Crystal - Rotator-I - Rotator-II Phase Transitions in the Mixtures of Alkanes

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ABSTRACT

Using the combination of Flory–Huggins theory of isotropic mixing and Landau theory, we discuss the crystal – rotator-I – rotator-II phase transitions in the binary mixture of alkanes. The influence of concentration on the order parameters and the transition temperatures is discussed. Theoretical results show the first order character of both the rotator-I to crystal and rotator-II to rotator-I phase transitions in the mixture of alkanes. A good agreement between theoretical and experimental results are presented in this paper.

Keywords: Rotator Phases; Alkanes; Phase Transitions; Landau Theory

1. Introduction

Rotator phases are the states which exhibited by normal alkanes and alcohols consisting of layered structures with three dimensional crystalline order of the center of mass, but no long range orientational order of the molecules about their long axes. So far five different rotator phases have been identified with respect to the molecular arrangements: rotator-I (RI) phase, rotator-II (RII) phase, rotator-III (RIII) phase, rotator-IV (RIV) phase and rotator-V (RV) phase[1-4]. The RI phase is composed of untiled molecules with respect to the layers and there is rectangularly distorted hexagonal lattice. The RII phase is described as composed of molecules that are untiled with respect to the layers that are packed in a hexagonal lattice. The RV phase is the same as the RI phase except that the molecules are tilted towards their next nearest neighbour (NNN).

Over the past few decades considerable experimental progress has taken place toward the understanding of the rotator phases and transitions among them[1-10]. There has been also a great deal of experimental studies on binary mixtures of alkanes[11-15]. Denicolo et al.[11] studied the rotator phase transitions for the binary mixtures of C_{23}H_{48}+C_{26}H_{58}. In pure form both the alkanes include three rotator phases R_I, R_{II}, R_{V} including the crystalline phase (X). In this study they only observed the R_I-X and R_{II}-R_{I} phase transitions although the R_{V} phase was present in pure alkanes. So the R_{V} phase is suppressed. It was observed that the R_{II}-R_{I} transition temperature increases with the increase of the concentration of the second compound C_{26}H_{58}. However, the R_{I}-X transition temperature decreases with the increase of the concentration of C_{26}H_{58}. The lattice distortion changes with the change of concentration. Both the R_{I}-X and R_{II}-R_{I} phase transitions are observed to be first order transitions. Snyder et al.[12-13] studied the phase separation and mixing in binary n-alkanes crystal phases. Sirotta et al.[14-15] studied the rotator phase transitions in the binary mixture of alkanes C_{23}H_{48}+C_{26}H_{58} using x-ray scattering. This binary mixture was found to exist RII, RI phases and an intervening mesophase was reported to be the hexatic phase. The stability of the RI phase increases with the increase of concentration, squeezing out of the RV phase. Dutta et al.[16] also observed the hexatic phase in the same alkanes mixture C_{23}H_{48}+C_{26}H_{58} but with nanometer confinement condition. Mixtures of alkanes with nanoparticles and liquid crystals were also studied extensively[17-20].

In our previous works[21-24], we extensively studied the rotator phase transitions in the binary mixtures of alkane+alkane, alkane+nanoparticles and alkane+liquid crystal. The purpose of the present work is to study the
rotator phase transitions in the binary mixture of alkanes C_{23}H_{48}+C_{24}H_{50} with the combination of Flory–Huggins theory of isotropic mixing and Landau theory.

2. Theory

This paper considers the mixture of two alkanes C_{23}H_{48} and C_{24}H_{50}. Pure C_{23}H_{48} and C_{24}H_{50} alkanes exhibit the four phases: crystalline phase (X), R_v phase, R_i phase and R_u phase. The X phase exhibits a layered structure consisting of bilayer stacking of the lamellas. It has orthorhombic (distorted-hexagonal) packing within a layer as well as long range herringbone order of the rotational degrees of freedom of the backbones. Thus the X phase is described by herringbone order parameter \( \psi \) and lattice distortion order parameter \( \xi \). The R_v phase is described by two order parameters: tilt angle \( \theta \) and lattice distortion parameter \( \tilde{\xi} \). The R_i phase is described by lattice distortion parameter \( \tilde{\xi} \). Thus three order parameters \( \psi, \theta \) and \( \tilde{\xi} \) are to describe the experimental results of the binary mixture C_{23}H_{48} + C_{24}H_{50}. This paper uses the combination of Flory-Huggins theory and Landau theory. Then the total free energy per unit volume of the C_{23}H_{48} + C_{24}H_{50} mixture can be written as

\[
F = \frac{N k_B T}{V} [\varphi \ln \varphi + (1 - \varphi) \ln (1 - \varphi) + \chi \varphi (1 - \varphi)] + (1 - \varphi) \left[ \frac{1}{2} \delta \xi^2 - \frac{1}{3} b \xi^3 + \frac{1}{4} c \xi^4 + \frac{1}{2} a \theta^2 + \frac{1}{2} b \theta^4 + \frac{1}{2} \frac{\partial^2}{\partial \theta^2} \ln \varphi + \frac{1}{4} \frac{\partial^2}{\partial \theta^2} \ln \psi + \frac{1}{2} \frac{\partial^2}{\partial \psi^2} \ln \psi + \frac{1}{2} \frac{\partial^2}{\partial \theta^2} \ln \psi + \frac{1}{2} \delta \theta^2 \xi + \frac{1}{2} G \theta^2 \xi^2 + \frac{1}{2} \gamma \psi \xi + \frac{1}{2} H \psi^2 \xi^2 + \frac{1}{2} \eta \theta^2 \psi^2 \right]
\]

The terms in the first bracket represent the isotropic mixing of two components. The terms in the second bracket are the contribution of the order parameters of the X, R_v, and R_i phases. \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature. \( \varphi \) and \( 1 - \varphi \) are the volume fractions of C_{24}H_{50} and C_{23}H_{48}. \( \chi \) is known as Flory–Huggins interaction parameter and is function of temperature. We choose \( b > c > 0, q > 0, \gamma > 0 \) and \( \beta > 0 \) for the stability of the free energy (1). \( G, H, \delta, \gamma \) and \( \eta \) are coupling constants. \( \delta \) and \( \gamma \) are chosen negative to favour the R_v and X phases over the R_i phase. \( G, H \) and \( \eta \) is assumed to be positive. We assume \( a = a_0(T - T_i) \), \( \alpha = a_0(T - T_{ii}) \) and \( p = p_0(T - T_{ii}) \) with \( a_0 > 0, a_0 > 0, p_0 > 0, T_{i}, T_{ii} \) and \( T_{ii} \) are the virtual transition temperatures and described by \( T_{i} = T_{01} + u_1 (1 - \varphi)^2 + u_2 (1 - \varphi)^3, T_{ii} = T_{02} + v_1 (1 - \varphi) + v_2 (1 - \varphi)^2 \).

The free energy (1) describes four phases: (i) X phase (ii) R_v phase (iii) R_i phase (iv) R_u phase. Thus the free energy (1) describes the following six transitions: (i) \( R_u - R_i \) (ii) \( R_u - R_v \); (iii) \( R_i - R_v \); (iv) \( R_v - X \) and (v) \( R_u - X \) and (vi) \( R_v - R_u \). However the mixture C_{23}H_{48} + C_{24}H_{50} shows only two \( R_u - R_i \) and \( R_v - X \) transitions observed in experiment[11]. The presence of the cubic term \( b \) describes the first order \( R_i - X \) and \( R_v - R_i \) transitions.

Minimization of Eq. (1) with respect to \( \theta \) and \( \psi \) we get

\[
\theta^2 = \frac{\alpha + \delta \xi + G \xi^2 + \eta \psi^2}{\beta}
\]

\[
\psi^2 = \frac{p + \gamma \xi + H \xi^2 + \eta \theta^2}{q}
\]

From Eqs. (2) and (3) it is clear that the conditions \( \alpha + \delta \xi + G \xi^2 + \eta \psi^2 = 0 \) and \( p + \gamma \xi + H \xi^2 + \eta \theta^2 = 0 \) define the boundary between the \( R_i \) and \( R_v \) phases. The \( R_v \) phase occur only for \( \alpha + \delta \xi + G \xi^2 + \eta \psi^2 < 0 \). Since \( \delta < 0, G > 0, \eta > 0 \) Further in the region of \( R_v \) phase \( \alpha < 0 \). So the existence of the \( R_v \) phase occurs for \( \alpha < 0, \delta < 0 \). In general sign of the coupling constant \( \delta \) can changes sign with change concentration. \( \delta \) can become positive for higher value of the concentration of second compound. Then the condition \( \alpha + \delta \xi + G \xi^2 + \eta \psi^2 < 0 \) does not hold any more. Then the \( R_v \) phase disappears and subsequently the \( R_v - X \) transition occurs. The experimental results[11] show the disappearance of the \( R_v \) phase in the binary mixture of C_{23}H_{48}+C_{24}H_{50} even though the pure components exhibit the \( R_i - R_v \) transition. We will now discuss on the \( R_u - X \) and \( R_u - R_i \) transitions in the binary mixture C_{23}H_{48}+C_{24}H_{50}.

Now \( \theta = 0, \psi = 0, \xi \neq 0 \) is the solution of the \( R_i \) phase. Then the free energy for the \( R_u - R_i \) phase transition can be written as

\[
F_{R_u} = \frac{N k_B T}{V} [\varphi \ln \varphi + (1 - \varphi) \ln (1 - \varphi)] + \chi \varphi (1 - \varphi)
\]

\[
+ (1 - \varphi) \left[ \frac{1}{2} \alpha \xi^2 - \frac{1}{3} b \xi^3 + \frac{1}{4} c \xi^4 \right]
\]

The conditions for the first order \( R_u - R_i \) phase transition is given by

\[
F_{R_u}(\xi, \varphi) = F_{R_u}(\xi, \varphi) = 0, F_{R_u}(\xi, \varphi) \geq 0
\]
In addition, the chemical potentials in the R₁ and R₁I phases are equivalent i.e \( \mu_{R₁I} = \mu_{R₁} \).

If \( \theta = 0, \psi \neq 0, \xi \neq 0 \) is the solution of the X phase. Then the free energy for the R₁-X phase transition in terms of \( \xi \) can be written as

\[
F_χ = \frac{NK_BT}{V} [\psi \ln \psi + (1 - \phi) \ln (1 - \phi) + \chi \phi (1 - \phi)] \\
+ (1 - \phi) \left[ -\frac{\gamma^2}{4} - \frac{H_p}{Y} \xi + \frac{1}{2} b^* \xi^2 + \frac{1}{2} c^* \xi^3 \right]
\]

where

\[
a^* = a - \frac{\gamma^2}{q} - \frac{H_p}{q} \\
b^* = b - 3 \frac{\gamma^2}{q} \\
c^* = c - \frac{H^2}{q}
\]

The conditions for the first order R₁-X phase transition is expressed as

\[
F_X^I(\xi, \phi) = F_RI(\xi, \phi), \ F_X^I(\xi, \phi) = 0, \ F_X^I(\xi, \phi) \geq 0
\]

Further, the chemical potentials in the R₁ and X phases are equivalent i.e \( \mu_{R₁} = \mu_X \).

Solving Eqs. (5) and (7) simultaneously one can observe the phase diagram showing R₁-X and R₁I-R₁ phase transitions respectively.

3. Results and discussion

This paper now discusses our theoretical results by plotting various figures. Figures 1 and 2 show the temperature dependence of the order parameters \( \xi \) and \( \psi \) for different concentration of C₁₂H₂₅ in the R₁ and X phases respectively. This is done for a particular set of parameter values. It is clear from Figures 1 and 2 that both the order parameters \( \xi \) and \( \psi \) vary discontinuously with temperature both for pure compound as well as for the mixture of C₅H₁₂+24H. Figure 1 shows the increase of the lattice distortion parameter \( \xi \) with the increase of the concentration of C₂₃H₄₅. From Figure 1, we observe that the jump of the lattice distortion order parameter for the R₁-R₁I transition increases from \( \xi_{R₁I-R₁} = 0.26 \) at \( T_{R₁I-R₁} = 38.4 \) °C for \( \phi=0 \) to \( \xi_{R₁I-R₁} = 0.3 \) at \( T_{R₁I-R₁} = 39 \) °C for \( \phi=0.3 \). This behaviour indicates the strong first order character of the R₁I-R₁ transition even in the binary mixture of alkanes. Figure 2 shows the decrease of the herringbone order parameter \( \psi \) with the increase of the concentration of C₂₃H₄₅. From Figure 2, we observe that the jump of the herringbone order parameter for the R₁-X transition changes from \( \psi_{R₁-X} = 0.078 \) at \( T_{R₁-X} = 29.7 \) °C for \( \phi=0 \) to \( \psi_{R₁-X} = 0.022 \) at \( T_{R₁-X} = 28 \) °C for \( \phi=0.3 \). This observation clearly indicates the possibility of the critical point \( \phi>0.3 \) at the R₁-X transition in the binary mixture of alkanes. Temperature vs. concentration curve is shown in Figure 3. Figure 3 shows that the R₁I-R₁ transition temperature increases with the increase of concentration of C₁₂H₂₅. The above theoretical analysis supports the experimental results.[11]
4. Conclusion

This paper studies the \( R_1-X \) and \( R_0-R_1 \) transitions for the binary mixture of \( C_{23}H_{48}+C_{24}H_{50} \). The theoretical analysis is based on free energy expansion using the combination of Flory Huggins theory and Landau theory. Theoretical results show that both the \( R_1-X \) and \( R_0-R_1 \) transitions are first order even in the mixture of \( C_{23}H_{48}+C_{24}H_{50} \). The possibility of the critical point at the \( R_1-X \) transition in the binary mixture of alkanes are also observed.

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