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Calculation of phase diagram and the thermodynamic quantities by the Landau mean field model close to the solid – liquid and solid – solid transitions in n-paraffins

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ABSTRACT

We calculate the phase diagrams and predict the temperature dependence of the thermodynamic quantities at high pressures for the solid – liquid and solid – solid transitions in n-paraffins. This calculation is performed by fitting the phase line equations as obtained from the Landau model to the experimental data from the literature. On the basis of the Landau model, phase diagram of the solid – solid transition is predicted at 0.1 MPa for the binary mixtures of n-tridecane + (n-hexane and cyclohexane). For the calculation of the heat capacity the extended mean field is employed for the n-paraffins studied here. We find that our calculated phase diagrams explain the observed behaviour of the liquid – solid transitions at high pressures in those binary mixtures. Our phase diagrams predicted at 0.1 MPa and our predictions for the thermodynamic quantities can be compared with the experiments for those binary mixtures.

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1. Introduction

Solid – liquid equilibria (SLE) in n-alkanes have been studied extensively because of its industrial and scientific concern. As phase change materials (PCMs), n-alkane mixtures have been proved to be very important for thermal protection and energy storage [1–3] as also indicated previously [4,5]. There have been a number of studies concerning the phase diagrams which include the regions of single phase and multiphase coexistence [6–8], in particular, the equilibrium phase diagram of n-octadecane ($C_{18}H_{38}$) + n-nanodecane ($C_{19}H_{40}$) [6], tetradecane, pentadecane + hexadecane [9] and hexadecane/octadecane mixtures (mC_{16}/C_{18}) [5]. Regarding the phase diagrams in n-alkanes, the effect of pressure on the liquid – solid transition, in particular, on the phase boundary between the liquid phase and the two – phase liquid – solid phase domain has been studied experimentally [9–11]. As a continuous series of solid solutions, temperature – composition ($T - X$) phase diagram has been obtained experimentally [12]. The properties and characteristic of normal alkanes with the $T - X$ phase diagrams of some alkane mixtures have been considered in earlier studies [13–15], as also indicated previously [12]. The rotator phases which are intermediate phases occur between the crystalline and the isotropic phases in n-alkanes. They have been observed experimentally by using neutron scattering [16], computer simulations [17] and X-ray scattering [16], as reported in an earlier study [18]. Theoretically, the solid – liquid phase equilibrium has been modelled by the group – contribution method (UNIFAC) [19]. The model of Won [20] has improved representation of solid –

liquid equilibrium and Won's model has been modified by Pedersen and Skovborg [21] for its description, as also indicated previously [12]. The phase diagrams were then calculated using both ideal and nonideal thermodynamic models [19-21]. A local composition model for paraffinic solid solutions and g^E model known as chain delta lattice parameter (CDLP) model have been introduced for the rotator - orthorhombic solid phases in paraffins by Coutinho et al. [22,23]. Thermal behavior of degassed oil at atmospheric pressure has been modelled by Lira-Galeana et al. [24]. Also, the description of both fluid - fluid and solid - fluid phase boundaries of paraffinic solutions has been modelled by Pauly et al. [25]. Additionally, by the molecular dynamics simulation (MD) solid - liquid and solid - solid phase transitions in alkanes have been studied recently [26,27]. The solid - liquid - vapour phase behaviour of n-alkanes has also been modelled by thermodynamic perturbation theory (TPT) very recently [28]. The pressure effect on the rotator I - II transition [29] and the liquid - rotator I - II phase sequence of alkanes have been studied within the Landau phenomenological model [30]. We have also investigated the liquid - solid phase transition in n-alkanes by the Landau mean field theory using the experimental data from the literature in our recent studies [31-35]. By expanding the free energy in terms of the order parameter within the framework of the Landau phenomenological model, the phase line equations can be obtained for the solid - liquid solution transitions in n-alkanes. The crystal order parameter (ψ) describes the crystal phase of a small molecule system with the $\psi = 0$ for the melt state, $\psi = 1$ for a perfect crystal and $0 < \psi < 1$ for imperfect crystal, as stated previously [36].

Regarding high-pressure (solid + liquid) equilibria of n-alkane mixtures, in particular, (n-tridecane, n-hexadecane, n-octadecane) + n-hexane and cyclohexane, as studied experimentally [11], phase diagrams can be obtained and the thermodynamic quantities can be predicted within the Landau mean field theory. Also, α and β crystalline forms of n-tridecane + n-hexane and cyclohexane mixtures with their intermolecular and intramolecular interactions, can be studied for the transitions of solid - liquid and solid - solid (at 0.1 MPa) using the experimental data [11] by this model. To predict the thermodynamic quantities, in particular, for the heat capacity, we employ the extended mean field model [37] that was applied to the smectic A-C transition in liquid crystals [38]. Phase line equations are fitted to the experimental data [11] for the first order solid - liquid transition in the binary mixtures studied. The solid - solid ($\alpha - \beta$) transition is considered as of a second order with the quadratic coupling of the order parameters as stated above within the extended mean field theory. This coupling is important in determining the nature of this transition and their stability. Positive or negative sign of the coefficient for the quadratic coupling can drive the system towards the α or β phase, as also indicated for the $R_I - R_V$ transition in alkanes [36,39]. High value of the coupling constant shows that there is a strong coupling between the order parameters of the solid phases of α and β in n-paraffins. Since the experimental measurements are lacking to explain the solid - solid phase transition type ($\alpha \rightarrow \beta$) and the pressure effect on the transition temperatures, which characterizes melting solid phase for those binary mixtures as indicated previously [11], the solid - solid transition can be investigated. This has motivated us to study SLE for those binary mixtures by establishing the phase diagrams and the temperature dependence of the thermodynamic quantities under high pressures using the Landau mean field model.

Below, in section 2 we give an outline of the mean field theory. In section 3, our calculations and results are given. We discuss our results in section 4 and conclusions are given in section 5.

2. Theory

We present here the Landau phenomenological model to describe the phase transitions of the liquid - α , liquid - β and $\alpha - \beta$ crystalline forms of n-tridecane. By expanding the free energy in terms of the order parameter of the α and β solid phases, $T - X$ and $P - X$ phase diagrams are

calculated and the temperature dependence of the thermodynamic quantities is predicted for the binary mixtures of n-tridecane, n-hexadecane and n-octadecane. For the calculations of the $T - X$ and $P - X$ phase diagrams, the phase line equations are obtained from the Landau phenomenological model and they are fitted to the experimental data from the literature for those binary mixtures.

2.1 Liquid - α transition

The free energy of the α crystalline form of the binary mixtures can be expanded in terms of the order parameter ψ of this phase as

$$F_\alpha = a_2\psi^2 + a_4\psi^4 + a_6\psi^6 \quad (1)$$

where the coefficients a_2 , a_4 and a_6 are in general the temperature (T), concentration (x) and pressure (P) dependent. For the first order transition between liquid (L) and the α phase, $a_4 < 0$ and $a_6 > 0$. The free energy of the liquid (L) phase is

$$F_L = 0 \quad (2)$$

since there is no ordering in this phase. By using the condition for the first order transition

$$F_L = F_\alpha \quad (3)$$

we find that

$$a_2\psi^2 + a_4\psi^4 + a_6\psi^6 = 0 \quad (4)$$

F_α can be minimised with respect to the ψ ($\partial F_\alpha / \partial \psi = 0$), then we get

$$a_2 + 2a_4\psi^2 + 3a_6\psi^4 = 0 \quad (5)$$

By solving Equation 4 and Equation 5, we obtain the order parameter ψ in terms of the coefficients as

$$\psi^2 = -a_4/2a_6 \quad (6)$$

We can find the phase line equation for the $L - \alpha$ transition by means of Equation 6. When we substitute ψ^2 (Equation 6) into the free energy F_α (Equation 1), we find that

$$F_\alpha = -\frac{a_2^2}{4a_4} - \frac{a_2^3 a_6}{8a_4^3} \quad (7)$$

Using Equation 2 and Equation 3 the phase line equation can be obtained as

$$a_2 a_6 = -2a_4^2 \quad (8)$$

For the $\alpha - L$ transition, by equating

$$F_\alpha = F_L = 0 \quad (9)$$

ψ^2 (Equation 6) can be equivalently expressed as

$$\psi^2 = a_2/4a_4 \quad (10)$$

2.2 Liquid - β transition

Similar to the $L - \alpha$ transition, the free energy of the β phase can be expressed as Equation 1 by replacing the coefficients a_2 , a_4 and a_6 with the b_2 , b_4 and b_6 , respectively. By the first order condition that

$$F_L = F_\beta \quad (11)$$

with the Equation 2, we get Equation 4 where the b 's coefficients are used. This can be solved for the order parameter η^2 as the ψ^2 (Equation 6) with the coefficients b_4 and b_6 . Similar to the expressions F_α (Equation 7) and the Equation 8 and Equation 9, η^2 can be obtained as ψ^2 (Equation 10) with the b 's coefficients.

2.3. $\alpha - \beta$ transition

For the solid-solid ($\alpha - \beta$) transition in the binary mixtures studied, the free energy can be expanded in terms of both the order parameters ψ and η of the crystalline phases α and β , respectively, with their quadratic coupling ($\psi^2\eta^2$) as

$$F_{\alpha-\beta} = a_2\psi^2 + a_4\psi^4 + a_6\psi^6 + b_2\eta^2 + b_4\eta^4 + b_6\eta^6 + c\psi^2\eta^2 \quad (12)$$

where c is the coupling constant between the two order parameters.

In our treatment, we consider the $\alpha - \beta$ transition as of a second order and on that basis, the phase line equation is obtained for the binary mixtures. Firstly, by minimising the free energy $F_{\alpha-\beta}$ with respect to ($\partial F_{\alpha-\beta}/\partial\psi = 0$) we get

$$a_2 + 2a_4\psi^2 + 3a_6\psi^4 + c\eta^2 = 0 \quad (13)$$

Secondly, by means of the minimisation ($\partial F_{\alpha-\beta}/\partial\eta = 0$) we find that

$$b_2 + 2b_4\eta^2 + 3b_6\eta^4 + c\psi^2 = 0 \quad (14)$$

We can either solve η^2 (Equation 13) or ψ^2 (Equation 14). Solving η^2 from Equation 13 gives

$$\eta^2 = -\frac{1}{c}(a_2 + 2a_4\psi^2 + 3a_6\psi^4) \quad (15)$$

or

$$\psi^2 = -\frac{1}{c}(b_2 + 2b_4\eta^2 + 3b_6\eta^4) \quad (16)$$

by solving ψ^2 from Equation 14. By substituting Equation 15 into Equation 16, one obtains

$$\psi^2 = -\frac{1}{c} \left\{ b_2 + 2b_4 \left(-\frac{1}{c} \right) (a_2 + 2a_4\psi^2 + 3a_6\psi^4) + 3b_6 \left(-\frac{1}{c} \right)^2 \left[(a_2 + 2a_4\psi^2 + 3a_6\psi^4)^2 \right] \right\} \quad (17)$$

By expanding the parenthesis and after some algebra, we find the expression as

$$A + B\psi^2 + C\psi^4 + D\psi^6 + E\psi^8 = 0 \quad (18)$$

where the parameters are defined as

$$A = \frac{a_2}{c^3} (2b_4c - 2b_2c^2 - 3a_2b_6)$$

$$B = \frac{a_4}{c^3} (4b_4c - 2b_2c^2 - 12a_2b_6 - c^3)$$

$$C = \frac{3}{c^3} (2a_6b_4c - a_6b_4c^2 - 4a_4^2b_6 - 6a_2a_6b_6)$$

$$D = -\frac{36a_4a_6b_6}{c^3} (1 + 3a_2)$$

$$E = -27a_6^2b_6/c^3 \quad (19)$$

For the second order $\alpha - \beta$ transition, we have a condition that the coefficient of the ψ^2 term should be equal to zero ($B = 0$). This gives that

$$c(4a_4b_4 - 2a_4b_2c - c^2) = 12a_2a_4b_6 \quad (20)$$

as the phase line equation for the $\alpha - \beta$ transition in the binary mixtures studied here.

For the solid-liquid equilibria of n-alkane mixtures by considering the solid-solid ($\alpha - \beta$) transition, the temperature dependence of the thermodynamic quantities such as the order parameter, susceptibility, heat capacity, entropy and enthalpy can be predicted from the Landau phenomenological model. Their critical behaviour including the free energy close to the solid-liquid equilibria in those binary mixtures can be described by associating with the critical exponents. For this purpose, we employ the extended mean field model [37] for the heat capacity, that was applied to the smectic A-smectic C (AC) transition in liquid crystals [38], as stated above.

2.4 Order parameter and susceptibility

Regarding the quadratic coupling ($\psi^2\eta^2$) between the order parameters ψ and η (Equation 12) for the $\alpha - \beta$ transition in the binary mixtures studied, Equation 15 and Equation 16 can be expressed in terms of the coefficients which depend on the temperature (T), pressure (P) and concentration (X). By substituting Equation 6 into Equation 15, one gets

$$\eta^2 = -\frac{1}{c} \left(a_2 - \frac{a_4^2}{4a_6} \right) \quad (21)$$

Similarly, $\eta^2 = -b_4/2b_6$ as ψ^2 Equation 6 can be substituted into Equation 16, which gives

$$\psi^2 = -\frac{1}{c} \left(b_2 - \frac{b_4^2}{4b_6} \right) \quad (22)$$

For the $\alpha - \beta$ transition, susceptibility of the order parameters ψ and η can also be obtained. Using the definition of the susceptibility of ψ , the inverse susceptibility can be obtained as

$$\chi_\psi^{-1} = \frac{\partial^2 F_{\alpha-\beta}}{\partial \psi^2} = 4a_4\psi + 12a_6\psi^3 \quad (23)$$

by means of Equation 13. Similarly, the inverse susceptibility

$$\chi_\eta^{-1} = \frac{\partial^2 F_{\alpha-\beta}}{\partial \eta^2} = 4b_4\eta + 12b_6\eta^3 \quad (24)$$

which can be obtained by using Equation 14, expresses in terms of the order parameter η (β phase) for the $\alpha - \beta$ transition in the binary mixtures considered. As a further step, Equation 22 can be substituted into Equation 23, which gives

$$\chi_{\psi}^{-1} = 4a_4 \left(-\frac{1}{c}\right)^{1/2} \left(b_2 - \frac{b_4^2}{4b_6}\right)^{1/2} - \frac{12a_6}{c^{3/2}} \left(b_2 - \frac{b_4^2}{4b_6}\right)^{3/2} \quad (25)$$

For the χ_{η}^{-1} , this time Equation 21 is substituted into Equation 24 from which we get

$$\chi_{\eta}^{-1} = 4b_4 \left(-\frac{1}{c}\right)^{1/2} \left(a_2 - \frac{a_4^2}{4a_6}\right)^{1/2} - \frac{12b_6}{c^{3/2}} \left(a_2 - \frac{a_4^2}{4a_6}\right)^{3/2} \quad (26)$$

2.5 Heat capacity, entropy, enthalpy and free energy

The temperature dependence of the heat capacity can be expressed as

$$C = C_0 + AT(T_c - T)^{-1/2} \quad (27)$$

on the basis of the extended mean field model [37] for the solid-liquid equilibria in n-alkanes. In Equation 27, the critical exponent $\phi = 1/2$ according to $C \propto (T - T_c)^{-\phi}$, where $(T - T_c)/T_c$ is the reduced temperature with the critical temperature T_c . Equation 27 describes the temperature dependence of the heat capacity in the vicinity of the critical temperature T_c as it was applied to the binary mixtures of liquid crystals [38] as stated above. Considering that, we also apply $C - T$ relation (Equation 27) to solid - solid and solid - liquid transitions of the binary mixtures of n-tridecane + (n-hexane and cyclohexane). For the solid - liquid equilibria of those mixtures, the critical temperature T_c is replaced by the melting temperature T_m on the assumption that the phase transition occurs in the vicinity of T_m . Thus, in our treatment the temperature dependence of the heat capacity C (Equation 27) refers to the solid - solid and solid - liquid transitions of the binary mixtures. In Equation 27, A is the amplitude. The parameter C_0 is nonsingular (background) heat capacity as the heat capacity C diverges with the critical exponent $-1/2$ in the vicinity of T_c (or T_m) according to Equation 27. From the definition $C/T = \partial S/\partial T$, the entropy can be written as

$$S = \partial F/\partial T = S_0 + A_0(T_m - T)^{1/2} \quad (28)$$

where S_0 is the entropy at the melting temperature ($T = T_m$) and $A_0 = -2A$.

This also gives the functional form of the free energy as

$$F = F_0 + a(T_m - T)^{\phi'} \quad (29)$$

or

$$\Delta F = F - F_0 = a(T_m - T)^{\phi'} \quad (30)$$

with the critical exponent $\phi' = 3/2$ and $a = 4A/3$, where F_0 is the free energy at the melting temperature ($T = T_m$) in the binary mixtures.

The temperature dependence of the enthalpy can be obtained from the heat capacity (Equation 27) using the definition $C = \partial H/\partial T$ as

$$H = H_0 + A_0 \left[T(T_m - T)^{1/2} + (2/3)(T_m - T)^{3/2} \right] \quad (31)$$

From the functional forms of C , S and H , which exhibit anomalous behaviour near the first order solid - liquid phase transition, discontinuities in the heat capacity (ΔC), entropy (ΔS) and enthalpy (ΔH) can also be extracted. The above relations confirm the following definitions:

$$\Delta C = \frac{\partial(\Delta H)}{\partial T} = AT(T_m - T)^{-1/2} \quad (32)$$

and

$$\frac{\Delta C}{T} = \frac{\partial(\Delta S)}{\partial T} = A(T_m - T)^{-1/2} \quad (33)$$

Regarding the Gibbs free energy $G(T, P)$, discontinuity ΔG becomes using the thermodynamic relation $\Delta G = \Delta H - T\Delta S$,

$$\Delta G = a(T_m - T)^{3/2} \quad (34)$$

where $a = 4A/3$ as before.

The temperature dependence of the order parameter ψ of the solid phase can also be deduced from the heat capacity (Equation 27) on the basis of the extended mean field model [37,38] according to the integral relation

$$\psi = \left[\int_T^{T_m} \left(\frac{C}{T} \right) dT \right]^{1/2} \quad (35)$$

By integrating C (Equation 27) in the solid phase ($T < T_m$), one gets

$$\psi = \psi_0(T_m - T)^\phi \quad (36)$$

with the critical exponent $\phi = 1/4$ and the amplitude $\psi_0 = (A)^{1/2}$.

3. Calculations and results

In this section, the phase line equations which we obtained for the $L - \alpha$, $L - \beta$ and $\alpha - \beta$ (at 0.1 MPa) transitions, were fitted to the experimental data for the $T - X$ phase diagrams, and the thermodynamic quantities of interest were predicted for the systems of n-tridecane (1) + n-hexadecane (2) and n-tridecane (1) + cyclohexane (2) at atmospheric and higher pressures. We also predicted $T - X$ phase diagrams for n-alkane (1) (n-hexadecane, n-octadecane and n-eicosane) + cyclohexane (2) at 300 MPa.

3.1 Liquid - α ($L - \alpha$) transition

We assume the temperature, concentration and pressure dependence of the coefficients a_2 , a_4 and a_6 (Equation 8) as

$$a_2 = a_{20}(T - T_\alpha) + a_{21}(P - P_\alpha) \quad (37)$$

where T_α represents liquidus for the α crystalline form and P_α the corresponding pressure. a_{20} and a_{21} are constants. We can also assume the concentration dependence of a_4 as

$$a_4 = a_{40} + a_{41}(x - x_\alpha) + a_{42}(x - x_\alpha)^2 \quad (38)$$

where x_α denotes the concentration of the first component (1) of the binary mixture in the α crystalline form. a_{40} , a_{41} and a_{42} with the $a_6 = a_{60}$ (Equation 8) are constants. By substituting Equation 37 and Equation 38 into the phase line equation (Equation 8), we then obtain after arranging the terms,

$$T - T_\alpha = a_0' + a_1'(x - x_\alpha) + a_2'(x - x_\alpha)^2 + a_3'(x - x_\alpha)^3 + a_4'(P - P_\alpha) \quad (39)$$

where

$$a_0' = -\frac{2a_{40}^2}{a_{20}a_{60}}, a_1' = -\frac{4a_{40}a_{41}}{a_{20}a_{60}}, a_2' = -\frac{2}{a_{20}a_{60}}(a_{41}^2 + 2a_{40}a_{42}), a_3' = -\frac{4a_{41}a_{42}}{a_{20}a_{60}}, a_4' = -a_{21}/a_{20} \quad (40)$$

Equation 39 was fitted to the experimental data [11] for the $L - \alpha$ transition in the binary mixture of n-tridecane (1) + n-hexane (2) system at $P = P_\alpha = 0.1$ MPa, as plotted in Figure 1. The coefficients a_0' , a_1' , a_2' and a_3' were determined as given in Table 1.

3.2 Liquid - β ($L - \beta$) transition

As we assumed the dependences of the coefficients for the $L - \alpha$ transition (Equation 37 and Equation 38), we can also assume the coefficients b_2 , b_4 and b_6 in the same form where a_{20} , a_{21} with the T_α , P_α are replaced by b_{20} , b_{21} with the T_β , P_β , respectively. T_β is the liquidus for the β crystalline form and P_β is the corresponding pressure. b_{20} and b_{21} are constants. Similarly, the coefficient b_4 can depend on the concentration in the same form as a_4 (Equation 38) where a_{40} , a_{41} , a_{42} with the x_α are replaced by b_{40} , b_{41} , b_{42} with the x_β , respectively. The coefficient x_β is the concentration of the first component (1) of the binary mixture in the β crystalline form. b_{40} , b_{41} and b_{42} are also constants ($b_6 = b_{60} = \text{constant}$). As we considered for the $L - \alpha$ transition, Equation 37 and Equation 38 with the coefficients b_2 , b_4 and b_6 can be substituted into the phase line equation (Equation 8) we get Equation 39 with the replacements b_0' , b_1' , b_2' , b_3' , b_4' . Equation 39 with those replacements was then fitted to the experimental data [11] for the solid + liquid ($L - \beta$) equilibria of n-tridecane (1)

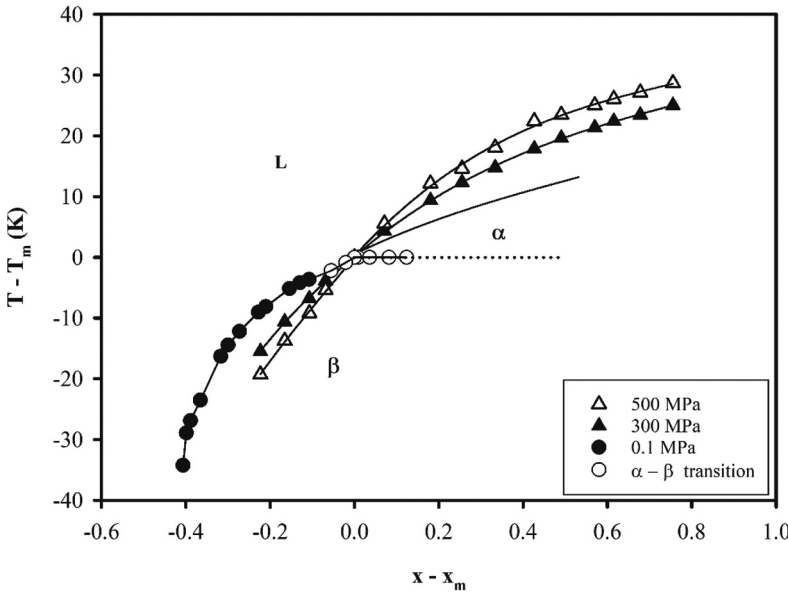


Figure 1. $T - X$ phase diagram calculated for the transitions of $\alpha - L$ and $\beta - L$ (eq. 39) at the pressures of 0.1, 300 and 500 MPa for the mixtures of n-tridecane (1) + n-hexane (2) using the experimental data [11]. For the $\alpha - \beta$ transition at 0.1 MPa, eq. (41) was fitted to the experimental data [11] along the dotted line (open circles) and additional data along the $\beta - L$ phase line (closed circles) for this mixture. T_m and x_m denote the melting temperature and concentration, respectively. For the $\alpha - \beta$ transition, transition temperature and concentration are T_t and x_t , respectively. The dotted line for the $\alpha - \beta$ transition is also indicated [11].

Table 1. Values of the coefficients for the $\alpha - L$ and $\beta - L$ transitions according to Equation 39 at $P = P_\alpha$ and the replacement of coefficients b 's at $P = P_\beta$, for the mixtures of n-tridecane (1) + n-hexane (2) at constant pressures of 0.1, 300 and 500 MPa with the melting temperatures (T_m) and concentrations (x_m). For the 0.1 MPa, (T_α, x_α) and (T_β, x_β) indicate the transition temperature and concentration for the α and β phases, respectively.

n-tridecane (1) + n-hexane (2)	α - phase	$\alpha - L$	β - phase	$\beta - L$
		$\left(\begin{array}{l} x > x_m \\ T > T_m \end{array} \right)$		$\left(\begin{array}{l} x < x_m \\ T < T_m \end{array} \right)$
0.1 MPa	a_0'	0.5602	b_0'	0.2054
$x_\alpha = 0.4685$	a_1'	33.3734	b_1'	56.0889
$T_\alpha = 255.18$ K	a_2'	-26.3658	b_2'	246.6010
$x_\beta = 0.4328$	a_3'	15.6869	b_3'	745.7749
$T_\beta = 253.11$ K				
300 MPa	a_0'	0.1531	b_0'	0.0271
$x_m = 0.2446$	a_1'	59.3037	b_1'	55.4300
$T_m = 292.96$ K	a_2'	-50.5350	b_2'	-47.8548
	a_3'	20.7005	b_3'	67.0293
500 MPa	a_0'	0.2126	b_0'	0.0369
$x_m = 0.2446$	a_1'	76.1465	b_1'	83.3366
$T_m = 315.39$ K	a_2'	-73.6111	b_2'	15.0335
	a_3'	29.8286	b_3'	132.2664

+ n-hexane (2) system at $P = P_\beta = 0.1$ MPa as plotted with the solid-liquid ($L - \alpha$) equilibria in Figure 1. The coefficients b_0' , b_1' , b_2' and b_3' , which we determined from this fit, are given in Table 1.

3.3 $\alpha - \beta$ transition

For the solid - solid ($\alpha - \beta$) transition, we obtained the phase line equation (Equation 20) where we substituted the dependences of the coefficients a_2 (Equation 37), a_4 (Equation 38), b_2 and b_4 with the coupling constant c and $b_6 = b_{60}$. By arranging terms and neglecting all the cross terms such as $(x - x_t)(T - T_t)$ with the fourth order term of $(x - x_t)^4$ in the expansion, we arrived at the phase line equation

$$T - T_t = c_0' + c_1'(x - x_t) + c_2'(x - x_t)^2 + c_3'(x - x_t)^3 + c_4'(P - P_t) \quad (41)$$

where

$$\begin{aligned} c_0 &= 6a_{20}a_{60} + b_{20}c, c_0' = \frac{c}{2a_{40}c_0} (4a_{40}b_{40} - c^2), c_1' = \frac{2c}{a_{40}c_0} (a_{40}b_{41} + a_{41}b_{40}), c_2' \\ &= \frac{2c}{a_{40}c_0} (a_{40}b_{42} + a_{41}b_{41} + a_{42}b_{40}), c_3' = \frac{2c}{a_{40}c_0} (a_{41}b_{42} + a_{42}b_{41}), c_4' = -\frac{1}{c_0} (b_{21}c + 6a_{21}a_{60}) \end{aligned} \quad (42)$$

In Equation 41, T_t , x_t and P_t represent the transition temperature, concentration and pressure, respectively, for the $\alpha - \beta$ transition.

At the transition pressure, $P = P_t = 0.1$ MPa, Equation 41 was fitted to the data for the $\alpha - \beta$ transition for the binary mixtures of n-tridecane (1)+n-hexane (2) system. Figure 1 gives in our $T - X$ plot the $\alpha - \beta$ transition with the dotted line, as also given previously [11] for this binary mixture at $P = 0.1$ MPa. The coefficients determined are given in Table 2.

For the solid-liquid transition in those binary mixtures, Equation 39 was fitted to the experimental data [11] at the pressures of $P = 300$ and 500 MPa. Figure 1 gives our $T - X$ plots for those transitions. The coefficients of Equation 39, which were determined by means of those fittings, are tabulated in Table 1.

Table 2. Values of the coefficients for the $\alpha - \beta$ transition according to Equation 41 for the mixtures indicated at $P = 0.1$ MPa with the transition temperatures (T_t) and concentrations (x_t).

0.1 MPa	Equation 41 (K)	n-tridecane (1) + n-hexane (2) ($x_t = 0.4328, T_t = 253.11$ K)	n-tridecane (1) + cyclohexane (2) ($x_t = 0.1418, T_t = 241.71$ K)
$\alpha - \beta$ transition	c_0'	-0.9591	-0.1402
	c_1'	11.86	11.70
	c_2'	-21.30	-90.94
	c_3'	328.00	64.47

We also calculated the $T - X$ phase diagram of n-tridecane (1) + cyclohexane (2) system at different pressures of 0.1, 200, 300 and 400 MPa as we performed for n-tridecane (1) + n-hexane (2) system (Figure 1) by using the experimental data [11]. For the atmospheric pressure (0.1 MPa), we were able to study the solid-solid ($\alpha - \beta$) transition for the mixture of n-tridecane (1) + cyclohexane (2) as we also studied for n-tridecane (1) + n-hexane (2) system (Figure 1). By fitting Equation 39 to the experimental data [11] for the α -liquid and β -liquid transitions, respectively, the coefficients were determined (Table 3). This is plotted in Figure 2. Similarly, by Equation 41, the phase line for the solid - solid ($\alpha - \beta$) transition was determined with the coefficients (Table 2) at $p = 0.1$ MPa, as plotted in Figure 2. For the higher pressures of 200, 300 and 400 MPa, Equation 39 was fitted to the experimental data [11] to obtain the phase lines for the solid-liquid transition in the mixture of n-tridecane (1) + cyclohexane (2), as also plotted in Figure 3. Coefficients determined are given in Table 3.

3.4 Calculation of the order parameter

The order parameters ψ and η of the solid phases α and β , respectively, can be calculated at various temperatures, as an example, we calculated the order parameter ψ of the α phase at the pressures of 0.1, 300 and 500 MPa of the n-tridecane (1) + n-hexane (2). Using the expressions of a_2 (Equation 37) and a_4 (Equation 38) in the order parameter η , or b_2 and b_4 in the order parameter ψ (Equation 22) for the $\alpha - \beta$ transition (0.1 MPa), we calculated ψ as a function of the temperature. This was done by means of the expression,

$$\psi^2 = -\frac{1}{c} \left[b_{20}(T - T_\beta) + b_{21}(P - P_\beta) - \frac{b_{40}^2}{4b_{60}} \right] \quad (43)$$

Table 3. Values of the coefficients for the $\alpha - L$ and $\beta - L$ transitions according to Equation 39 at $P = P_\alpha$ and at $P = P_\beta$ ($b_2' = 0$ and $b_3' = 0$), respectively, for the mixtures of n-tridecane (1) + cyclohexane (2) at constant pressures of 200, 300 and 400 MPa with the melting temperatures (T_m) and concentrations (x_m).

n-tridecane (1) + cyclohexane (2)	Equation 39 (K)	$\alpha - L$	Equation 39 (K)	$\beta - L$
		$\left(\begin{matrix} x > x_m \\ T > T_m \end{matrix} \right)$		$\left(\begin{matrix} x < x_m \\ T < T_m \end{matrix} \right)$
200 MPa $x_m = 0.1952$ $T_m = 277.27$ K	a_0'	-0.2786	b_0'	-2.690
	a_1'	42.28	b_1'	-519.1
	a_2'	-26.79		
	a_3'	19.27		
	300 MPa $x_m = 0.1970$ $T_m = 290.86$ K	a_0'	-0.2987	b_0'
a_1'		27.75	b_1'	-676.9
a_2'		29.98		
a_3'		-27.53		
400 MPa $x_m = 0.1978$ $T_m = 304.10$ K		a_0'	-0.5991	b_0'
	a_1'	22.56	b_1'	-1.001×10^3
	a_2'	47.41		
	a_3'	-39.15		

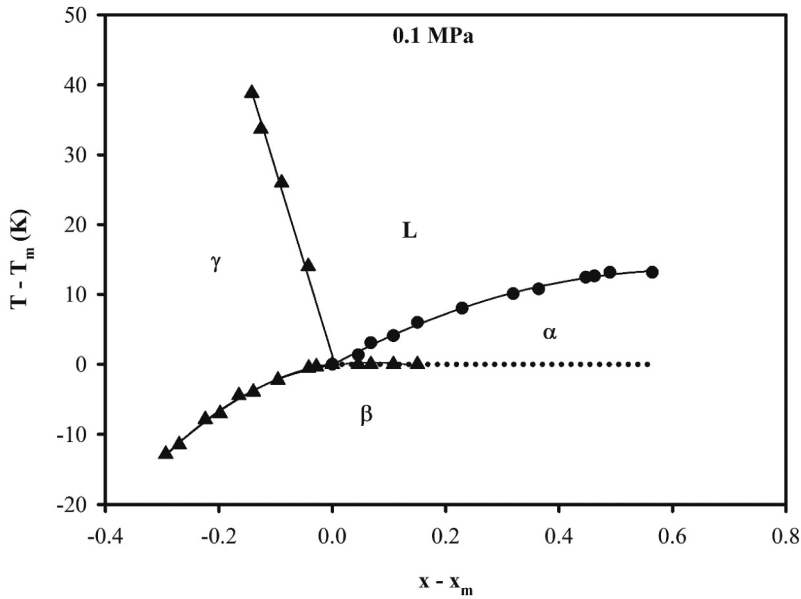


Figure 2. $T - X$ phase diagram calculated for the transitions of $\alpha - L$, $\gamma - L$ (eq. 39), $\beta - \gamma$ and $\alpha - \beta$ (eq. 41) at the pressure of $P = 0.1$ MPa for the mixtures of n-tridecane (1) + cyclohexane (2) using the experimental data [11]. For the $\alpha - \beta$ transition at 0.1 MPa, eq. (41) was fitted to the experimental data [11] along the dotted line and additional data [11] along the $\gamma - \beta$ transition line (solid triangles) for this mixture. T_m and x_m denote the melting temperature and concentration, respectively. For the $\alpha - \beta$ transition, transition temperature and concentration are T_t and x_t , respectively. The dotted line for the $\alpha - \beta$ transition is also indicated [11].

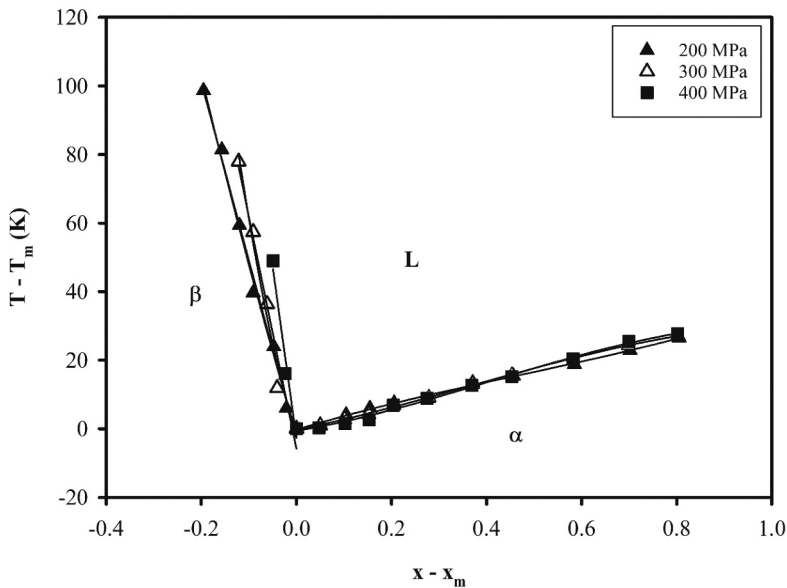


Figure 3. $T - X$ phase diagram calculated for the transitions of $\alpha - L$ (eq. 39) and $\beta - L$ (eq. 39) at the pressures of 200, 300 and 400 MPa for the mixtures of n-tridecane (1) + cyclohexane (2) using the experimental data [11]. T_m and x_m denote the melting temperature and concentration, respectively.

at the melting mole fraction $x = x_m$. At the melting pressure ($P = P_m$), the temperature dependence of the order parameter ψ can be written as

$$\psi^2 = B_0 + B_1(T - T_\beta) \quad (44)$$

where

$$B_0 = b_{40}^2/4a_{60}c, B_1 = -b_{20}/c \quad (45)$$

This can be written for the order parameter η of the β phase similar to the Equation 43 by replacing the b 's coefficients by a 's coefficients. The temperature dependence of ψ (or η) can be, as a general power-law formula, written as

$$\psi \sim |T - T_t|^{1/2} \quad (46)$$

with the transition temperature T_t ($\alpha - \beta$ transition) in the mean field approximation. At higher pressures, by substituting a_2 (Equation 37), a_4 (Equation 38) into Equation 1 and also b_2, b_4 which reduces to Equation 46 with the replacement of T_t by the melting temperature T_m for the transitions of $\alpha - L$ and $\beta - L$ in the binary mixtures of n-tridecane (1) + n-hexane (2). We plot in Figure 4 the order parameter ψ (normalized) as a function of the temperature at the pressures of 0.1, 300 and 500 MPa for $T < T_m$ (Figure 4a) and $T > T_m$ (Figure 4b) for the n-tridecane (1) + n-hexane (2). Similar treatment was conducted at the pressures of 0.1 (Figure 5a) and, 200, 300 and 400 MPa (Figure 5b) for n-tridecane (1) + cyclohexane (2) according to Equation 46, where T_t is the transition between $\alpha - \beta, \beta - \gamma$ and $\alpha - \gamma$ (solid phases) with the replacement of T_m ($\alpha - L$ transition).

In the following, we calculated the temperature dependence of the susceptibility, heat capacity, entropy, enthalpy and the free energy for the mixtures of n-tridecane (1) + n-hexane (2) and n-tridecane (1) + cyclohexane (2) systems at 0.1 MPa (atmospheric pressure) and at higher pressures.

3.5 Calculation of the susceptibility

Temperature dependence of the susceptibility (χ_ψ) can also be predicted by means of Equation 37 and Equation 38 according to Equation 23 in the binary mixtures. In order to simplify the expression for the inverse susceptibility, a non-divergent term to the power 3/2 was ignored. This gives at constant concentration ($x = x_m$) and pressure ($P = P_m$),

$$\chi_\psi^{-1} = C_0 [b_0' + b_1'(T - T_m)]^{1/2} \quad (47)$$

where the parameters are defined as

$$b_0' = -b_{40}^2/4b_{60}, b_1' = b_{20}, C_0 = 4a_{40}(-1/c)^{1/2} \quad (48)$$

As we predicted the temperature dependence of the order parameter (ψ), the inverse susceptibility was also predicted at the pressures of 0.1, 300 and 500 MPa for the binary mixtures of n-tridecane (1) + n-hexane (2) according to Equation 47. χ_ψ^{-1} is plotted as a function of temperature for this mixture in Figure 6a. For the mixture of n-tridecane (1) + cyclohexane (2), our predicted inverse susceptibility (Equation 47) at the pressures of 0.1, 200, 300 and 500 MPa is also plotted in Figure 7. For both figures (Figures 6 and 7), normalized inverse susceptibility, $[(\chi^{-1}/C_0)^2 - b_0']/b_1'$, is plotted as a function of temperature.

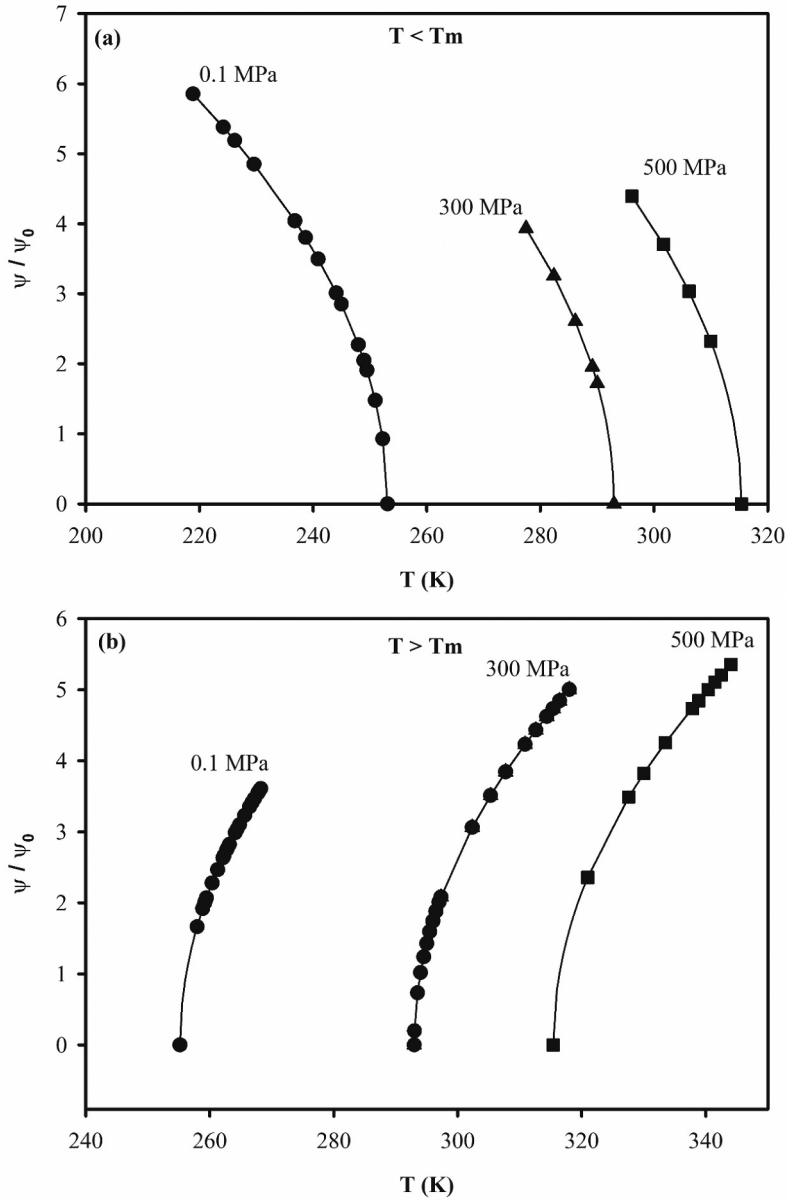


Figure 4. Variation of the order parameter ψ (normalized) with the temperature above and below T_m at the pressures of 0.1, 300 and 500 MPa according to eq. (44) for the mixture of n-tridecane (1) + n-hexane (2). T_m represents the melting temperature for the $\alpha - L$ and $\beta - L$ transitions. For 0.1 MPa, the transition temperature between the phases α and β is T_r .

3.6 Calculation of the heat capacity, entropy, enthalpy and free energy

The heat capacity was calculated as a function of temperature according to Equation 27 from the extended mean field model [37] for the $\alpha - \beta$ transition in the systems of n-tridecane (1) + n-hexane (2) and n-tridecane (1) + cyclohexane (2) at $P = 0.1$ MPa, as plotted in Figures 8 and 9, respectively, within the temperature intervals of the α and β phases as indicated experimentally [11]. Calculation of the heat capacity for the liquid - solid transition was also performed at higher pressures of 300 and 500 MPa for n-tridecane (1) + n-hexane (2) (Figure 8) and at the pressures of

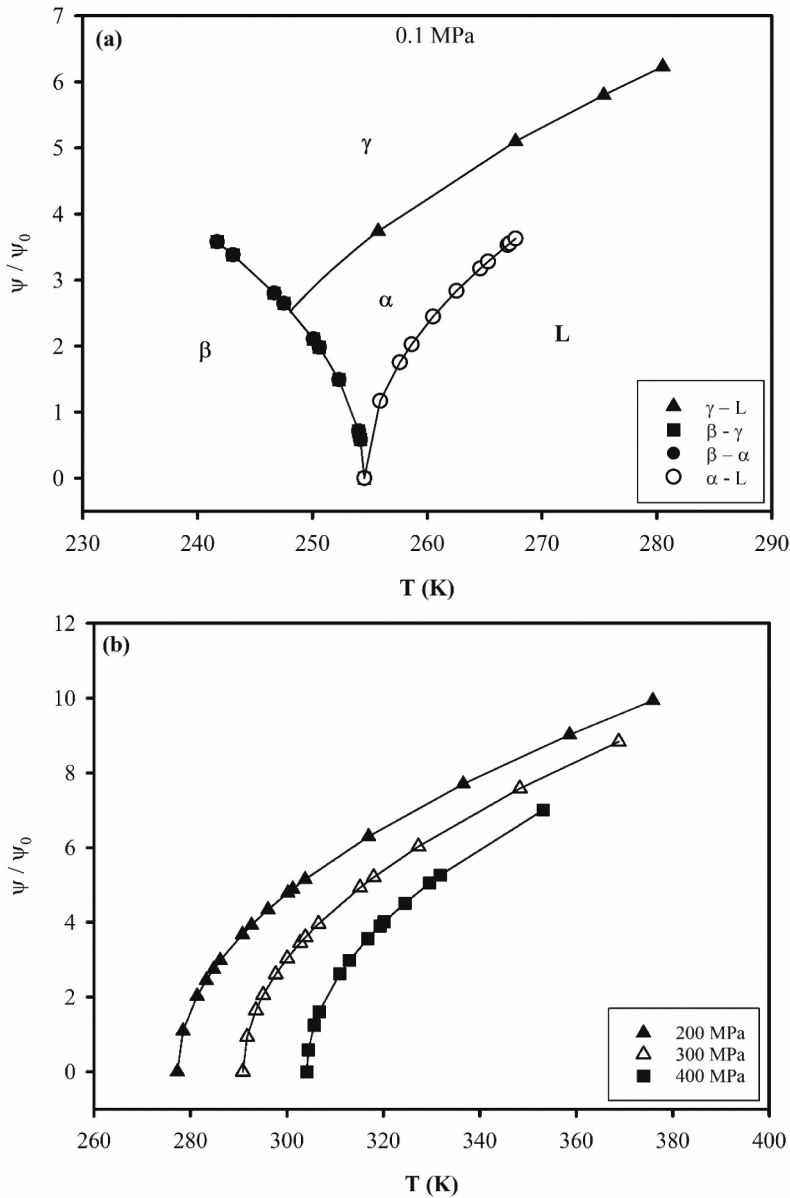


Figure 5. Variation of the order parameter ψ (normalized) with the temperature above and below T_m at the pressures of 0.1, 200, 300 and 400 MPa according to eq. (44) for the mixture of n-tridecane (1) + cyclohexane (2).

200, 300 and 400 MPa for n-tridecane (1) + cyclohexane (2) (Figure 9) using the temperature intervals of the experimental data [11]. Note that we also indicated the solid phases (α , β , γ) and the liquid phase (L) at 0.1 MPa (Figure 9) for the binary mixtures of n-tridecane (1) + cyclohexane (2) as we indicated for the $T - X$ phase diagram (Figure 2).

Since we obtained the temperature dependence of the entropy (Equation 28) from the heat capacity on the basis of the extended mean field model [37], it was predicted for the $\alpha - \beta$ transition at 0.1 MPa and the solid - liquid transition for the n-tridecane (1) + n-hexane (2) (300 and 500 MPa) and for the n-tridecane (1) + cyclohexane (2) (200, 300 and 400 MPa). We plot the temperature dependence of the entropy in Figures 10 and 11 for the mixtures of n-tridecane (1) + n-hexane (2) and n-tridecane (1) + cyclohexane (2), respectively. Note that in Figure 11 (a), we indicated the

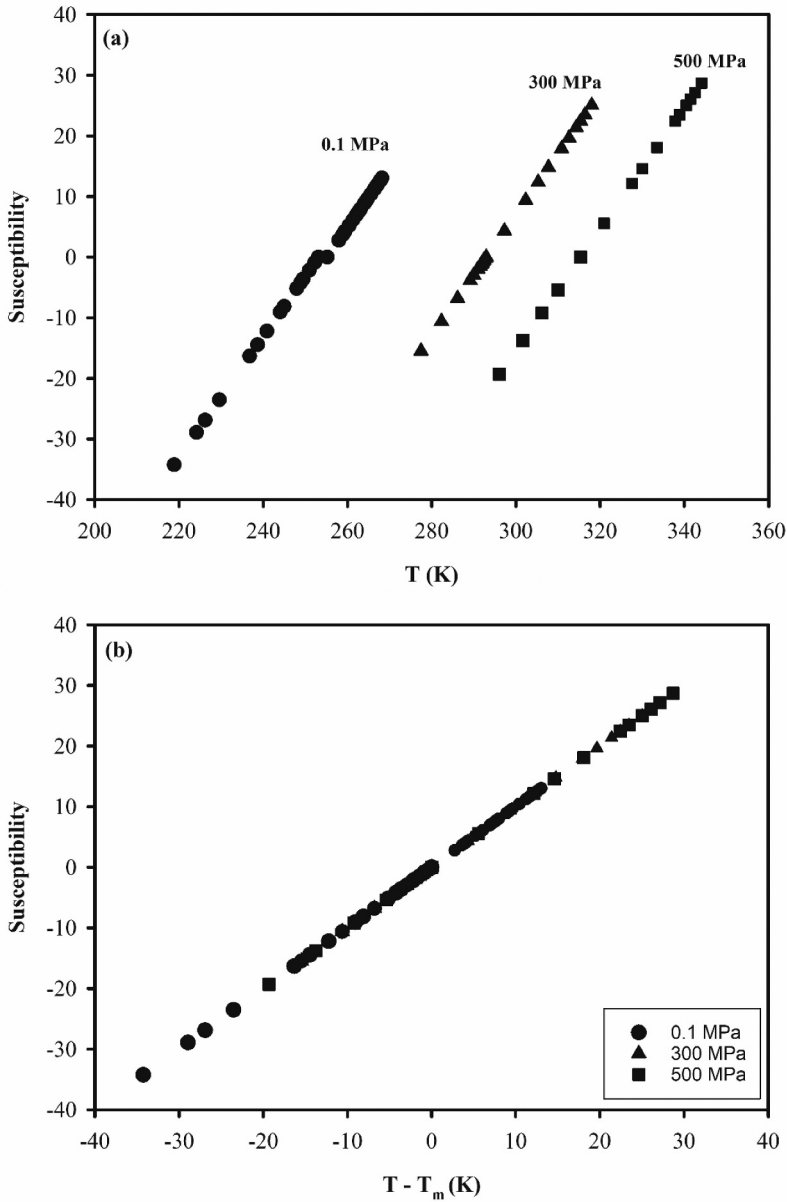


Figure 6. Variation of the inverse susceptibility with the temperature at the pressures of 0.1, 300 and 500 MPa according to eq. (47) for the mixtures of n-tridecane (1) + n-hexane (2) for both above and below the melting temperature (T_m).

solid phases of α , β and γ with the liquid (L) phase for n-tridecane (1) + cyclohexane (2) at 0.1 MPa. For this mixture, the prediction of the entropy S was performed for both regions ($T < T_m$ and $T > T_m$) at the pressures of 200, 300 and 400 MPa by using the absolute value of $|T - T_m|^{1/2}$ according to Equation 28, as for the order parameter ψ (Equation 46).

Similarly, enthalpy was predicted (Equation 31) as a function of temperature for both transitions, $\alpha - \beta$ ($P = 0.1$ MPa) and solid - liquid transition at higher pressures as indicated for the mixtures of n-tridecane (1) + n-hexane (2) and tridecane (1) + cyclohexane (2), as plotted respectively, in Figures 12 and 13. As given in Figure 12, the enthalpy H was predicted at the pressures of 0.1, 300 and 500 MPa, as before for the n-tridecane (1) + n-hexane (2). For the

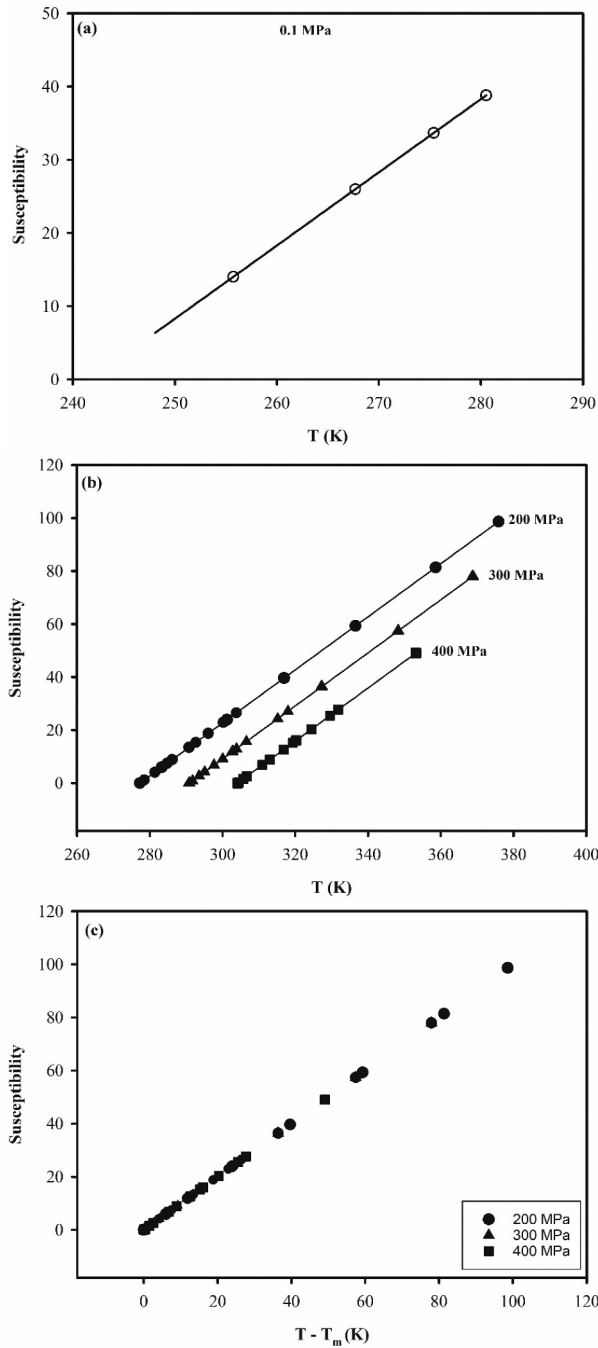


Figure 7. Variation of the inverse susceptibility with the temperature at the pressures of 200, 300 and 400 MPa according to eq. (47) for the mixtures of n-tridecane (1) + cyclohexane (2) for both above and below the melting temperature (T_m).

n-tridecane (1) + cyclohexane (2), the enthalpy H was also predicted at the pressures of 200, 300 and 400 MPa above and below T_m according to $|T - T_m|^{1/2}$ (Equation 31) with the solid phases α, β, γ and the liquid phase L at 0.1 MPa (Figure 13). Also, the Helmholtz free energy F (Equation 29) and the Gibbs free energy G (Equation 34) were predicted for both transitions as

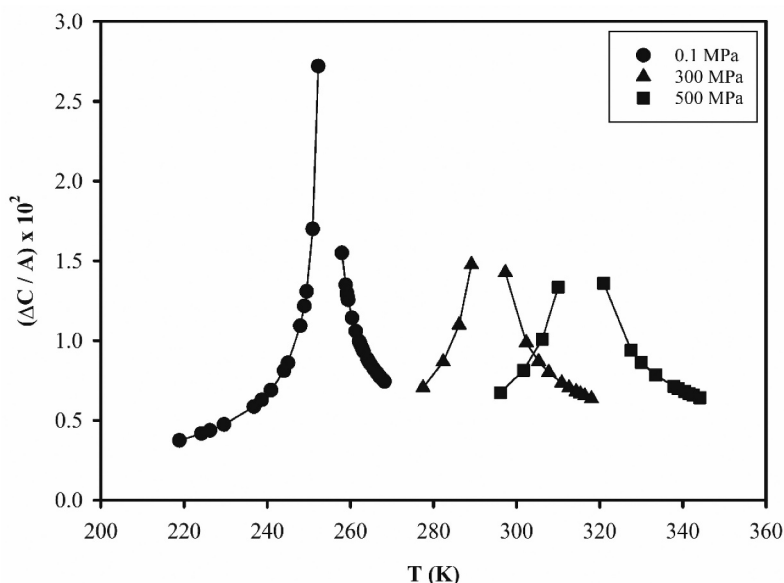


Figure 8. Variation of the heat capacity (normalized) with the temperature at the pressures of 0.1, 300 and 500 MPa according to eq. (27) for the mixture of n-tridecane (1) + n-hexane (2). For 0.1 MPa, the transition temperature between the phases α and β is T_t .

in the prediction of the heat capacity, entropy and enthalpy for the mixtures studied here. Plots are given for the F and G (Figures 14 and 15) for the n-tridecane + n-hexane (2) and n-tridecane (1) + cyclohexane (2), respectively.

4. Discussion

$T - X$ phase diagrams were calculated for the transition of the solid (α and β phases) – liquid (at 0.1 MPa and higher pressures) and the $\alpha - \beta$ transition (at 0.1 MPa) for the binary mixtures of n-tridecane (1) + n-hexane (2) (Figure 1) and n-tridecane (1) + cyclohexane (2) (Figures 2 and 3). As seen from those figures, our fits are reasonably good. This shows that Equation 37 describes adequately the observed behavior of the liquid - α (solid) and liquid - β (solid) transitions, respectively. As we see from those figures (Figures 1–3) solid – liquid equilibrium curves depend on the pressure and they shift to higher temperatures with the increasing pressure, as observed experimentally [11].

As we considered above, the coefficients a_2 , a_4 and a_6 in the free energy expansion (Equation 1) can depend on the temperature, pressure and concentration in general. For simplicity, we assumed the temperature and pressure dependence of a_2 (Equation 37), concentration dependence of a_4 (Equation 38) and a_6 as constants according to the phase line equation (Equation 8). With the linear dependence of a_2 (Equation 37) and the quadratic dependence of a_4 (Equation 38), we neglected the fourth power of the concentration dependence in Equation 8 in order to get Equation 39 as simple as possible, which was fitted to the experimental data [11] without using adjustable parameters for our analysis. In the case that all the coefficients (a_2 , a_4 and a_6) were dependent on the temperature, pressure and concentration in general according to the phase line equation (Equation 8), Equation 39 would carry a number of adjustable parameters due to the terms such as $(T - T_\alpha)(P - P_\alpha)$, $(T - T_\alpha)(x - x_\alpha)$, $(P - P_\alpha)(x - x_\alpha)$ although at constant pressures ($P = P_\alpha$) some of those terms disappear. As a result of this, for the $T - X$ phase diagrams at constant pressures (Figures 1–3), analysis of the experimental data would be based on all those adjustable parameters in the binary

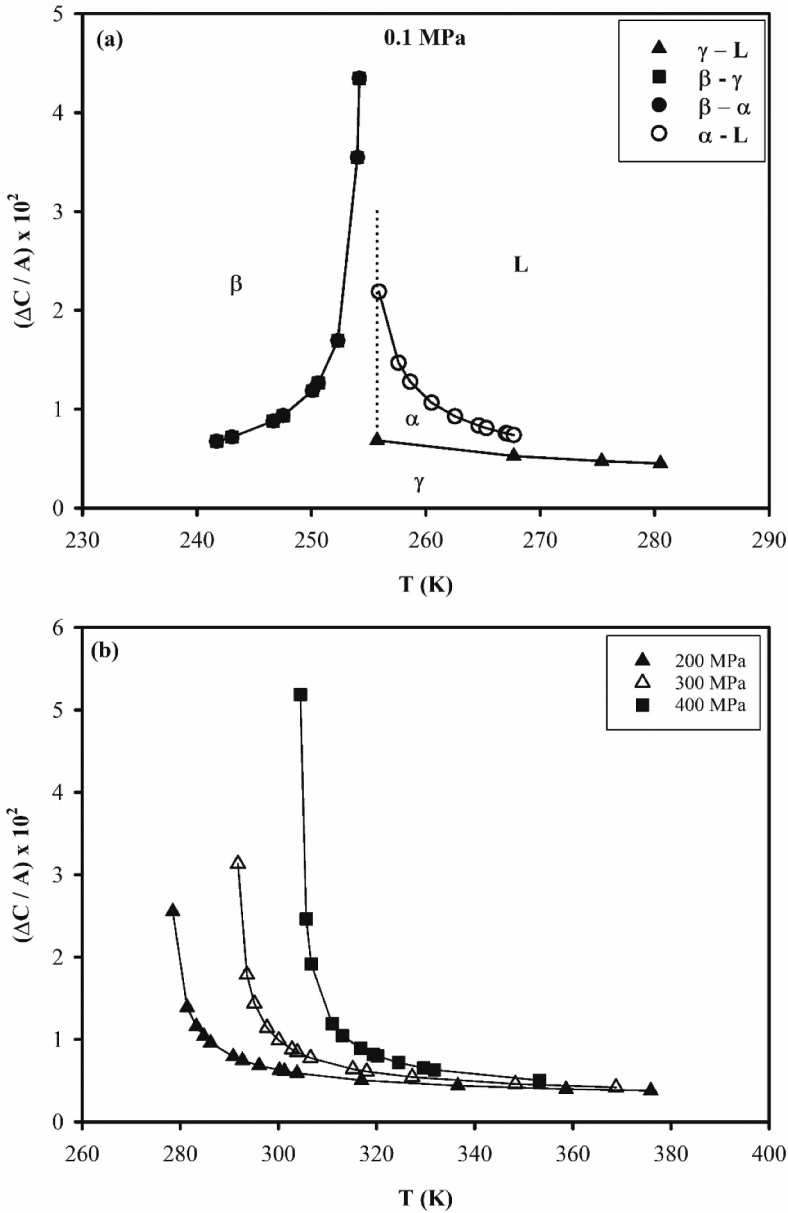


Figure 9. Variation of the heat capacity (normalized) with the temperature at the pressures of 0.1 (a), 200, 300 and 400 MPa (b) according to eq. (27) for the mixture of n-tridecane (1) + cyclohexane (2). For 0.1 MPa, the transition temperature between the phases α and β is T_i .

mixtures studied. Consequently, this would result in the thermodynamic properties expressed in the complicated forms, as predicted at various temperatures (at constant pressures) for the binary mixtures of n-tridecane (1) + n-hexane (2) and n-tridecane (1) + cyclohexane (2) (Figures 4–15). This however causes some difficulties in analyzing the experimental data. In the fitting procedure, the fitting parameters according to Equation 39, are only a_0' , a_1' , a_2' , a_3' and a_4' . The parameters T_α , x_α and P_α are fixed, which denote the liquidus temperature, concentration of the first component (1) of the binary mixture and the liquidus pressure, respectively, of the α phase, as defined earlier. Their values at constant pressures for the phases of α and β are given in Tables (1–4), as stated above. On the basis of constant values of T_α , x_α and P_α with the fitting parameters, namely, a_0' , a_1' ,

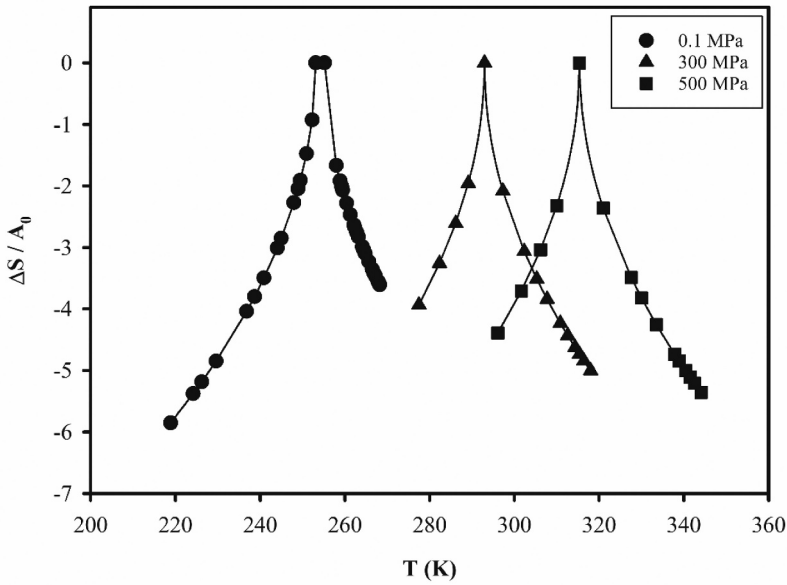


Figure 10. Variation of the entropy (normalized) with the temperature at the pressures of 0.1 (a), 300 and 500 MPa (b) according to eq. (28) for the mixture of n-tridecane (1) + n-hexane (2). For 0.1 MPa, the transition temperature between the phases α and β is T_t .

a_2', a_3', a_4' (Equation 39) of the α phase ($\alpha - L$ transition), $b_0', b_1', b_2', b_3', b_4'$ of the β phase ($\beta - L$ transition) and, $c_0', c_1', c_2', c_3', c_4'$ (Equation 41) for the $\alpha - \beta$ transition, the thermodynamic properties were subsequently predicted.

In our treatment, we considered nonlinear dependence on concentration of the free energy coefficients a_4 and b_4 (Equation 38). Nonlinear dependence on concentration was also considered for the calculation of $T - X$ phase diagrams of binary eutectic mixtures with a coupling between order parameters in a liquid – solid transition [40]. On that basis, the solid – solid ($\alpha - \beta$) transition was predicted for those mixtures at $P = 0.1$ MPa, which can be compared with the experimental measurements.

The $T - X$ phase diagram contains two solid crystalline (α and β) phases limited by the solidus and solvus curves emerging at the eutectic isotherm $T = T_E$ (minimum temperature) with the two phase regions of $\alpha + L$, $\beta + L$ and $\alpha + \beta$ [40]. This is similar structure of the binary mixtures of n-tridecane (1) + n-hexane (2) and n-tridecane (1) + cyclohexane (2) with the additional γ phase as studied here, regarding their $T - X$ phase diagrams at 0.1 MPa, as given in Figures 1–3.

Temperature dependence of the order parameter ψ (Equation 43) was predicted for the α and β phases to describe the $\alpha - \beta$ transition at 0.1 MPa and also transitions of α -liquid and β -liquid in the mixtures studied at higher pressures (Figures 4 and 5). As shown in the figures, the order parameter ψ exhibits a continuous decrease for the $\alpha - \beta$ transition (at 0.1 MPa), whereas this decrease turns out to be more discontinuous at higher pressures for the liquid – solid ($\alpha - L$ and $\beta - L$) transition as the TCP temperature (T_1) is approached for those binary mixtures studied. This is a similar behaviour as reported previously that based on the Landau mean-field theory, the ambient pressure increase can cause a first order ($R_I - R_V$) transition to turn to the second order passing through a tricritical (TCP) point [36,41]. Our results also indicate that the $\alpha - \beta$ transition occurring at atmospheric pressure can be considered as the tricritical transition since both the continuous (second order) and discontinuous (first order) transitions take place. As the pressure increases, discontinuity (first order) is more dominant that occurs for the liquid – solid ($\alpha - L$ and $\beta - L$) transition in those binary mixtures (Figures 4 and 5).

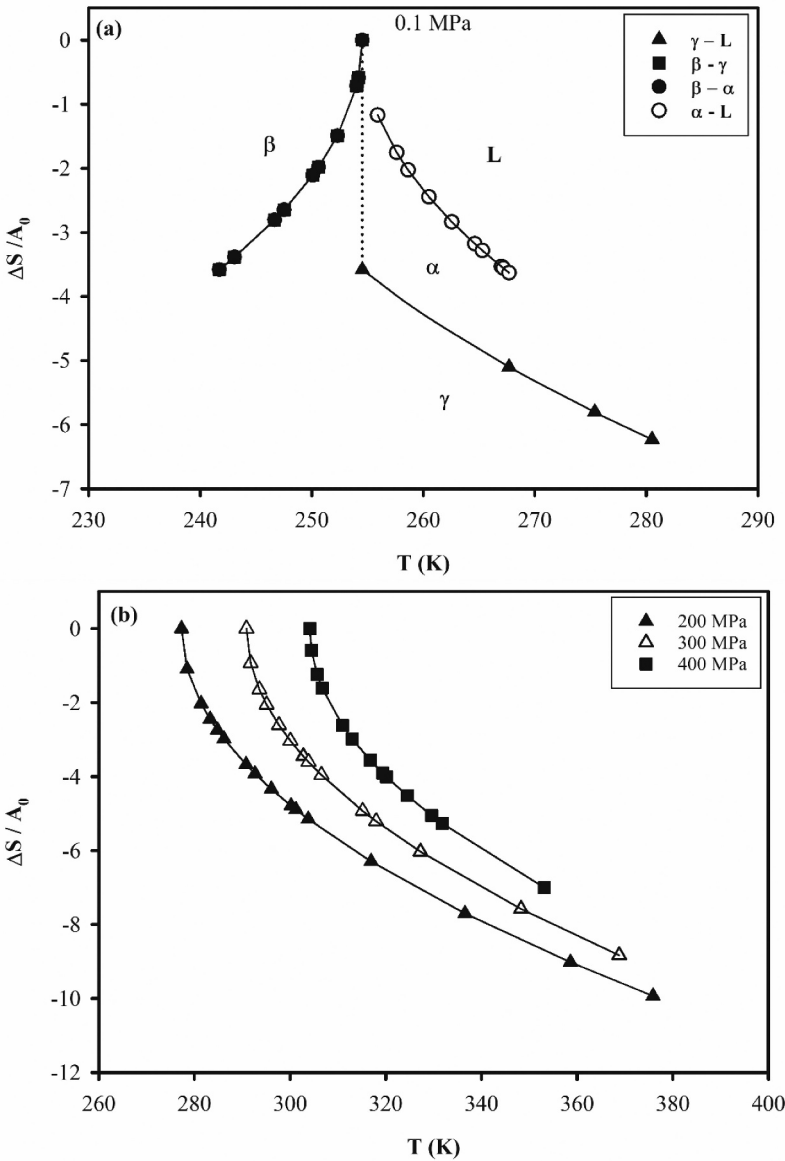


Figure 11. Variation of the entropy (normalized) with the temperature at the pressures of 0.1 (a), 200, 300 and 400 MPa (b) according to eq. (28) for the mixture of n-tridecane (1) + cyclohexane (2). For 0.1 MPa, the transition temperature between the phases α and β is T_i .

It can be argued that the order parameter (ψ or η) varies with the temperature according to the power-law formula (Equation 36) with the critical exponent $\phi = 1/4$ on the basis of the extended mean field model [37] at the pressures for the binary mixtures studied here. In fact, this is the tricritical exponent value for the order parameter [42,43], which can be considered for the solid – solid ($\alpha - \beta$) transition at the atmospheric pressure (0.1 MPa) as we studied for those binary mixtures. From this point of view, we can suggest that the temperature dependence of the order parameter (ψ or η) is described by Equation 46 with the critical exponent 1/2 for the binary mixtures studied at higher pressures. On that basis, variation of the order parameter with the temperature can be tested by the experimental measurements at atmospheric and higher pressures

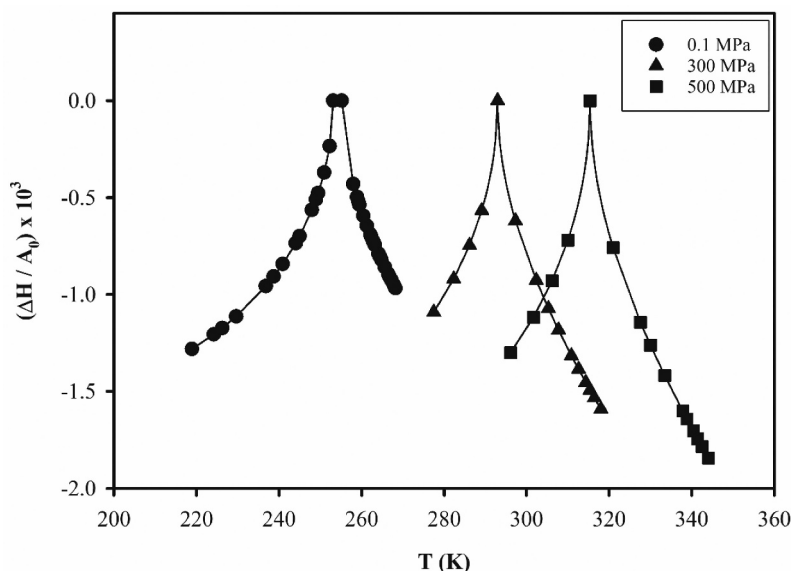


Figure 12. Variation of the enthalpy (normalized) with the temperature at the pressures of 0.1, 300 and 500 MPa according to eq. (31) for the mixture of n-tridecane (1) + n-hexane (2). For 0.1 MPa, the transition temperature between the phases α and β is T_c .

for those binary mixtures studied, whether Equation 46 with the critical exponent $1/2$ or Equation 36 with the exponent value of $1/4$, holds for the liquid – solid and solid – solid transitions.

Regarding the susceptibility (χ_ψ) of the order parameter, which was predicted (Equation 47) for the $\alpha - \beta$ transition (at 0.1 MPa) for the binary mixtures studied (Figures 6 and 7), we find that the inverse susceptibility increases linearly with the temperature toward the tricritical point, as expected from the mean field model employed in this study. Similar behavior can be obtained for the $\alpha - L$ and $\beta - L$ transitions for those binary mixtures at high pressures. This confirms that the critical exponent $\gamma = 1$ for the susceptibility according to the power-law formula, $\chi \sim^{-\gamma}$ where $\tau = (T - T_c)/T_c$ is the reduced temperature with the critical temperature T_c , as expected from the mean field model.

Predictions of the thermodynamic quantities of the heat capacity (C), entropy (S), enthalpy (H) and the free energy (F and G), were also studied for the binary mixtures within the framework of the Landau mean field model, as stated above. Heat capacity which was obtained at atmospheric (0.1 MPa) and higher pressures for those binary mixtures considered according to Equation 27 as given by Figures 8 and 9, exhibits the critical behaviour close to the TCP. It increases anomalously with the temperature increasing in the α phase (below T_1) toward the T_1 . Particularly, both continuous and discontinuous (tricritical) behaviour of C at 0.1 MPa (atmospheric pressure) and more discontinuous change of C with the temperature at higher pressures as obtained from the mean field model for those binary mixtures, can be compared with the experimental measurements. This would suggest the $\alpha - \beta$ transition (at 0.1 MPa) and liquid – solid (α -liquid and β -liquid) transition at higher pressures as the tricritical transition (first and second order) and the first order transition, respectively, in those binary mixtures studied here.

Anomalous behaviour of the heat capacity (C) leads to the entropy change (ΔS) during the transitions of liquid – solid (at high pressures) and solid – solid (at atmospheric pressure) for the binary mixtures according to the definition $S = (C/T)dT$ by means of Equation 28, as shown in Figures 10 and 11. This occurs in the enthalpy change $\Delta H = H - H_0$, (Equation 31) for those mixtures studied (Figures 12 and 13). Discontinuous change in the entropy ($\Delta S = S - S_0$) and in enthalpy ΔH occurs with the critical exponent $1/2$ as described by Equation 28 and Equation 31, respectively,

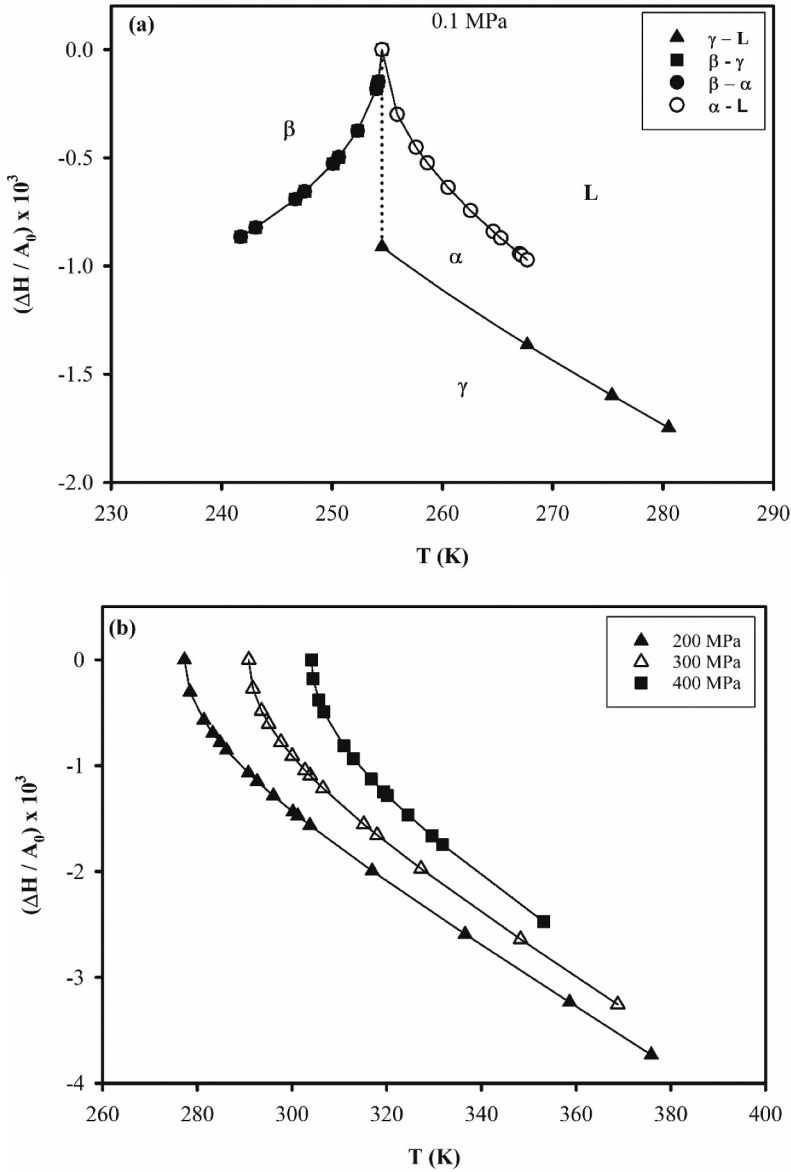


Figure 13. Variation of the enthalpy (normalized) with the temperature at the pressures of 0.1 (a), 200, 300 and 400 MPa (b) according to eq. (31) for the mixture of n-tridecane (1) + cyclohexane (2). For 0.1 MPa, the transition temperature between the phases α and β is T_i .

whereas the Helmholtz free energy changes continuously with the critical exponent $3/2$ (Equation 30) as the Landau model predicts, which we predicted for the binary mixtures studied at 0.1 MPa and higher pressures for the n-tridecane (1) + n-hexane (2) (Figure 14) and for the n-tridecane (1) + n-hexane (2) (Figure 15). The free energy (F) is plotted below and above the melting temperature (T_m) for the pressures of 0.1 MPa (the transition temperature between α and β phases is T_i), 300 and 500 MPa in the case of n-tridecane (1) + n-hexane (2), as given in Figure 14. Increasing ($T < T_m$) and decreasing ($T > T_m$) behaviour of the free energy, as plotted in Figures 14a and 14b, respectively, shift to the higher temperatures as the pressure increases for this binary mixture. In the case of the tridecane (1) + cyclohexane (2), we predicted similar behaviour of the free energy with respect to the temperature below and above T_m at 0.1 MPa (Figure 15a) and also at higher pressures (Figure 15b). This indicates

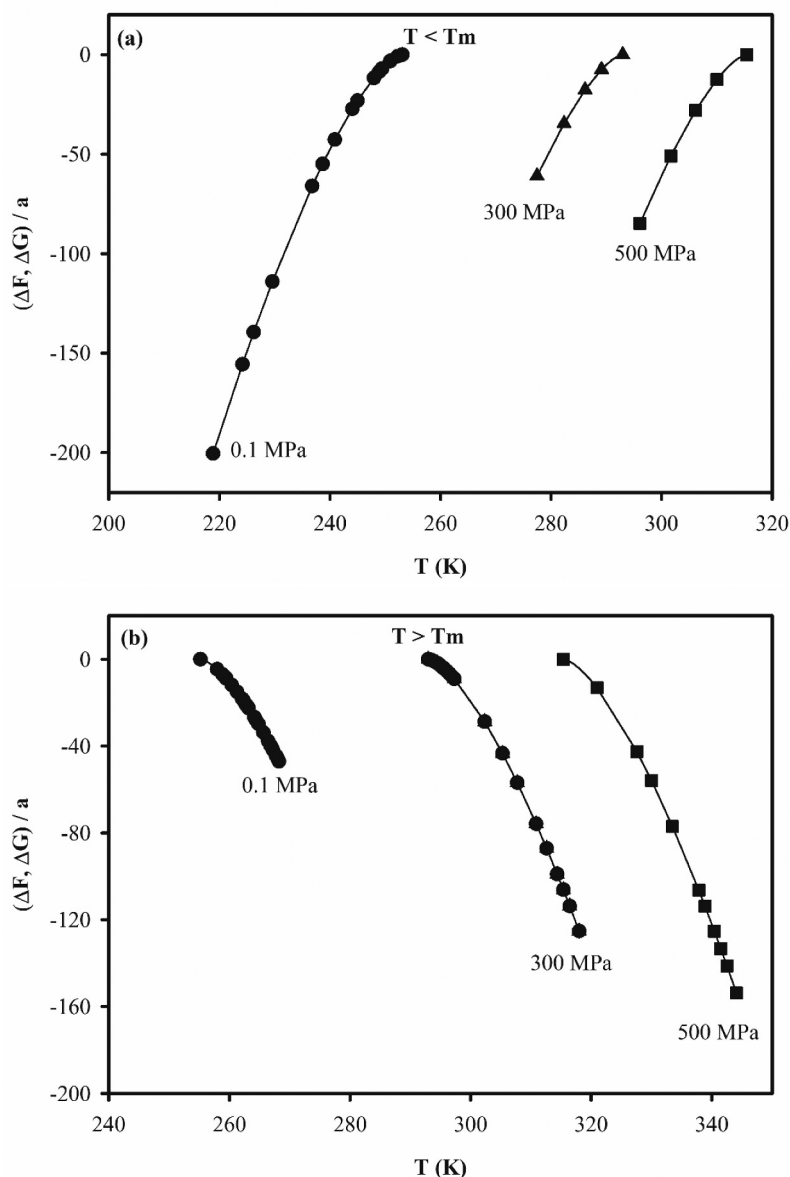


Figure 14. Variation of the Helmholtz free energy F (normalized) and the ΔG (normalized), with the temperature at the pressures of 0.1, 300 and 500 MPa according to eq. (30) for the mixture of n-tridecane (1) + n-hexane (2) for $T < T_m$ (a) and $T > T_m$ (b). For the 0.1 MPa, the transition temperature is T_t .

that regarding the thermodynamic quantities (heat capacity, entropy, enthalpy and the free energy), their temperature dependences at atmospheric and higher pressures exhibit similar critical behaviour for the binary mixtures studied as shown in Figures 8 – 15. In this study, as a start we considered a first order transition for the solid – liquid equilibria ($\alpha - L$ and $\beta - L$ transitions) and second order transition at 0.1 MPa for the solid – solid ($\alpha - \beta$) transition. At atmospheric pressure, as usual, the solid – liquid transition is considered a first order type as we also considered in the present study for the binary mixtures studied. As the pressure increases, the nature of the phase transition can change from the first order toward a second order close to the tricritical point (TCP) at which both transitions (continuous and discontinuous) take place, as stated above. Considering the temperature dependence of the thermodynamic quantities which we predicted according to the Landau phenomenological

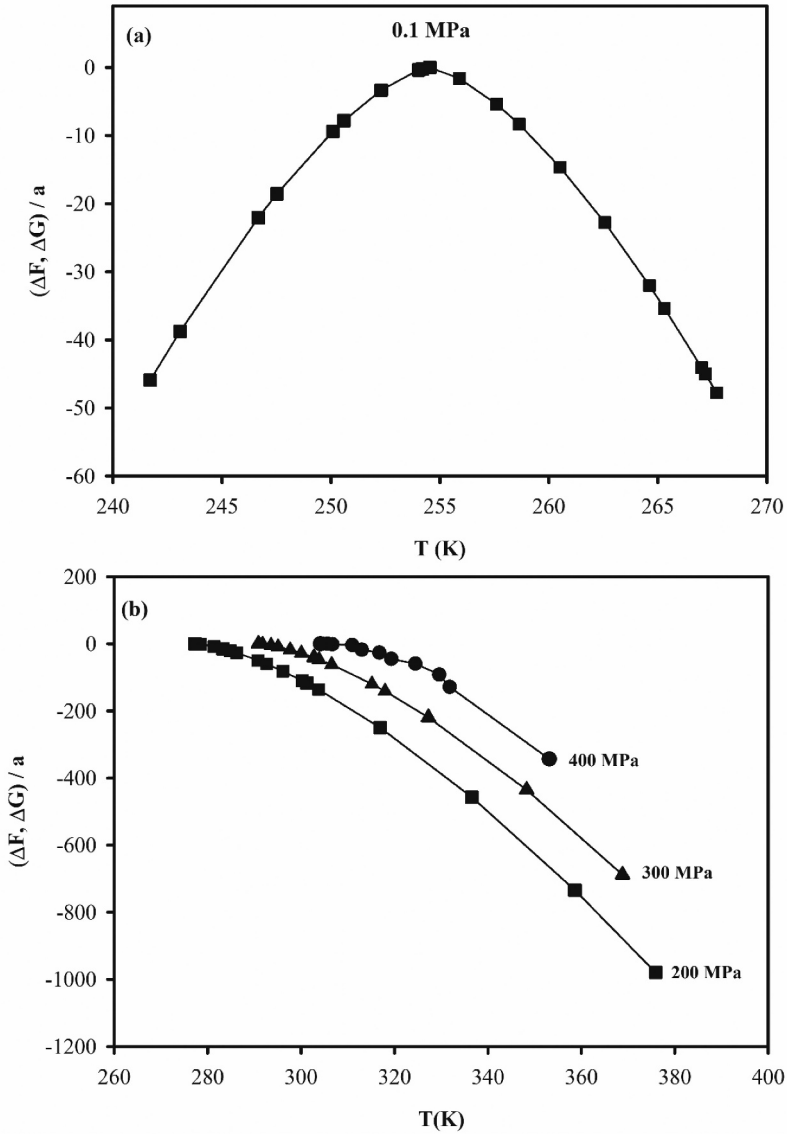


Figure 15. Variation of the Helmholtz free energy F (normalized) and the ΔG (normalized), with the temperature at the pressures of 0.1 (a), 200, 300 and 400 MPa according to eq. (30) for the mixture of n-tridecane (1) + cyclohexane (2) below and above T_m . At 0.1 MPa, the transition temperature is T_r .

model, they exhibit some changes for the second order solid – solid ($\alpha - \beta$) transition (at 0.1 MPa) at higher pressures and also for the first order solid – liquid equilibria ($\alpha - L$ and $\beta - L$) at 0.1 MPa and at higher pressures (Figures 5–15). Their temperature dependences are associated with the critical exponents for the second order ($\alpha - \beta$) and the first order ($\alpha - L$ and $\beta - L$) transitions, as considered above. From this point of view, it is reasonable to consider solid – solid ($\alpha - \beta$) transition as of a second order initially at 0.1 MPa. Also, we can consider the solid – liquid equilibria ($\alpha - L$ and $\beta - L$) as of a first order, as usual, at 0.1 MPa and its change if occurs, toward a second order (more continuous) or tricritical (both discontinuous and continuous) at higher pressures, as predicted here for the binary mixtures studied. Finally, our predictions of C , S , H and F as a function of temperature at the higher

Table 4. Values of the coefficients for the $\alpha - L$, $\gamma - L$ and $\beta - \gamma$ transitions according to Equation 39 with $b_3' = 0$ and Equation 41 at $P = P_m (= P_t)$, respectively, for the mixture of n-tridecane (1) + cyclohexane (2) at 0.1 MPa with the melting temperature (T_m) and concentration (x_m). T_t and x_t represent the transition temperature and concentration, respectively (P_t is the transition pressure).

0.1 MPa n-tridecane (1) + cyclohexane (2)	Equation 39 (K)	$\alpha - L$ ($x > x_m$) ($T > T_m$)	Equation 39 (K)	$\gamma - L$ ($x < x_m$) ($T > T_m$)	Equation 41 (K)	$\beta - \gamma$ ($x < x_t$) ($T < T_t$)
$(\alpha - L)$	a_0'	-0.2786	b_0'	0.2586	c_0'	0.04
$x_m = 0.4355$ $T_m = 254.59$ K	a_1'	42.28	b_1'	-328.632	c_1'	10.97
$(\gamma - L)$	a_2'	-26.79			c_2'	-118.6
$x_m = 0.1418$ $T_m = 241.71$ K	a_3'	19.27	b_2'	-438.067	c_3'	-18.53
$(\beta - \gamma)$						
$x_t = 0.4355$ $T_t = 254.53$ K						

pressures studied for those binary mixtures, can be compared with the experimental measurements. This then examines our predictions within the Landau phenomenological (mean field) model.

5. Conclusions

The $T - X$ phase diagrams were constructed on the basis of the Landau phenomenological model and the thermodynamic quantities which were extracted from the free energy, were predicted for the n-tridecane + (n-hexane and cyclohexane) at the atmospheric and high pressures. This was done for the liquid - solid and solid - solid (at 0.1 MPa) transitions for those binary mixtures.

Our phase line equations for the $T - X$ phase diagrams which were fitted to the experimental data, describe adequately the solid - liquid transitions ($\alpha - L$ and $\beta - L$) at high pressures in those mixtures. Also, our predictions for the solid - solid ($\alpha - \beta$) transitions (at 0.1 MPa), are expected to describe the observed behaviour in the mixtures studied, which can be tested by the experimental measurements. Additionally, the observed data can be compared with our calculated thermodynamic quantities (at zero and high pressures) for those n-paraffins. This also gives an experimental support to the validity of the Landau mean field model to describe the liquid - solid and solid - solid transitions in n-paraffins.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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