ORIGINAL RESEARCH ARTICLE

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 (R_I) phase, rotator-II (R_{II}) phase, rotator-III (R_{III}) phase, rotator-IV (R_{IV}) phase and rotator-V (R_V) phase[1-4]. The R_I phase is composed of untilted molecules with respect to the layers and there is rectangularly distorted hexagonal lattice. The R_{II} phase is described as composed of molecules that are untilted with respect to the layers that are packed in a hexagonal lattice. The R_V phase is the same as the R_I 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 $C_{23}H_{48}$ + $C_{24}H_{50}$. In pure form both the alkanes exhibit 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 RIIRI transition temperature increases with the increase of the concentration of the second compound $C_{24}H_{50}$. However, the R_I-X transition temperature decreases with the increase of the concentration of $C_{24}H_{50}$. 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. Ungar et al.[12] and Snyder et al.[13] studied the phase separation and mixing in binary n-alkanes crystal phases. Snyder et al.[14] and Sirota et al.[15] studied the rotator phase transitions in the binary mixture of alkanes $C_{23}H_{48} + C_{28}H_{58}$ using x-ray scattering. This binary mixture was found to exist R_{II}, R_I phases and an intervening mesophase was reported to be the hexatic phase. The stability of the R_I phase increases with the increase of concentration, squeezing out of the R_V phase. Dutta et al.[16] also observed the hexatic phase in the same alkanes mixture $C_{23}H_{48} + C_{28}H_{58}$ 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 $C_{23}H_{48} + C_{28}H_{58}$ 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_{II} 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 ψ and lattice distortion order parameter ξ. The R_V phase is described by two order parameters: tilt angle θ and lattice distortion parameter ξ. The R_I phase is described by lattice distortion parameter ξ. Thus three order parameters ψ, θ and ξ 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

$$F = \frac{Nk_BT}{V}[\varphi\ln\varphi + (1-\varphi)\ln(1-\varphi) + \chi\varphi(1-\varphi)]$$
$$+ (1-\varphi)\left[\frac{1}{2}a\xi^2 - \frac{1}{3}b\xi^3 + \frac{1}{4}c\xi^4 + \frac{1}{2}\alpha\theta^2 + \frac{1}{4}\beta\theta^4 + \frac{1}{2}p\psi^2 + \frac{1}{4}q\psi^4 + \frac{1}{2}\delta\theta^2\xi \right.$$
$$\left. + \frac{1}{2}G\theta^2\xi^2 + \frac{1}{2}\gamma\psi^2\xi \right| + \frac{1}{2}H\psi^2\xi^2 + \frac{1}{2}\eta\theta^2\psi^2 \right] \quad (1)$$

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. φ and $(1-\varphi)$ are the volume fractions of $C_{24}H_{50}$ and $C_{23}H_{48}$. χ is known as Flory-Huggins interaction parameter and is function of temperature. We choose $b>$, $c>0$, $q>0$, and $\beta > 0$ for the stability of the free energy (1). G, H, δ, γ and η are coupling constants. δ and γ are chosen negative to favour the R_V and X phases over the R_I phase. G, H and η is assumed to be positive. We assume $a = a_0(T - T_1^*)$, $\alpha = \alpha_0(T - T_2^*)$ and $p = p_0(T - T_3^*)$ with $a_0 > 0$, $\alpha_0 > 0$, $p_0 > 0$. T_1^*, T_2^* and T_3^* are the virtual transition temperatures and described by $T_1^* = T_{01} + u_1(1-\varphi) + u_2(1-\varphi)^2$, $T_2^* = T_{02} + v_1(1-\varphi) + v_2(1-\varphi)^2$, $T_3^* = T_{03} + w_1(1-\varphi) + w_2(1-\varphi)^2$. The free energy (1) describes four phases: (i) X phase (ii) R_V phase (iii) R_I phase (iv) R_{II} phase. Thus the free energy (1) describes the following six transitions: (i) R_{II}-R_I; (ii) R_{II}-R_V; (iii) R_I-R_V; (iv) R_I-X; (v) R_{II}-X and (vi) R_V-X. However the mixture $C_{23}H_{48} + C_{24}H_{50}$ shows only two R_{II}-R_I and R_I-X transitions observed in experiment[11]. The presence of the cubic term b describes the first order R_I-X and R_{II}-R_I transitions.

Minimization of Equation (1) with respect to θ and ψ we get

$$\theta^2 = -\frac{\alpha + \delta\xi + G\xi^2 + \eta\psi^2}{\beta} \tag{2}$$

Minimization of Equation (1) with respect to θ and ψ we get

$$\psi^2 = -\frac{p + \gamma\xi + H\xi + \eta\psi\theta^2}{q} \tag{3}$$

From Equations (2) and (3) it is clear that the conditions $\alpha + \delta\xi + G\xi^2 + \eta\psi^2 = 0$ and $p + \gamma\xi + H\xi + \eta\psi\theta^2 = 0$ define the boundary between the R_I, X and R_V phases. The R_V phase occur only for $+\delta\xi + G\xi^2 + \eta\psi^2 < 0$. 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 δ can changes sign with change concentration. δ 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_I-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_I-X and R_{II}-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_{II}-R_I phase transition can be written as

$$F_{RI} = \frac{Nk_BT}{V}[\varphi\ln\varphi + (1-\varphi)\ln(1-\varphi)] + \chi\varphi(1-\varphi) + (1-\varphi)\left[\frac{1}{2}\alpha\xi^2 - \frac{1}{3}b\xi^3 + \frac{1}{4}c\xi^4\right] \tag{4}$$

The conditions for the first order R_{II}-R_I phase transition are given by

$$F_{RI}(\xi,\varphi) = F_{RII}(\varphi), \ F'_{RI}(\xi,\varphi)=0, \ F''_{RI}(\xi,\varphi)\geq 0 \tag{5}$$

In addition, the chemical potentials in the R_I and R_{II} phases are equivalent i.e., $\mu_{RII} = \mu_{RI}$.

$\theta = 0$, $\psi \neq 0$, $\xi \neq 0$ is the solution of the X phase. Then the free energy for the R_I-X phase transition in terms of ξ can be written as

$$F_X = \frac{Nk_BT}{V}[\varphi\ln\varphi + (1-\varphi)\ln(1-\varphi) + \chi\varphi(1-\varphi)] + (1-\varphi)\left[-\frac{P^2}{4q} - \frac{Hp}{q}\xi + \frac{1}{2}a^*\xi^2 - \frac{1}{3}b^*\xi^3 + \frac{1}{4}c^*\xi^4\right] \tag{6}$$

where, $a^* = a - \frac{\gamma^2}{q} - \frac{Hp}{q}, b^* = b - \frac{3\gamma H}{q}, c^* = c - \frac{H^2}{q}$.

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

$$F_X(\xi,\varphi) = F_{RI}(\xi,\varphi), \ F'_X(\xi,\varphi)=0, \ F''_X(\xi,\varphi)\geq 0 \tag{7}$$

Further, the chemical potentials in the R_I and X phases are equivalent i.e., $\mu_{RI} = \mu_X$.

Solving Equations (5) and (7) simultaneously one can observe the phase diagram showing R_I-X and R_{II}-R_I 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 ξ and ψ for different concentration of $C_{24}H_{50}$ in the R_I 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 ξ and ψ vary discontinuously with temperature both for pure compound as well as for the mixture of $C_{23}H_{48} + C_{24}H_{50}$. **Figure 1** shows the increase of the lattice distortion parameter ξ with the increase of the concentration of $C_{24}H_{50}$. From **Figure 1**, we observe that the jump of the lattice distortion order parameter for the R_{II}-R_I transition increases from $\xi_{RII-RI} = 0.26$ at $T_{RII-} = 38.4\ °C$ for $\varphi = 0$ to $\xi_{RII-} = 0.3$ at $T_{RII-} = 39\ °C$ for $\varphi = 0.3$. This behaviour indicates the strong first order character of the R_{II}-R_I

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transition even in the binary mixture of alkanes. **Figure 2** shows the decrease of the herringbone order parameter ψ with the increase of the concentration of $C_{24}H_{50}$. From **Figure 2**, we observe that the jump of the herringbone order parameter for the R_I-X transition changes from $\psi_{RII} = 0.078$ at $T_{RII-X} = 29.7$ °C for $\varphi = 0$ to $\psi_{RII-R} = 0.022$ at $T_{RII-X} = 28$ °C for $\varphi = 0.3$. This behaviour indicates the weak first order character of the R_I-X transition in the binary mixture of alkanes. This observation clearly indicates the possibility of the critical point $\varphi > 0.3$ at the R_I-X transition in the binary mixture of alkanes. Temperature vs. concentration curve is shown in **Figure 3**. **Figure 3** shows that the RII-RI transition temperature increases with the increase of concentration of $C_{24}H_{50}$. The R_I-X transition temperature decreases with the increase of concentration of $C_{24}H_{50}$. The above theoretical analysis supports the experimental results[11].
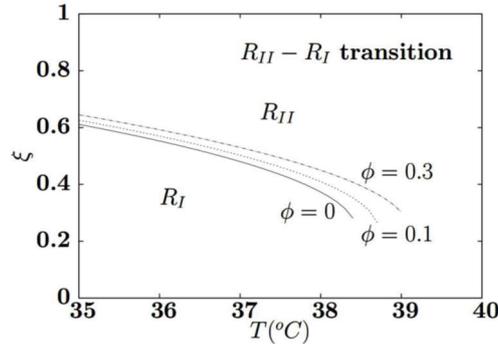
Figure 1. Temperature dependence of the lattice distortion parameter ξ for different concentration of $C_{24}H_{50}$ in the R_I phase of the R_{II}–R_I transition.
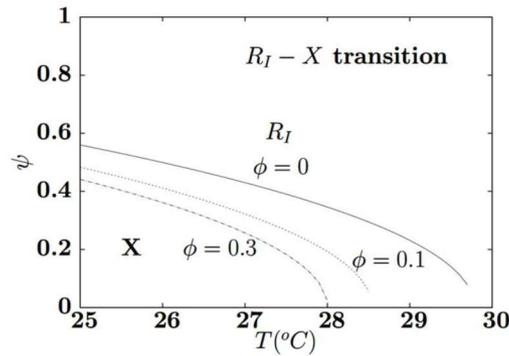
Figure 2. Temperature dependence of the herringbone order parameter ψ for different concentration of $C_{24}H_{50}$ in the X phase of the R_I-X transition.
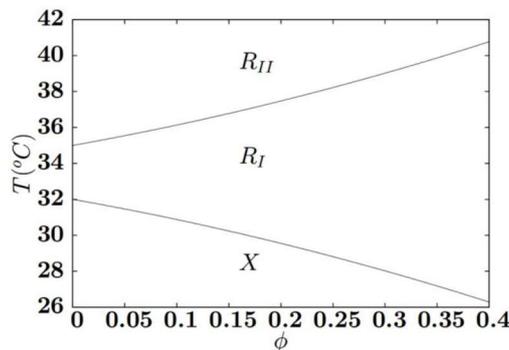
Figure 3. Temperature vs. concentration curve for the mixture of $C_{23}H_{48} + C_{24}H_{50}$.

4. Conclusion

This paper studies the R_I-X and R_{II}-R_I 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_I-X and R_{II}-R_I 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_I-X transition in the binary mixture of alkanes are also observed.

Conflict of interest

The author declares no conflict of interest.

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