13} \\ & + (A_{12} - A_{23} + A_{13}) \cdot n_3 - 2(A_{12} - A_{23} + A_{13}) \cdot n_2 n_3] \\ \frac{\partial \mu_1}{\partial n_3} = \frac{1}{n} \cdot [& -RT + 2n_3 A_{13} - 2n_3^2 A_{13} - 2n_2^2 A_{12} \end{aligned}$$

$$\begin{aligned}
 & + \left(A_{13} - A_{23} + A_{12} \right) \cdot n_2 - 2 \left(A_{13} - A_{23} + A_{12} \right) \cdot n_3 n_2 \Big] \\
 \frac{\partial \mu_2}{\partial n_3} = & \frac{1}{n} \cdot \left[-RT + 2n_3 A_{23} - 2n_3^2 A_{23} - 2n_1^2 A_{21} \right. \\
 & \left. + \left(A_{23} - A_{13} + A_{12} \right) \cdot n_1 - 2 \left(A_{23} - A_{13} + A_{12} \right) \cdot n_1 n_3 \right]
 \end{aligned}$$

For a dilute impurity near the critical point of a binary system, $n_3 \rightarrow 0$; $(n_1)_c = (n_2)_c = 0.5$.

Thus the above equation gets simplified as,

$$\begin{aligned}
 \left(\frac{\partial \mu_1}{\partial n_2} \right)_c &= 0; & \left(\frac{\partial \mu_1}{\partial n_3} \right)_c &= -\frac{1}{2n} \cdot \left[A_{12} - A_{13} + A_{23} \right]; \\
 \left(\frac{\partial \mu_2}{\partial n_3} \right)_c &= -\frac{1}{2n} \cdot \left[A_{12} - A_{23} + A_{13} \right].
 \end{aligned} \tag{12}$$

In a similar way one considers the temperature derivative $(\partial / \partial T) (\partial \mu_i / \partial n_j)$ and inserts the critical conditions (12) so that one has

$$\begin{aligned}
 \left(\frac{\partial}{\partial T} \right) \left[\frac{\partial \mu_1}{\partial n_2} \right]_c &= \frac{1}{n} \cdot \left[-R + \frac{1}{2} \cdot \frac{\partial A_{12}}{\partial T} \right] \\
 \left(\frac{\partial}{\partial T} \right) \left[\frac{\partial \mu_1}{\partial n_3} \right]_c &= \frac{1}{n} \cdot \left[-R + \frac{1}{2} \cdot \left(\frac{\partial A_{13}}{\partial T} - \frac{\partial A_{23}}{\partial T} \right) \right] \\
 \left(\frac{\partial}{\partial T} \right) \left[\frac{\partial \mu_2}{\partial n_3} \right]_c &= \frac{1}{n} \cdot \left[-R + \frac{1}{2} \cdot \left(\frac{\partial A_{23}}{\partial T} - \frac{\partial A_{13}}{\partial T} \right) \right].
 \end{aligned} \tag{13}$$

When these are substituted in $(\partial P / \partial T)$ from Eq. (11) one obtains,

$$\left(\frac{\partial P_1}{\partial T} \right)_c = \frac{1}{n^2} \cdot \frac{A_{12}}{2} \cdot \left(R - \frac{1}{2} \cdot \frac{\partial A_{12}}{\partial T} \right). \tag{14}$$

Combining equations (7), (8) and (14), one arrives finally,

$$\frac{\partial T_c}{\partial n_3} = -\frac{A_{12}^2 - (A_{13} - A_{23})^2}{2A_{12} \cdot \left(R - \frac{1}{2} \cdot \frac{\partial A_{12}}{\partial T} \right)}. \tag{15}$$

This equation gives the shift of T_c by the doping with the impurity n_3 .

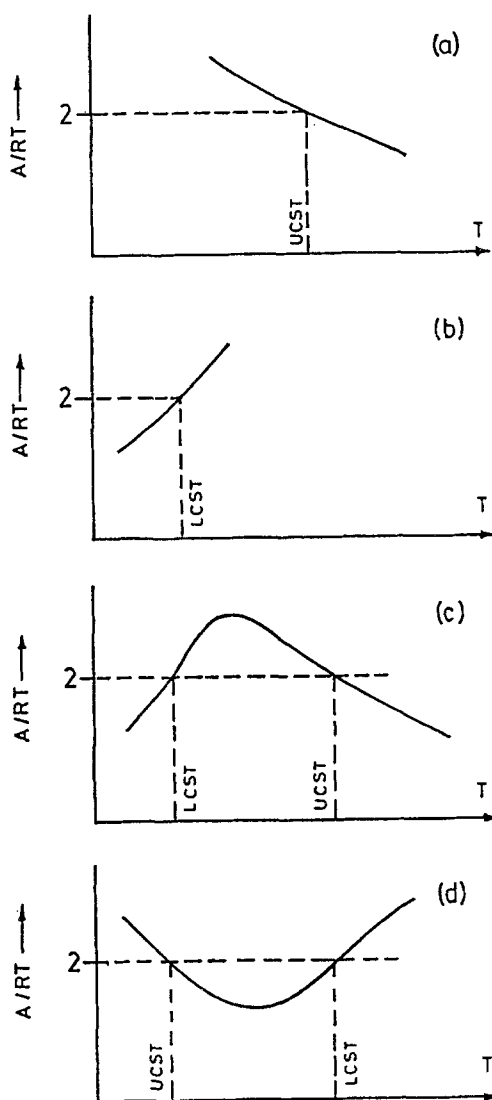


Fig. 1 Cases of phase separation depending on the variations of A/RT around the critical value 2.0. (a) A/RT decreases with increase of T , the situation when the parameter A is nearly constant. At low temperatures when $A/RT > 2$, two phase separation occurs with a single phase above UCST. The UCST phenomenon is thus the most common critical solution temperature in partially soluble mixtures. (b) A/RT increases with increase of T . Above LCST two phases separate out with the one phase region at low temperatures. (c) A/RT is parabolic convex upwards. This corresponds to a closed loop phase diagram with one phase region at high and low temperatures; two phases coexist at intermediate temperatures. (d) A/RT is parabolic convex downwards. A valley-saddle phase boundary occurs with a one phase region at intermediate temperatures; two phases coexist at high and low temperatures

Discussion

In the simple regular solution theory, the parameter A is taken as constant. If the system remains in a liquid state at sufficiently low temperatures, one can have the condition $A/RT > 2$ and phase separation occurs at low temperatures. This is the common UCST phenomenon [Fig. 1a]. If one has a temperature dependent A parameter, then A/RT can have other possible variations which yield LCST [Fig. 1b], closed loop phase diagrams [Fig. 1c] and valley-saddle type mutual solubility phase diagrams [Fig. 1d]. The quadratic dependence is the minimum requirement to ensure a description of all the cases with the same functional form of A .

The Eq. (15) is equivalent in spirit to the considerations of several workers [4, 12–15]. If $A_{13} \approx A_{23}$ i.e. impurity interacts equally with liquids (1) and (2) and so dissolves in both phases, then $\delta T_C / \delta n_3$ is negative and UCST moves down. An example [2] is the addition of acetic anhydride to the binary critical mixture of acetonitrile + cyclohexane. If $A_{23} \gg A_{12}$ and $A_{23} \gg A_{13}$, i.e. impurity (3) interaction with liquid (2) is much more than 3–1 and 2–1 interactions and the impurity dissolves only in (3); then UCST moves up with the addition of impurity n_3 . An example is the doping of acetonitrile + cyclohexane with water [2]. The semi-quantitative application of these ideas to specific systems requires information on the value of A and their temperature variations, which are not always readily available. These will be considered separately.

Finally it is to be noted that if the A_{ij} 's are independent of T , then Eq. (15) goes back to the equation of regular solution theory [5–7], namely

$$\frac{\delta T_C}{\delta n_3} = - \frac{A_{12}^2 - (A_{13} - A_{23})^2}{2RA_{12}} \quad (16)$$

As discussed earlier, this describes the qualitative features of UCST phenomena only. The temperature derivative of A is needed to describe correctly the features of other types of phenomena. It should also be noted that in this approximate model the impurity is assumed to affect T_C and not n_C . While the impurity effects on T_C are substantial to be noticed easily, the effect on n_C is quite small.

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Nomenclature

UCST	=	Upper critical solution temperature
LCST	=	Lower critical solution temperature
g^E	=	Gibbs free energy
n_i	=	no of moles of a component
A_{ij}	=	co-efficient of the regular solution theory
T_C	=	critical temperature
$(n_i)_C$	=	mole fraction at critical temperature
μ_i	=	chemical potential
R	=	molar gas constant
γ_i	=	Activity coefficient
P	=	Equation of the surface
μ_i°	=	the value of μ_i under standard conditions of concentration
n	=	total number of moles

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Zusammenfassung – In Ausdehnung der normalen Lösungstheorie wird eine Gleichung für die Änderung der kritischen Lösungstemperatur bei Zusatz einer dritten Komponente zu einem binärem flüssigen System entwickelt. Dieses Modell kann auf UCST, LCST und für geschlossene Schlefensysteme angewendet werden und besitzt die richtigen Charakteristika in Grenzfällen.