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Phase transitions of *n*-alkane systems

Part 2 *Melting and solid state transition of binary mixtures*

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The theory of Lauritzen, Passaglia and Di Marzio is used to investigate the melting of a number of *n*-alkane binary systems. A value for the interfacial surface free energy lateral to the chain direction σ_n of 3 erg cm^{-2} is obtained. For the system $n\text{C}_{19}\text{H}_{40}$–$n\text{C}_{44}\text{H}_{90}$ an estimate is made of the distribution of the free energy between the crystallization and the remelting processes. A comparison is made with other models of binary *n*-alkane systems. σ_n is used to calculate the equilibrium density of vacancies, and this is found to correlate with the behaviour of the solid state phase transition.

1. Introduction

The phase transitions of the *n*-alkanes and their mixtures have been studied extensively both experimentally and theoretically. Experimental data on a number of binary systems has been reported by Mazee [1, 2], Nechetailo *et al.* [3, 4] and Asbach and Kilian [5]. The earlier data has been reviewed by Mnyukh [6], and Würflinger and Schneider [7] have studied the system $n\text{C}_{19}\text{H}_{40}$–$n\text{C}_{21}\text{H}_{44}$ under high pressure. The theory of the crystallization of mixed alkanes has been investigated by Lauritzen, Passaglia and Di Marzio [8, 9] and by Asbach and Kilian [5]. The former theory, hereafter called the LPD theory, is attractive as it is microscopic in nature and can be applied to other systems, especially polymers [10]. An important parameter in this model is the interfacial surface free energy σ_n for the crystal facets orthogonal to the paraffin chain direction. This measures the difference between the specific free energy of the crystal facet and that of the liquid.

σ_n is of interest since the value obtained for paraffins has been applied in the case of polyethylene. The only experimental data available is that of Turnbull and Cormia [11]. Using a droplet freezing method they determined σ_n to be 7.2 erg cm^{-2}. However, this result was obtained at a supercooling of 13 to 15° C and crystallization with highly strained chain conformations has been observed at much smaller supercoolings [12]. Thus, this value is likely to be in error since it does not refer to equilibrium crystallization of linear chains. Generally a slightly higher value, for σ_n of 10 erg cm^{-2} has been used for polyethylene [13, 14]. We have obtained phase diagrams for a number of binary mixtures of zone-refined *n*-alkanes. These results, together with those of Mazee and Würflinger and Schneider, have been fitted to the LPD theory using σ_n as a variable parameter. This enables us to obtain a value for σ_n under conditions close to equilibrium crystallization.

For binary systems with nearly equal chain lengths, which form solid solutions, the difference between equilibrium and kinetic results is not sufficient to be clearly displayed in the calculations. This difference is significant for disparate chain lengths but in such binary systems non-solid-solution behaviour is more common. For the system $n\text{C}_{19}\text{H}_{40}$–$n\text{C}_{44}\text{H}_{90}$ solid solution behaviour is observed and the differences of crystallization under equilibrium and kinetic conditions can be observed.

σ_n can also be used to calculate vacancy densities in binary solid solutions. The onset of the solid state phase transition is likely to be affected by the density of vacancies since the upper, so-called "rotator" phase, involves both rotational and translational diffusive motions of the chains

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[15, 16]. The latter motions will be made easier by the presence of lattice vacancies. Vacancy densities were, therefore, calculated by a Monte Carlo method and compared with the compositional dependence of the solid-state phase transition.

2 Experimental

Paraffins with a nominal purity of 99.9% were zone refined with an average of forty zone passes. $nC_{20}H_{42}$ samples treated in this manner no longer showed evidence of a solid-state phase transition but solidified as large water white crystallites. This indicates a purity of at least 99.99% for the zoned refined materials [17].

Phase diagrams were determined using a Dupont differential thermal analyser (DTA) and a Dupont differential scanning calorimeter (DSC). The DTA data suffer little thermal lag and peak values were taken as transition temperatures. The DSC data was corrected for thermal lag by taking the transition temperature as the intersection of the slope of the peaks and the base line on the low temperature side of the peak. For broad DSC peaks the slope was taken to be that observed for pure metals and was drawn from the maximum of the peak [18]. For paraffins of nearly equal chain length the resolution of the DSC curves in the melting region, into solidus and liquidus peaks was difficult so that only the major peak assigned to the liquidus was used.

3. The melting of binary mixtures

Lauritzen *et al.* [9] calculated the melting and freezing curves for the system $nC_{24}H_{50}$–$nC_{26}H_{54}$ and found a value of 3 erg cm^{-2} for σ_n, though the fit was only fair. This fitting was repeated using an Algol computer programme written for an ICL 1900 series computer [19]. Using Broadhurst's data for the melting points and heats of fusion of the pure components [20] the results of Lauritzen *et al.* were reproduced within 0.1° C. This programme was used to obtain transition curves for the systems: $nC_{19}H_{40}$–$nC_{20}H_{42}$, $nC_{19}H_{40}$–$nC_{21}H_{44}$, $nC_{21}H_{44}$–$nC_{23}H_{48}$, $nC_{22}H_{46}$–$nC_{23}H_{48}$, $nC_{30}H_{62}$–$nC_{35}H_{72}$ and $nC_{19}H_{20}$–$nC_{44}H_{90}$. In all cases the molecules were treated as hexagonal blocks, as shown in Fig. 1. That is, the value of σ_n is assumed to be independent of choice of lateral facet and is calculated as an average 'molecular' value [9]. This approximation is reasonable since the structure of the pre-melting phase of odd-carbon paraffins is close to hexagonal and a similar phase is induced in the even-carbon triclinic paraffins by the presence of paraffinic impurities.

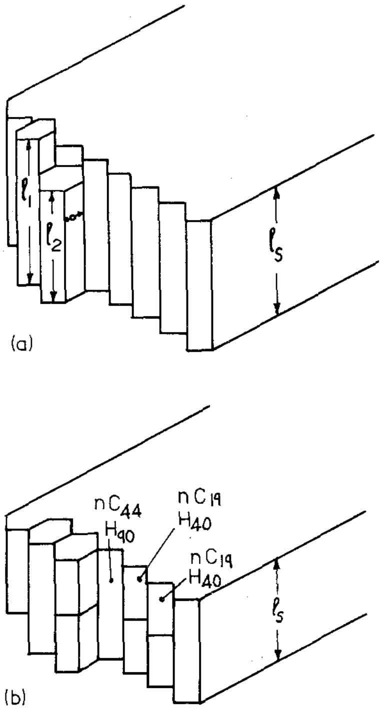

Figure 1 Stacking of paraffin molecules during the growth of a single molecular layer. (a) for a binary system with nearly equal chain lengths, (b) for a system with molecular lengths in the ratio 1 : 2.

All these systems are observed to form solid solutions. As noted in the introduction, the calculated transition curves are essentially identical for both equilibrium and kinetic conditions when the chain lengths of the paraffins are similar. Typical results are shown in Fig. 2 for the system $nC_{19}H_{40}$ –$nC_{21}H_{44}$ and $nC_{21}H_{44}$–$nC_{23}H_{48}$. The experimental results of this work and of Mazee are plotted together with the equilibrium curves calculated for σ_n equal to 3 erg cm^{-2}. Fig. 3 shows a similar calculation for the high pressure data of Würflinger and Schneider. In all cases, except $nC_{19}H_{40}$–$nC_{44}H_{90}$, the experimental data was fitted best with equilibrium curves calculated with σ_n equal to 3 erg cm^{-2}.

The system $nC_{19}H_{40}$–$nC_{44}H_{90}$ contains molecules with lengths in the approximate ratio one to two. Thus, a solid solution can be formed where two $nC_{19}H_{40}$ molecules occupy the lattice site of one $nC_{19}H_{40}$ molecule, see Fig. 1. The LPD model can then be applied using "double" $nC_{19}H_{44}$ molecules. The equilibrium diagrams for this system

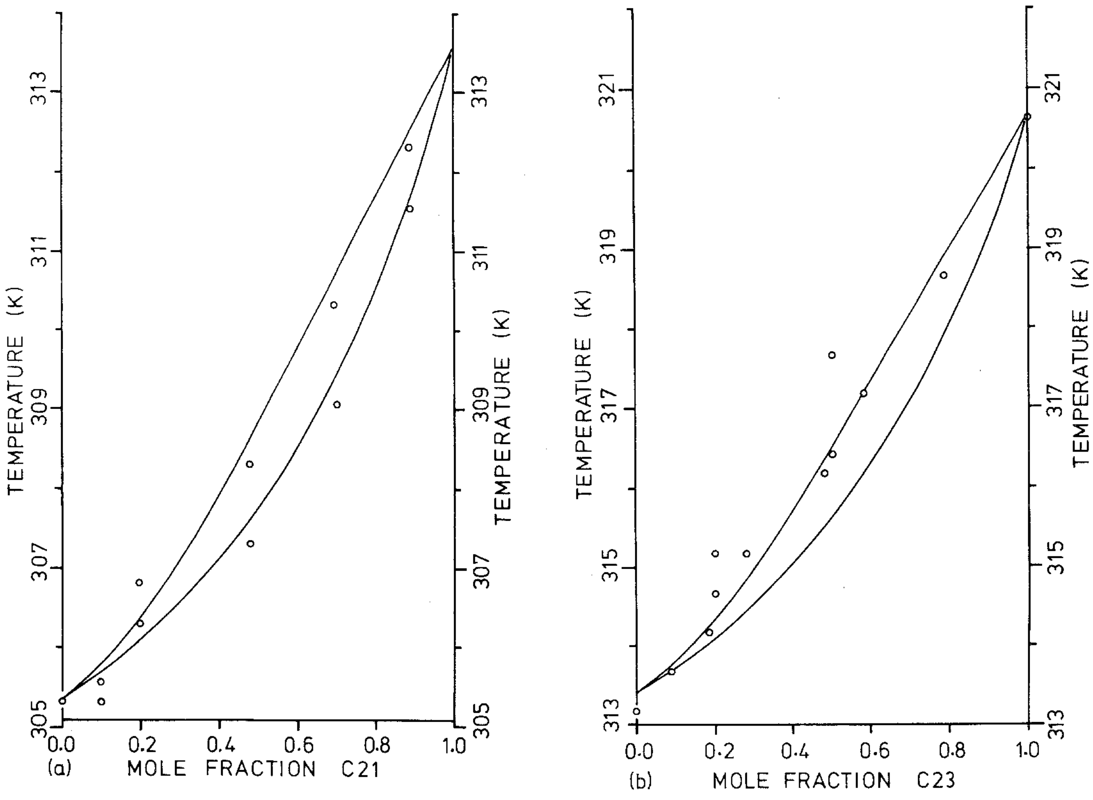

Figure 2 Phase diagrams for the binary systems (a) $nC_{19}H_{40}$–$nC_{21}H_{44}$ and (b) $nC_{21}H_{44}$–$nC_{23}H_{48}$. The full curves are calculated for σ_n equal to 3 erg cm^{-2} (data from Mazee and this work).

show a much smaller dependence on σ_n. A difference of less than 0.2° C results from changing the value of σ_n from 3 to 8 erg cm^{-2}. However, in the kinetic case the calculated curves depend on the distribution of the free energy between the forward, freezing, and backward, re-melting, processes. This can be described in terms of rate constants for the addition of a molecule j to a row of molecules terminating in molecule i, a_{ij} and for the removal of a similar molecule, b_{ij}:

$$a_{ij} = x_j \exp(\phi A),$$

$$b_{ij} = \exp[-(1-\phi)A]$$

$$0 \leqslant \phi \leqslant 1$$

x_j is the molar concentration of species j is the liquid. A is a function of several parameters including x_j, melting points, heats of fusion and molecular chain lengths of the individual pure substances. ϕ is an arbitrary variable parameter, having negligible effect on solidus and liquidus curves, when the two constituent chain lengths are very close to each other. Similar results are obtained with a calculation for normal, rather than "double" $nC_{19}H_{40}$ molecules.

The experimental data is, unfortunately, less reliable for this system since, as can be seen from Fig. 4, there is pronounced segregation of the components. Thus, for slowly cooled mixtures the solidus observed will be that of the finally freezing material which will be nearly pure $nC_{19}H_{40}$. Thus, only the liquidus will be unambiguous. However, at less than 15% $nC_{44}H_{90}$, differences were observed between the liquidus of the initial thermogram and that of subsequent thermograms. This effect, which was negligible for more than 15% $nC_{44}H_{90}$, reflects the sensitivity of the system to crystallization conditions. Both sets of data are plotted in Fig. 4. The results are fitted best by a calculation for "double" $nC_{19}H_{40}$ molecules with σ_n equal to 3 erg cm^{-2} and ϕ equal to zero, however this value of ϕ can be considered only as an estimate due to the uncertainties inherent in the experimental data.

Calculations were also made using the simple thermodynamic model of Mazee [1, 2]. These were found to give much poorer fits to the experimental data than the calculations described above. Differences between the LPD model and the calculations of Asbach and Kilian were found to be small in the case of the system $nC_{24}H_{50}$–$nC_{28}H_{58}$, the only system where a simple comparison is possible.

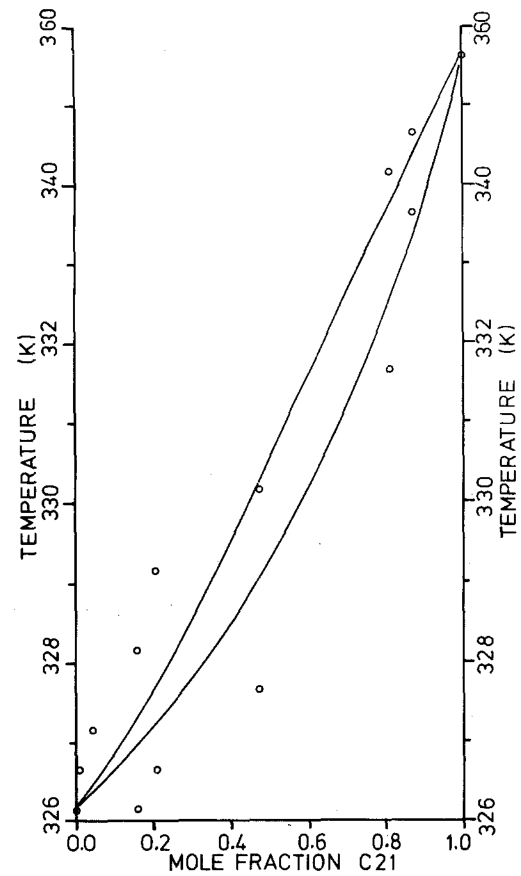

Figure 3 Phase diagram for $nC_{19}H_{40}$–$nC_{21}H_{44}$ at 1 kbar, the full curves are calculated with σ_n equal to 3 erg cm^{-2} and the experimental points are from [7].

4. The solid-state phase transition

The temperature of the solid-state transition from the orthorhombic to the near hexaognal "rotator" phase is observed to be decreased in binary systems [1–4]. Since the upper phase involves both diffusive rotary and translational motion of the paraffin molecules [15, 16] the presence of whole or partial lattice vacancies is likely to play a part in the observed composition dependence of the transition temperature. A Monte Carlo calculation was used in which molecules of two different lengths were stacked in random manner. Vacancies considered were complete absence of a molecule or smaller vacancies formed by partial filling of the complete molecular vacancy. The molecular array was constructed in a manner analogous to the LPD theory [19].

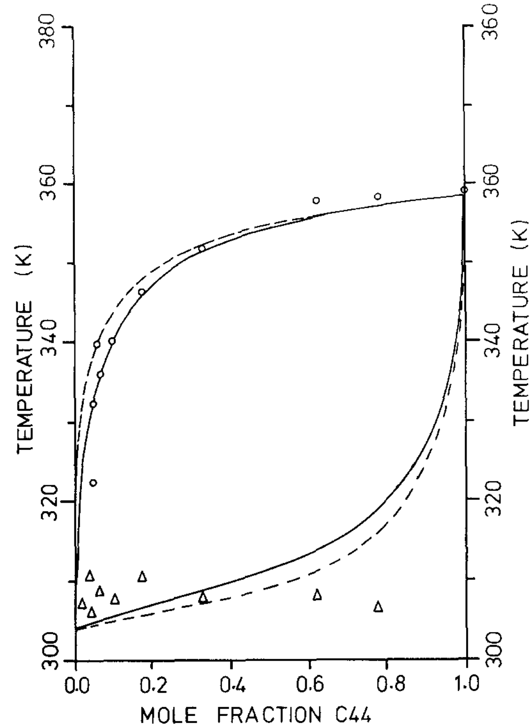

Figure 4 Phase diagram for $nC_{19}H_{40}$–$nC_{44}H_{90}$. The theoretical curves were calculated with σ_n equal to 3 erg cm^{-2} and $\phi = 1$(----); $\phi = 0$. (——) The experimental points are from this work (see text).

A partition function for the ensemble is obtained and the probabilities of a molecule occupying or leaving a site vacant deduced. The values of σ_n of 3, 4 and 8 erg cm^{-2} were used in the calculation, which was performed for an array of 65 x 65 x 65 molecules. The first fifteen layers were neglected to eliminate the effects of the "regular" stacking of the initial layer. Differences between the above and an array size of 50 x 50 x 50 were slight, indicating that such array dimensions are adequate.

Closest agreement between total CH_2 vacancy and the depression of the solid state transition was obtained for $\sigma_n = 3$ erg cm^{-2} and supports the value calculated in the previous section. For a value of $\sigma_n = 8$ erg cm^{-2}, a maximum in CH_2 vacancy distribution occurs for a mole fraction of $nC_{23}H_{48}$ of 0.5. The results of this calculation are compared with experimental data for the system $nC_{21}H_{44}$–$nC_{23}H_{48}$ for $\sigma_n = 3$ erg cm^{-2} in Fig. 5. The curves for total CH_2 unit vacancies and the depression of the solid-state transition are seen to follow one another. Measurements were also made

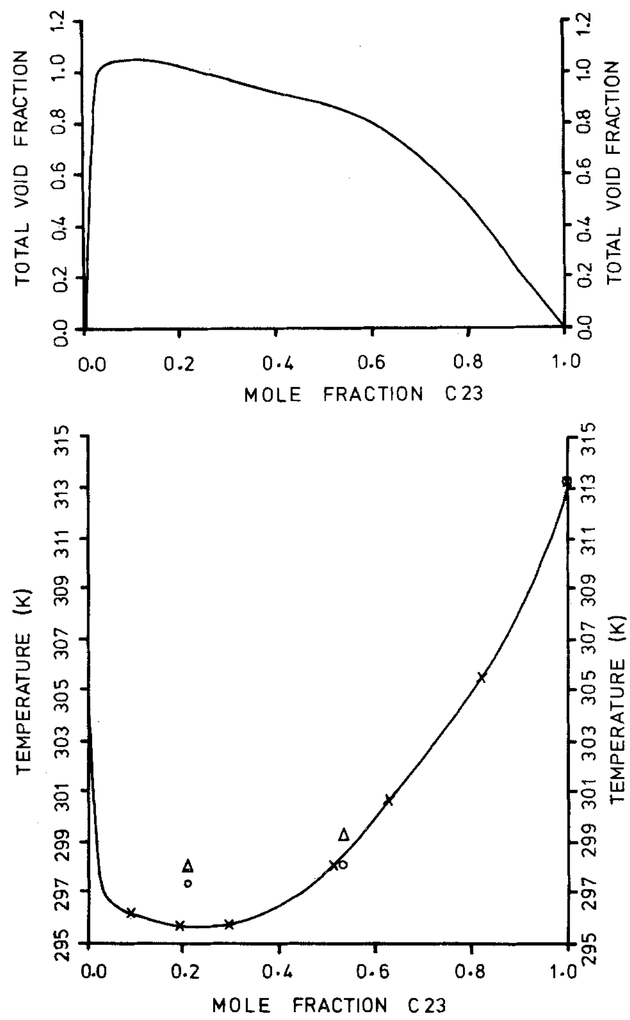

Figure 5 Comparison of the vacancy concentration and temperature dependence of the solid-state phase transition in the system $nC_{21}H_{44}$–$nC_{23}H_{48}$. Upper graph, CH_2 unit vacancy concentration calculated with σ_n equal to 3 erg cm^{-2}; lower graph, temperature dependence of the solid state phase trnasition, (data of Mazee △, ○ and this work ×.

of the density of samples from this binary system, since the presence of vacancies should lead to a decrease in density. This is indeed found to be the case as shown in Fig. 6, though the correspondence with the calculated vacancy density is not as good as that of Fig. 5.

5 Conclusions

A value of σ_n of 3 erg cm^{-2} has been found to give good fits to the near equilibrium freezing of *n*-alkane binary systems. The same value also gives vacancy densities which accord well with the experimentally observed behaviour of the solid state phase transition, however it is much smaller than the value found by Turnbull and Cormia, and certainly their higher value must reflect freezing of the molecules in strained conformations.

If the *n*-alkanes are a valid model system for polyethylene, the present value is much lower than the 10 erg cm^{-2} accepted for polyethylene. The

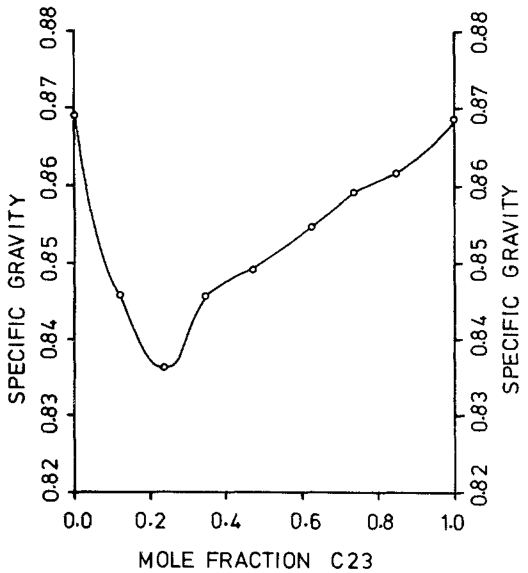

Figure 6 Relative densities of binary mxitures for the system $nC_{21}H_{44}$–$nC_{23}H_{48}$; compare with the upper graph of Fig. 5.

value chosen is important since it enables the surface energy of the chain fold surface of polyethylene crystals to be derived from crystal growth rates. This problem has been discussed by Keller and Pedemonte [14] who find values for the product $\sigma_n \sigma_e$ of 600 to 1000 $(\text{erg cm}^{-2})^2$ dependent on choice of melting point. Reducing the value of σ_n to 3 erg cm^{-2} increases the possible values of σ_e to 200 to 330 erg cm^{-2}, which is significantly above the values normally quoted for polyethylene, ~ 100 erg cm^{-2} [21]. Thus, it appears probably that *n*-alkanes melting from a highly disordered phase (i.e. a pre-melted phase) are not a good model for polyethylene melting from an ordered orthorhombic phase.

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