Investigation of equilibrium crystallization processes of n-alkane multicomponent systems

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The thermodynamic equilibrium between multicomponent melt and several solid solutions is computed for n-alkane mixtures consisting of many different homologues. The algorithm is based on the knowledge of the equations of state for the multicomponent melt and the solid solutions. Using pair interaction energies for the solid phases, which include the relative chain length differences of a pair of molecules, the sets of transcendental equations for the heterogeneous equilibrium can be solved by numerical methods. The results obtained from these calculations are compared with structure properties of the n-alkane solid solutions, which are evaluated from differential scanning calorimetry and X-ray measurements. It follows that the crystallization behaviour of the mixtures can be described by using just one pair interaction parameter, $K = 3500\,\mathrm{cal\,mol^{-1}}$, in a temperature range between liquidus and solidus. Further theoretical predictions for the miscibility of homologues in the solid state are obtained, which are of great interest for the crystallization processes in oligomer systems such as fractions of linear polyethylene with extended chain crystals.

(Keywords: crystallization; miscibility; solution)

INTRODUCTION

Studies of the morphology of fractions of linear polyethylene and samples of linear polyethylene, crystallized under elevated pressure, clearly show that the thickness distribution of the lamellae formed is closely related to the molecular weight distribution, as long as the macromolecules do not fold during crystallization[1–3]. Earlier thermodynamic calculations of the equilibrium crystallization processes started from known molecular weight distributions, assuming strict eutectic behaviour of the components in the solid state[1,2]. Although the dependences of the degree of crystallinity on temperature and the variation of the average crystal thicknesses with temperature agree quite satisfactorily with experimental results, the fact remains that molecules differing only little in chain length form continuous solid solutions. This follows from investigations of binary and ternary isobaric state diagrams of the n-alkanes, which show either eutectic phase separation or solutions in the solid state, depending on the difference in chain lengths compared to the mean chain lengths of the mixtures[4–7].

Thus a thermodynamic description of the extended chain crystallization of multicomponent systems of n-paraffins should be able to describe 'eutectoid' phase separation during crystallization from the melt. This can be detected experimentally according to two main features of the eutectoid solid state phases: first, the mean length distribution of the extended chain crystals still resembles the molecular weight distribution; and second, the lamellae are solid solutions composed of molecules differing in chain length by a certain amount. The appropriate theoretical approach is to calculate the crystallization at thermodynamic equilibrium, taking into account the melt and several solid phases as a multicomponents multiphase problem. The formulation of the fundamental Gibbs free energy equations for the possible phases in the solid state requires detailed knowledge of the interaction energies and excess entropies of the solid solutions as well as the multicomponent melt. The physical properties of the liquid state of n-paraffins are well known (equation of state theories[8,9]), whereas the equilibrium structure of an 'extended chain crystal', as a species of a multicomponent solid solution, is only studied for binary mixtures[4,5,10]. We discuss the Gibbs free energies of the solid state phases using a concept of an 'autonomous inhomogeneous microphase', which deals with three main thermodynamical aspects.

1. As the different components are homologues, a thermodynamic description which incorporates the dependences of the energies and entropies on chain lengths is a suitable approximation, as was shown by calculating the melting points of the pure n-alkanes[11,12].
2. As we will show in detail, the excess energy of the solid mixtures are simple functions of the chain lengths, chain length differences and concentrations.
3. The distribution of the crystal defects is inhomogeneous with respect to the direction of the molecular axes. The main contributions arise from chain ends and their next neighbours which are segregated in boundary layers of the lamellae.

Comparing a classical thermodynamic treatment of infinite homogeneous phases to our approach, we find that we neglect the free energy of stacking lamellae in

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the direction of the molecular axes. The packing of two lamellae on top of each other will depend on the defect structure of their boundary layers. We expect that the coupling between the lamellae decreases when the number of defects increases and thus the average density in the boundary layers of the lamellae decreases. On the other hand the major part of the heat of fusion is delivered by cooperative van der Waals interaction energies lateral to the chain directions, which are proportional to the chain lengths.

In this paper we present a method of solving the system of transcendent equilibrium equations for a multicomponent melt and several coexisting multicomponent solid solutions. The computer computations start from a simple strict regular model of pair interaction for the interaction energies between molecules of different chain lengths in the solid state. Variations of the number of components in the system and the molecular weight distribution are used to show possibilities and limits of this physical model for the solid state of n-paraffin mixtures. If the experimental results obtained by calorimetric and X-ray methods are analysed carefully and compared to the theoretical predictions based on the computations of the thermodynamic equilibrium, a refinement of the model for the excess enthalpy in the solid state will be necessary and thus a deeper insight will be obtained into the structure of extended chain lamellae at equilibrium.

EQUATIONS OF STATE

In equations (1) and (2) the first approximations of the Gibbs free energies for the multicomponent solid solutions and the multicomponent melt are presented.

The Gibbs free energy of the solid phase (c = crystal phase) is given by:

$$G^{c}=\sum_{i=1}^{N^{c}} G_{0i}^{c}n_{i}^{c}+RT\sum_{i=1}^{N^{c}} n_{i}^{c}\ln(x_{i}^{c})+\left(\sum_{j,k=1}^{N^{c}} A_{jk}^{c}x_{j}^{c}x_{k}^{c}\right)\sum_{i=1}^{N^{c}} n_{i}^{c} \tag{1}$$

where N^{c} = number of components in phase c, n_{i}^{c} = number of moles of component i in phase c, $x_{i}^{c}=n_{i}^{c}/(\sum n_{j}^{c})$ = mole fraction of component i in phase c, A_{jk}^{c} = pair interaction parameter, G_{0i}^{c} = hypothetical free energy of component i in the solid state c at the same temperature and pressure as the solid solution.

The Gibbs free energy of the melt (m = melt) is given by:

$$G^{m}=\sum_{i=1}^{M} G_{0i}^{m}n_{i}^{m}+RT\sum_{i=1}^{M} n_{i}^{m}\ln(\Phi_{i}^{m})+G_{ex}^{m} \tag{2}$$

where M = number of components in the system, n_{i}^{m} = number of moles of component i in the melt, $x_{i}^{m}=n_{i}^{m}/(\sum n_{j}^{m})$ = mole fraction of component i in the melt, $\Phi_{i}^{m}=(y_{i}x_{i}^{m})/(\sum y_{j}x_{j}^{m})$ = volume fraction of component i in the melt (the volume of a CH_3 group equals approximately the volume of a CH_2 group) and G_{ex}^{m} = Gibbs excess free energy in the melt.

Thermodynamic studies of the binary liquid mixtures of hydrocarbons show that the excess free enthalpy G_{ex}^{m} depends in a complicated way on volume sensitive functions of the pure components as well as on an additional pair interaction function[8]. For n-paraffins with only small differences in chain lengths the influence of G_{ex}^{m} is rather small but increases non-linearly if the chain length difference increases[6,8,13]. Therefore the crystallization temperature of binary mixtures that form eutectic solid phases is governed only by G_{ex}^{m} compared to the free enthalpy of the ideal athermal mixture[6]. On the other hand, binary systems that crystallize as solid solutions are composed of n-paraffins of similar chain lengths and thus G_{ex}^{m} is very small. For these systems the pair interaction parameters A_{ij}^{c} in the solid mixture determine the main features of the phase diagrams. We choose an analytical formulation of the pair interaction energy, which introduces the relative chain lengths difference:

$$A_{ij}^{c}=\frac{2K|y_{i}-y_{j}|}{y_{i}+y_{j}} \tag{3}$$

where $K=K(T,p)$, T = temperature and p = pressure. This representation of the excess enthalpy parameter can be interpreted in terms of the crystalline structure of the solid solution. *Figure 1a* shows a two-dimensional sketch of a stack of lamellae. Each lamella is built from molecules of different lengths and is a representative part of the solid solution. If one assumes that the CH_3 end groups of the hydrocarbons are excluded from the lamellae cores, as indicated in *Figure 1b*, the density distribution perpendicular to the lamellae surfaces gives quite a good model for the interpretation of the excess enthalpy. By introducing the relative chain lengths difference, equation (3), we relate the defect energy of the interfacial layers (*Figure 1b*) to the total energy of the crystallized lamella. This seems to be a very suitable estimate and is supported by calculations of isobaric state diagrams of binary systems[6].

To summarize this discussion the excess enthalpy terms for melt and solid phases are represented as follows:

Melt

$$G_{ex}^{m}=\sum_{i,j} A^{m}\Phi_{i}^{m}\Phi_{j}^{m}\sum_{k} y_{k}n_{k}^{m} \tag{4}$$

Solid solution

$$G_{ex}^{c}=K(T,p)\sum_{i,j}\frac{2|y_{i}-y_{j}|}{y_{i}+y_{j}}x_{i}^{c}x_{j}^{c}\sum_{k} n_{k}^{c} \tag{5}$$

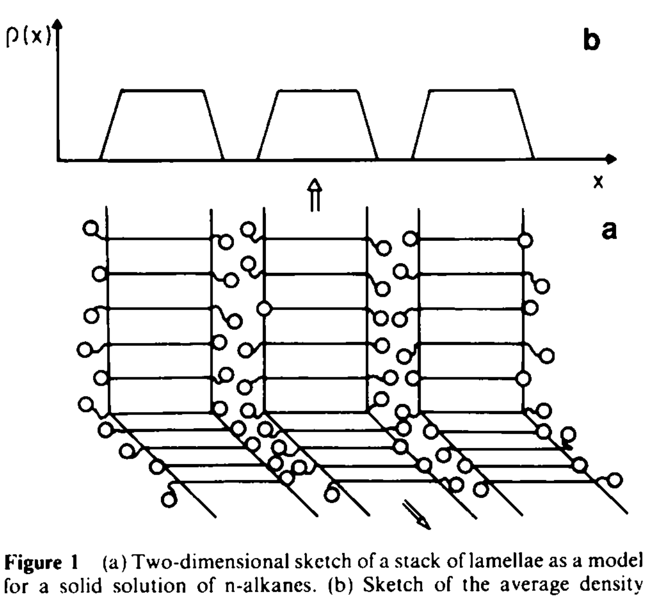

Figure 1 (a) Two-dimensional sketch of a stack of lamellae as a model for a solid solution of n-alkanes. (b) Sketch of the average density distribution in direction of the molecular axes

NUMERICAL CALCULATIONS, PHYSICAL BOUNDARIES AND CONSTRAINTS TO THE ALGORITHM

Calculations of the thermodynamic coexistence of melt and all possible solid phases are achieved by solving the set of transcendental equations:

$$\mu_i^{\mathrm{m}}(T,p)=\mu_i^{\mathrm{c}}(T,p) \tag{6}$$

where $\mu_i^{\mathrm{c}}=\partial G^{\mathrm{c}}/\partial n_i=$ chemical potential of component i in phase c. As N^{c} represents the number of components in the solid phase c the partial derivatives of the Gibbs free energies, according to equations (1) and (2), lead to N^{c} equations for phase c coexisting with the melt:

$$T\left[1-\frac{RT_i}{\Delta H_i}\ln\left(\frac{x_i^{\mathrm{m}}f_i^{\mathrm{m}}}{x_i^{\mathrm{c}}}\right)\right]-T_i\left[1-\frac{G_{\mathrm{ex},i}^{\mathrm{c}}}{\Delta H_i}\right]=0 \tag{7}$$

where T_i, $\Delta H_i=$ melting temperature and heat of fusion of the pure crystal phase containing only component i, $f_i^{\mathrm{m}}=$ activity coefficient for component i in the athermal melt given by:

$$f_i^{\mathrm{m}}=\frac{y_i}{\sum_j y_j x_j^{\mathrm{m}}}\exp\left(1-\frac{y_i}{\sum_j y_j x_j^{\mathrm{m}}}\right)$$

Interaction parameter $A^{\mathrm{m}}=0$ (equation (4)), and

$$G_{ex,i}^{\mathrm{c}}=\sum_{i>k}A_{ik}^{\mathrm{c}}(1-x_i^{\mathrm{c}})x_k^{\mathrm{c}}-0.5\sum_{k,1}A_{1k}^{\mathrm{c}}x_1^{\mathrm{c}}x_k^{\mathrm{c}}$$

The mole fractions x_i^{a} for each phase m and c are restricted by the boundary conditions:

$$\sum_i^{N^{\mathrm{a}}}x_i^{\mathrm{a}}=1 \tag{8}$$

for a = m, c . . . Equation (10) describes the conservation of the number of moles for each component i in the mixture with the help of the molar degree of crystallinity of the phase c.

$$w^{\mathrm{c}}=\frac{\sum_i^{N^{\mathrm{c}}}n_i^{\mathrm{c}}}{\sum_j^{M}n_j^0} \tag{9}$$

where $n_i^0=$ number of moles of component i in the system.

$$x_i^0=x_i^{\mathrm{m}}\left(1-\sum_{\mathrm{c}}w^{\mathrm{c}}\right)+\sum_{\mathrm{c}}x_i^{\mathrm{c}}w^{\mathrm{c}} \tag{10}$$

The numerical calculations can be supported by analytical expressions for T_i and ΔH_i, which describe how the thermodynamic functions of the pure systems i depend on chain lengths y_i[6,14,15]:

$$\Delta H_i=y_i\,\Delta H_{\mathrm{u}}(T) \tag{11}$$

$$\Delta H_{\mathrm{u}}(T)=\Delta H_{\mathrm{u}}(T_{\mathrm{A}})-\Delta c_{\mathrm{p}}(T_{\mathrm{A}}-T_i) \tag{12}$$

$$T_i=\frac{T_{\mathrm{A}}\left(1-\dfrac{2\sigma}{y_i\,\Delta H_{\mathrm{u}}}\right)}{1+\dfrac{RT_{\mathrm{A}}}{y_i\,\Delta H_{\mathrm{u}}}\ln(y_i)} \tag{13}$$

where $T_{\mathrm{A}}=$ limit T_i, i.e. asymptotic melt temperature, $\Delta c_{\mathrm{p}}=$ difference of the specific heats of the melt and the crystal and $\sigma=$ influence of the CH_3 end groups on the thermodynamic functions.

Usually the number of coexisting solid mixtures in the system is greater than one. The maximum number of different phases is given by Gibbs' phase rule. For each of these phases the set of unknown variables $\{x_i^{\mathrm{c}}, w^{\mathrm{c}}\}$ has to be calculated at a given coexistence temperature T, obeying the restrictions of the mass balance (equation (10)), which regulates the possible concentrations in the phases. Therefore the basic subroutine of the program is a procedure which minimizes the square of the double sum over c and i of equations (7) and (8). Routine E04KBF of the NAG-FORTRAN library was used in this work. This procedure requires the function values as well as the values of the first derivatives of the function with respect to the variables. As we have expressed the chemical potentials by analytical functions, we can derive them straightforwardly from equations (7) to (10).

The algorithm to compute the crystallization of an n-paraffin mixture is based on the following physical considerations.

Concentration range of a component in a solid solution

We restrict the concentration range of a component k of a solid solution to $0.01<x_k<=1$. A small amount of an additional component k in a solution ($x_k\approx10^{-3}$ or $x_k\approx10^{-4}$) will contribute to the entropy of mixing by $RTn_k\ln(x_k)$ and this exceeds the pair interaction energy even for fairly large A values. For mixtures with many phases this may lead to calculated concentrations of the components in the melt which deviate considerably from experimental values.

Concept for different solid phases

To keep the number of different solid solutions that coexist with the melt as low as possible, we look for mixed crystals which have a maximum number of components and consequently a maximum entropy of mixing. Furthermore it must be decided how to proceed in the case of a new solid phase developing, when the temperature T is reduced by an amount ΔT (refs 16, 17). The first step is to calculate whether all the existing solid solutions are stable at the lower temperature. If this is so we compute whether a new phase, which differs from the other solid phases by at least one component, can coexist. If a solid solution is not stable, the number of components of this phase is reduced and a new calculation of the set of phases is started. These results have to be controlled with respect to the 'contact rule for phase regions'[17]. We do not account for the problem of 'peritectic phases', i.e. phases composed of the same components differing only in concentration. These peritectic phases are formed when a solution is metastable with respect to the decay into two adjacent phases.

Order of crystallization of the components

The order in which the components take part in the crystallization processes is calculated from their 'hypothetical eutectic crystallization temperatures', which are obtained by calculating the coexistence temperature of a pure crystal of component i leaving the other components in the melt.

EXPERIMENTAL

The n-alkane mixtures were prepared by weighing the pure component n-alkanes (Humphrey Chemical Company, Connecticut, USA) with purities >97% for n-paraffins with more than 32 C atoms and 99% for shorter molecules. The mixtures were heated up to their liquid state and slowly cooled down, at 0.5 K min^{-1}, to room temperature.

The solid phase structure of the samples was investigated by differential scanning calorimetry (d.s.c.) and X-ray diffraction methods in dependence on temperature. From d.s.c. measurements, the Δc_p curve is proportional to $\mathrm{d}w^c(T)/\mathrm{d}T$, and the degree of crystallinity $w^c(T)$ is obtained by appropriately integrating the melting curve. The X-ray diffraction experiments were performed either with synchrotron radiation at DESY in Hamburg or at our laboratory using a Guinier de Wolff camera with CuKα radiation. The analysis of the X-ray diffraction pattern at diffraction angles in the range of $1° < \theta < 10°$ gives the long periods of stacks of lamellae. This means that whenever a solid solution phase is built by 'equivalent lamellae' stacked on top of each other, we obtain a long period which depends on the average lengths of the molecules within the lamellae and to a minor degree on the structure of the interfacial layers. The different solid solution phases of the mixtures can easily be distinguished by their different long periods. Interpreting the diffraction pattern in this simple way may lead to mistakes, because regions may exist where single lamellae of different average thicknesses are stacked in a random manner. This type of structure can be found, for instance, at eutectic mixtures of binary systems.

As the numeric calculations give very detailed information about the concentrations of each component in every phase at a given temperature, samples were crystallized isothermally using a filter device, shown in *Figure 2*. The crystals were separated from the melt by filtering under elevated pressure and then melt and crystals were analysed by gel permeation chromatography to obtain the concentrations of the components.

RESULTS

Neppert[18] studied a number of mixtures, selected to demonstrate that broad mixtures of n-alkanes fractionate into several solid solutions during crystallization. There are various published examples of this[19,20]. Structural properties of the solid solutions were best predicted by using a value of $K = 8000\ \mathrm{cal\ mol^{-1}}$ for the pair interaction parameter in the thermodynamic calculations. With this value the phases, which are stable at room temperature, and their compositions could be computed in good agreement with experimental results obtained from X-ray analysis. On the other hand, the calculated temperature dependences of the degree of crystallinities do not agree very well with the results from d.s.c. measurements.

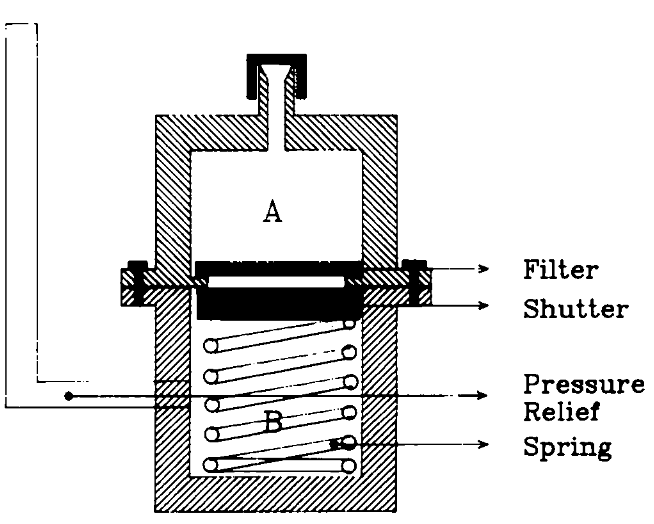

Figure 2 Diagram of spring-loaded filter device, used for isothermal crystallization of n-alkane mixtures

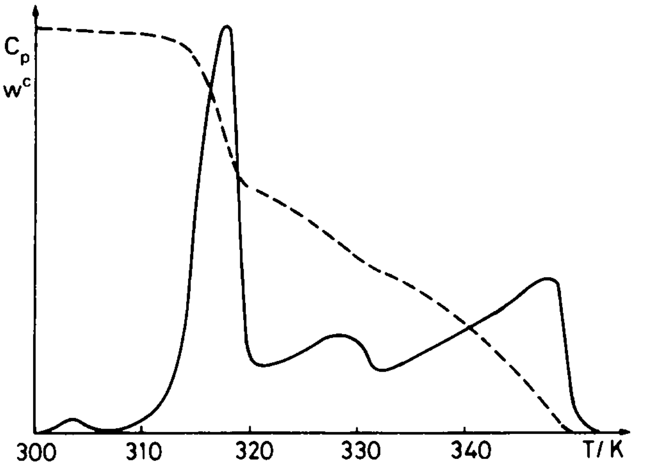

Figure 3 D.s.c. melting curve for n-alkane mixture M6 ( ). The composition is given in the text. $w^c(T)$ (- - -) is obtained by integrating the Δc_p curve stepwise

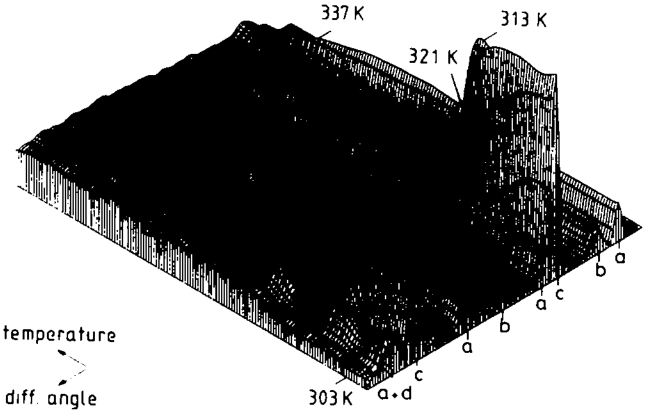

Figure 4 Small angle X-ray pattern of n-alkane mixture M6 and dependence on temperature as obtained with synchrotron radiation at DESY in Hamburg. a, b, c and d indicate different solid phases. The composition of M6 is given in the text

Motivated by these discrepancies we investigated two mixtures, one composed of six n-alkanes (M6) of equal weight, the second composed of seven n-alkanes (M7) of equal weight. The components for M6 are n-$C_{20}H_{42}$, n-$C_{22}H_{46}$, n-$C_{24}H_{50}$, n-$C_{32}H_{66}$, n-$C_{40}H_{82}$ and n-$C_{44}H_{90}$. The components for M7 are n-$C_{24}H_{50}$, n-$C_{26}H_{54}$, n-$C_{28}H_{58}$, n-$C_{30}H_{62}$, n-$C_{32}H_{66}$, n-$C_{36}H_{74}$ and n-$C_{40}H_{82}$.

Figure 3 shows the d.s.c. measurement and the related $w^c(T)$ curve for M6, while *Figure 4* shows the X-ray pattern of the mixture M6 and dependence on temperature. The measurements were obtained with synchrotron radiation at DESY in Hamburg. The evaluation of the long periods shows that up to four solid phases coexist in different temperature ranges: phase (a) solid solution of n-$C_{40}H_{82}$/n-$C_{44}H_{90}$; $T < 347$ K; phase (b) pure phase of n-$C_{32}H_{66}$; $T < 325$ K; phase (c) solid solution of n-$C_{22}H_{46}$/n-$C_{24}H_{50}$; $T < 313$ K; and phase (d) pure phase of n-$C_{20}H_{42}$; $T < 302$ K. Using a set of thermodynamic parameters for orthorhombic solid solutions of

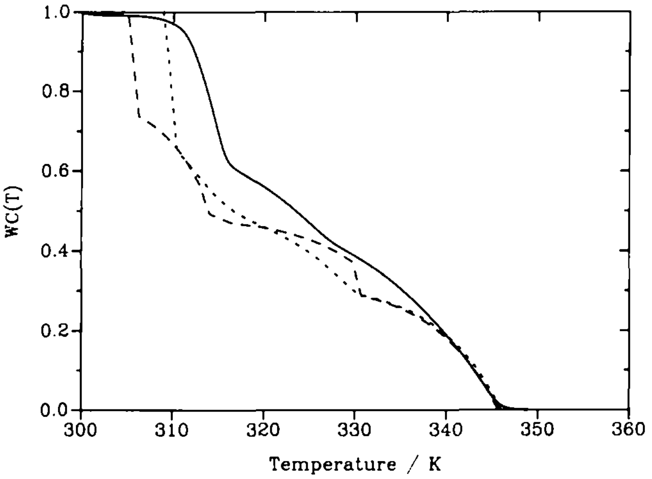

Figure 5 Comparison of the computed degree of crystallinity with experimental values (——) for mixture M6. The pair interaction energy $K = 5000$ cal mol^{-1} (– – –); $K = 3500$ cal mol^{-1} (- - -). The composition of M6 is given in the text

n-paraffins, $T_A = 415.3$ K, $\Delta H_u = 970$ cal mol^{-1}–CH$_2$–, $\Delta c_p = 1.4$ cal mol^{-1}–CH$_2$–, and $\sigma = 2800$ cal mol^{-1}–CH$_2$–, and a value of $K = 5000$ cal mol^{-1}, we compute that during crystallization in coexistence with the melt, just these four phases will develop. The calculated $w^c(T)$ for this curve is represented in *Figure 5* by the dashed trace. The dotted curve in *Figure 5* represents a computation with $K = 3500$ cal mol^{-1}. If we compare these theoretical approaches with the experimental result (the continuous curve in *Figure 5*) we observe that the calculation with $K = 3500$ cal mol^{-1} for the pair interaction energy resembles the main features of $w^c(T)$ in a better way than the graph with $K = 5000$ cal mol^{-1}. The main difference between the two theoretical predictions is that for $K = 3500$ kcal mol^{-1} a solid solution consisting of n-$C_{22}H_{46}$/n-$C_{24}H_{50}$/n-$C_{32}H_{66}$ coexists with the melt for temperatures up to 328.7 K, in contrast to the calculations with $K = 5000$ cal mol^{-1} where there is a pure solid phase of n-$C_{32}H_{66}$ in the temperature range up to 329.6 K followed by a binary solution of n-$C_{22}H_{46}$/n-$C_{24}H_{50}$ at 314 K. The ternary mixture ($K = 3500$ cal mol^{-1}) is stabilized by a greater entropy of mixing and thus $w^c(T)$ descends more smoothly to higher temperature. The temperature range of coexistence between melt and crystals extends over 40 K and the increasing temperature difference between calculated and measured degree of crystallinity is mainly due to neglecting an excess free enthalpy for the melt and a temperature dependence for $K(T, p)$ approximations, as discussed earlier.

For the mixture M6 it is found that in the temperature range of coexistence between melt and solid phases the pair interaction parameter K is approximately 3000–4000 cal mol^{-1}. At lower temperatures the pair interaction energy within the solid phases is increasing and therefore solid solutions formed at higher temperatures become unstable. The solubility for different long components within the solid phases is reduced. A hypothetical calculation in the temperature range of coexistence with the melt can account for the stable low temperature phases by taking K values of about 8000 cal mol^{-1}. These hypothetical calculations do not mirror the physical situation within the temperature range between solidus and liquidus.

The mixture M7 also demonstrates that a crystallized n-alkane mixture undergoes phase separation in the solid state. *Figure 6* shows a d.s.c. melting curve (continuous line) for a mixture kept at room temperature for 26 weeks after preparation of the sample. The second curve (dashed line) was obtained by crystallizing the sample with a cooling rate of 0.1 K min^{-1} in the d.s.c. apparatus. In the temperature range 310–325 K, solid phase transitions take place from the orthorhombic crystal phases to hexagonal 'rotator-phases'. These solid phase transitions are followed by melting processes in a temperature range 327–343 K. An interpretation of the melting processes for the tempered sample is quite difficult, because it is not clear which phases are in a hexagonal state and which phases are still orthorhombic crystals. The hypothetical calculations with an interaction energy parameter of $K = 8000$ cal mol^{-1} predict four solid phases for M7 at room temperature with the following long periods (LP): phase (a) two components n-$C_{36}H_{74}$/n-$C_{40}H_{82}$; LP = 5.0 nm; phase (b) two components n-$C_{26}H_{54}$/n-$C_{28}H_{58}$; LP = 3.61 nm; phase (c) four components n-C_{26}/n-C_{28}/n-C_{30}/n-C_{32}; LP = 3.95 nm; phase (d) pure phase n-$C_{24}H_{50}$; LP = 3.25 nm. These theoretical results agree very well with measurements of the long periods obtained with a Guinier de Wolff camera. The long periods *versus* temperature are represented in *Figure 7*.

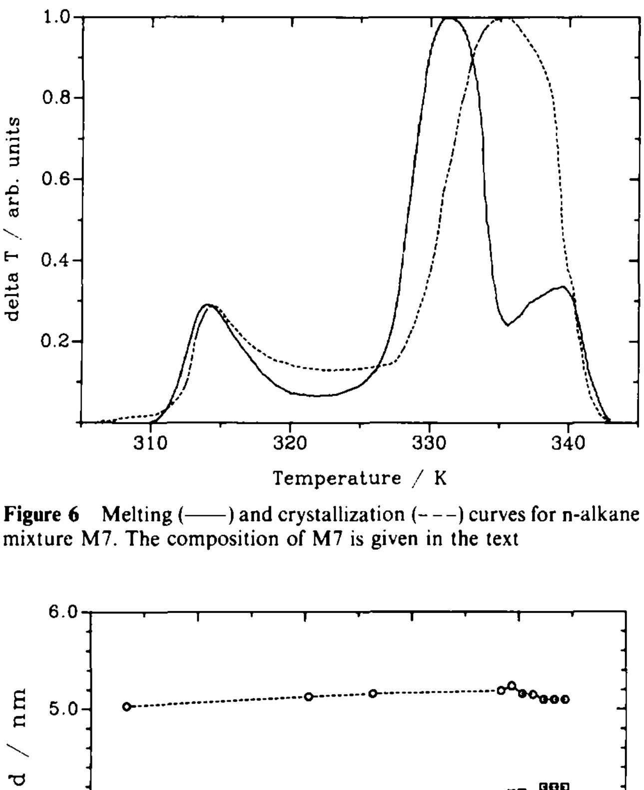

Figure 6 Melting (——) and crystallization (– – –) curves for n-alkane mixture M7. The composition of M7 is given in the text

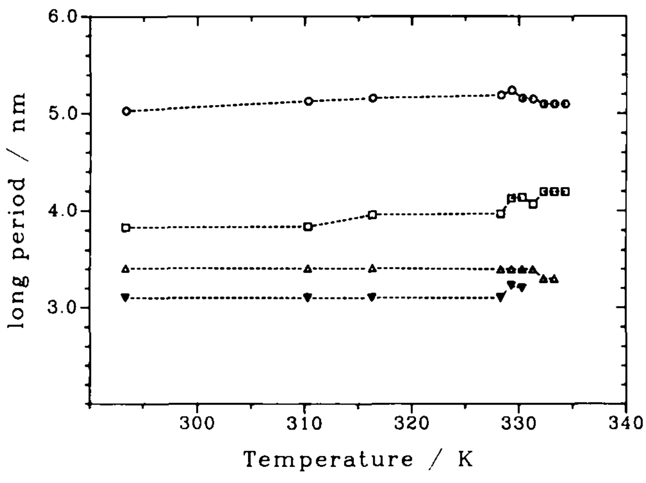

Figure 7 Long periods *versus* temperature for n-alkane mixture M7. The values were obtained from X-ray exposures in a Guinier de Wolff Camera. The composition of M7 is given in the text

The crystallization curve of the n-alkane mixture M7 (dashed curve in *Figure 6*) is now analysed by computer calculations, to find out which solid phases are built in coexistence with the multicomponent melt. *Figure 8* compares the experimental $w^c(T)$ of the crystallization processes with the calculation for a seven-component solid solution in the hexagonal rotator state, assuming a pair interaction energy of $K = 2000$ cal mol^{-1}. The thermodynamic parameters for the rotator phase are $T_A = 418.2$ K, $\Delta H_u(T_A) = 700$ cal mol^{-1} -CH$_2$-, $\Delta c_p = 1.4$ cal mol^{-1} -CH$_2$-, and $\sigma = 1280$ cal mol^{-1}.

This excellent agreement between experiment and theory encouraged us to investigate the crystallization process in more detail. As the computer calculations give all the concentrations in the phases at a certain temperature as well as the overall degree of crystallinity, a sample of the mixture M7 was crystallized isothermally. For this purpose the sample was heated in the pressure filter device (*Figure 2*) to 353 K, a temperature at which there is pure multicomponent melt. The temperature was then lowered to 336.1 K and the mixture was crystallized isothermally for 24 h. At the same temperature the crystal phase was separated from the melt by applying nitrogen gas with a pressure of 1 MPa, which opened the shutter and filtered the system.

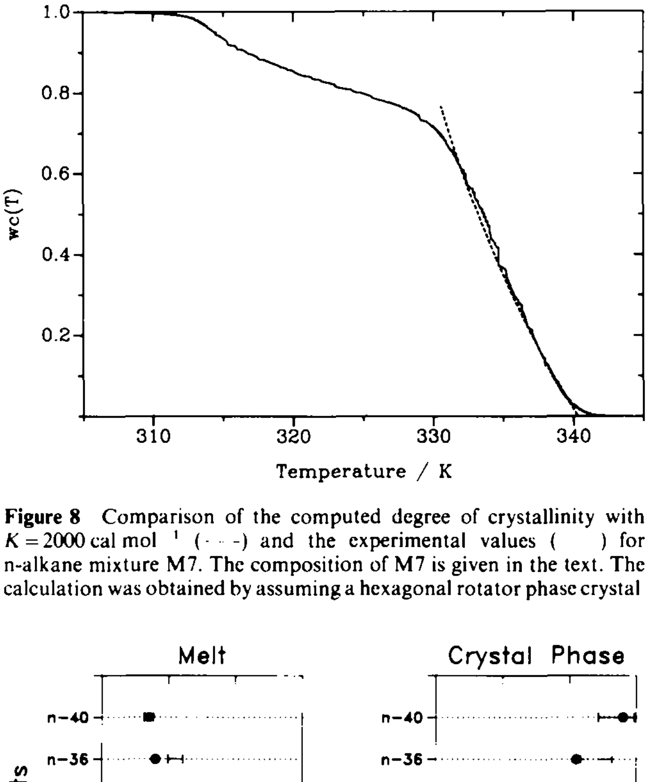

Figure 8 Comparison of the computed degree of crystallinity with $K = 2000$ cal mol^{-1} (- - -) and the experimental values ( ) for n-alkane mixture M7. The composition of M7 is given in the text. The calculation was obtained by assuming a hexagonal rotator phase crystal

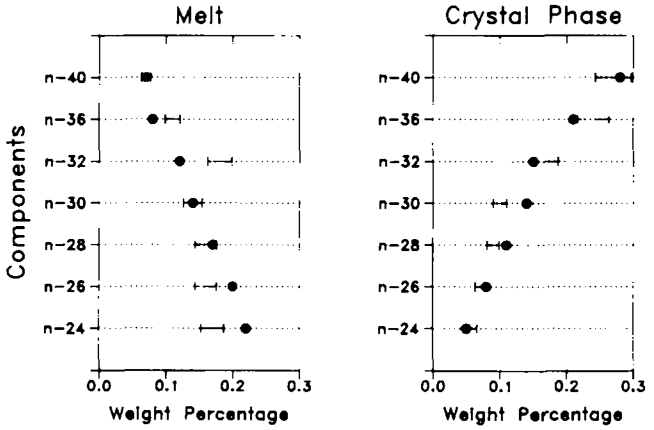

Figure 9 Composition of the melt and the crystal phase obtained by isothermally crystallizing n-alkane mixture M7 at 336.1 K. Solid symbols represent calculated values; bars indicate experimental values and errors as evaluated from g.p.c. analysis. The composition of M7 is given in the text

Both phases were analysed with respect to the concentrations of the components by means of g.p.c. with a relative experimental error of about 10%. *Figure 9* shows the concentrations of the components for the two phases. The solid symbols show the computed values while the bars show the experimental concentrations. From these comparisons we conclude that the n-alkane-mixture M7 crystallizes to a solid solution containing all seven components in a hexagonal rotator phase in the temperature range where the solid phase coexists with the melt. At temperatures of 320 310 K a solid phase transition to the orthorhombic crystal phase occurs. By cooling down, the solid mixture becomes unstable at lower temperatures and by diffusion processes in the solid state, rearrangement of the molecules into four solid phases is achieved.

CONCLUSIONS

The computations of the equilibrium crystallization process in n-alkane multicomponent multiphase systems give a deep insight into the energetic and entropic situation of the solid phases. The investigations into many multicomponent systems of n-paraffins show that the eutectoid behaviour of n-alkane systems is described by a pair interaction energy which is related to structural elements of the components, such as the chain lengths and the chain lengths difference of a pair of molecules. This concept seems to be very adequate for the n-alkane mixtures, because the interaction is a van der Waals type and is therefore an interaction of short range influence. The reduction of the excess energy $K\,\Delta y$ to the mean lengths of the molecules $\langle y \rangle$ describes the influence of the cooperative energy of the crystal lamellae. The solid solutions are stabilized by the entropy of mixing; the mutual dependence of increasing excess energy and increasing mixing entropy, by adding more components to the phase, leads to solid phases which are 'defect-saturated'. Unseld[21] showed that these systems have very interesting physical properties related to the longitudinal density distributions in the lamellae, which show pronounced differences to systems which are not defect-saturated. For all the defect-saturated phases, a value for the pair interaction energy of $K = 3500$ cal mol^{-1} described the equilibrium between melt and multicomponent solid phases sufficiently accurately.

Based on these results one can obtain theoretical predictions for defect-saturated phases with average chain lengths greater than 40 -CH$_2$- distances, a range where pure n-alkanes are no longer commercially available. The computations were carried out with the following inputs: the mixture consists of M n-alkanes, the lengths of the components differ by just one CH$_2$-group, and the fraction of weight is $1/M$. If one varies M, leaving the mean lengths of the M components unchanged, the calculations give the maximum value of chain lengths disparity Δy for a solid solution of M components with a pair interaction energy of $K = 3500$ cal mol^{-1}.

In *Figure 10* the dependence of $\Delta y/\langle y \rangle$ on $\langle y \rangle$ is represented. The curve shows that the miscibility of the components in the solid solutions leads to an asymptotic value of $\Delta y/\langle y \rangle = 0.36$. For numerical reasons it is not possible to extend the calculations to main chain lengths

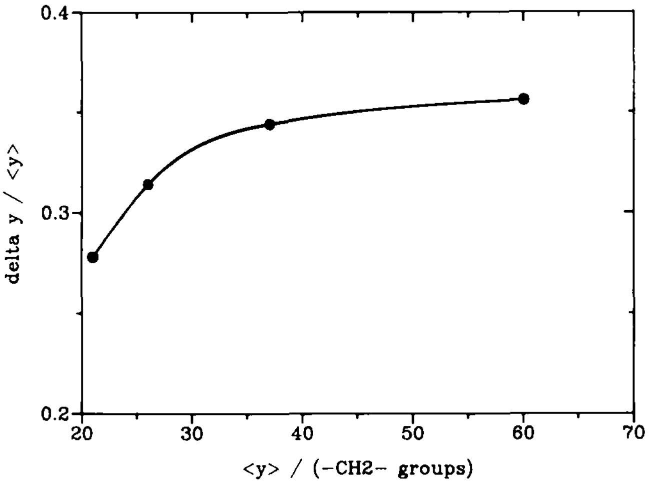

Figure 10 Theoretical computations for the miscibility $\Delta y/\langle y\rangle$ for n-alkane mixtures as a function of $\langle y\rangle$ using a pair interaction energy parameter of $K=3500$ cal mol^{-1}

of 100 -CH_2- groups or more, because then the number of different components in the phase becomes greater than 35–40.

As stated earlier in discussing the structures of mixtures M6 and M7, the miscibility of the components in the solid phases in the temperature range between liquidus and solidus is greater than at room temperature. Therefore $\Delta y/\langle y\rangle = 0.36$ is the maximum miscibility in the solid state. For low temperatures $\Delta y/\langle y\rangle$ must be reduced to values of 0.25–0.30 to describe the eutectoid features of multicomponent systems of n-alkanes.

Let us now reconsider the situation for predicting theoretically the low temperature solid phases. A correct analysis would start at the temperature range of coexistence between melt and solid phases. For temperatures below the solidus each solid phase must be analysed with respect to its stability, or the possible decay into neighbouring phases. Theoretical investigations of the determinants of the second derivatives $\partial^2 G/\partial n_i\,\partial n_j$ in dependence on the parameter K could describe this fractionation effect at low temperatures, when appropriate experimental data are available. In this way a list of $K(T)$ values would describe the phase diagrams of the multicomponent multiphase systems.

By taking a value of $K \approx 8000$ cal mol^{-1} for predicting the low temperature solid state, we transmit the low temperature structure to a temperature range of about 50 K above room temperature. Again the physical interpretation of the pair interaction energy is difficult, because the mutual dependence of defect energy and the entropy of mixing of the solid phases determine the composition of the phases. As the entropy of mixing is directly proportional to T and a non-linear function of the composition, $K = 8000$ cal mol^{-1} is an upper limit for the pair interaction energy. The corrections at lower temperature are about 20% or more. Nevertheless, the good agreement between theoretical predictions and experimental observations for a great number of n-alkane mixtures shows that the pair interaction energy increases continuously to lower temperatures. Abrupt changes in K must only be expected when solid phase transitions to and from the hexagonal rotator phase occur.

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