Summary of thesis

The traditional methods for the determination of liquid-solid phase diagrams of mixtures are based on the assumption that the overall equilibrium is established between the phases. Although these methods reveal valuable information about the phase behaviour and the mixing properties of the phases, one should realize that on a relevant time scale overall equilibrium will hardly be reached between the entire amounts of the solid and liquid phases. Typically, the result of the crystallization of a liquid mixture will be a non-equilibrium or metastable state of the solid. For a proper description of the crystallization process the equilibrium approach is practically insufficient. In Chapters 2 and 3, it has been shown that a kinetic approach is required for successful prediction of the state of the solid phase.

In Chapter 2, the slow crystallization of binary mixtures of 1,4-dichlorobenzene and 1,4-dibromobenzene was performed in the adiabatic calorimeter. For slow transition process that takes place at near equilibrium conditions, we could assume that the liquid phase was in equilibrium only with the growing solid phase, i.e., the solid phase at the surface. Then, the compositions of the liquid phase and the surface layer of the solid change along the liquidus and solidus lines of the equilibrium phase diagram. This assumption was quantitatively expressed in a kinetic model, which successfully reproduced the experimental enthalpy curve of the mixture, measured during slow cooling in the adiabatic calorimeter. The applicability of the introduced model was extended to a new method for the determination of the excess properties when the cooling path of the mixture was at disposal. In this way, the excess quantities can be obtained by using a relatively simple method, which basically requires only the knowledge of the cooling curve of the mixture. Finally, the phase diagram was achieved having the advantage over traditionally determined phase diagrams, in the sense that both excess enthalpy and entropy were derived without assuming complete equilibrium between totally homogeneous phases. However, this method is appropriate only for slow crystallization and it cannot be applied for conditions away from near-equilibrium, which often occur in the practice.

The crystallization mostly takes place at a certain degree of undercooling, i.e. at conditions well away from equilibrium. For the description of crystal growth at conditions far from equilibrium, the non-equilibrium or kinetic segregation has to be defined, by which the actual composition of the growing solid phase can be determined for the given composition of the liquid phase and temperature. The compositions of the growing solid, i.e. the kinetic segregation, may considerably deviate from that predicted by the equilibrium phase diagram. To study the crystallization of the mixture of 1,4-dichlorobenzene and 1,4-dibromobenzene at non-equilibrium conditions we designed an experimental set-up described in Chapter 3. The composition of the grown solid phase was measured by the gas chromatography and the results were compared to that calculated from the equilibrium and kinetic segregation model. Additionally, we took into account that the segregation induced composition gradients, as well as the temperature gradients in the liquid phase, allowing the properties of liquid phase near the solidification front to be different from those in the bulk. Thus, for the description of the crystallization process we included mass and heat transport limitations, which enabled the determination of so-called effective segregation. The experimental results, showing a reduced segregation, agreed very well with the solid compositions calculated from the proposed kinetic model, while the solid compositions predicted by equilibrium show too strong segregation. In this way, we have verified the performance of the kinetic model coupled with mass and heat transport limitations. These results show the effect of interfacial undercooling on the segregation during growth in mixed molecular systems. It appears that for the presented model system, this effect is still moderate. However, for molecular systems with higher melting entropy, such as fats, the effect of the interfacial undercooling will be considerably larger.

Triacylglycerols (TAGs) are the main constituents of edible fats and oils, which make the knowledge of their thermodynamic properties very important for food industry. These compounds exhibit polymorphism and thereby introduce complex phase behaviour in the food products. In Chapter 4, the thermal behaviour of different polymorphs of the three pure TAGs, being tristearin (SSS), tripalmitin (PPP) and trielaidin (EEE), was studied. A detailed thermal analysis of SSS and the investigation of its polymorphism were performed by means of adiabatic and differential scanning calorimetry. Specific heat capacities of the α- and β-polymorphic forms of SSS, together with the enthalpies of fusion and melting temperatures are reported and compared to the literature values. Additionally, we examined the fleeting existence of the β'-polymorph of SSS and its transformation to the β-phase under isothermal conditions in the DSC. The adiabatic data from melting of the β-polymorphs of SSS, EEE and PPP were used for the determination of their purities. The purities were calculated by two methods, both based on the assumption that the compound and impurity form a eutectic mixture. The results of these methods, for the first and the second melting of the compounds, show some discrepancies due to crystal imperfections in the β-polymorph formed after the first melting. Nevertheless, we concluded that the investigation of the phase behaviour of the binary mixtures of the mentioned TAGs would not be disturbed by the estimated amounts of impurities.

In Chapter 5, the thermal analysis of three binary mixtures of TAGs, being EEE-SSS, EEE-PPP and PPP-SSS, was performed in the DSC and the adiabatic calorimeter. The phase diagrams of the β-polymorph of the mixtures were constructed using the DSC data obtained from slow cooling of the melts and subsequent melting of the formed solid phases. In all three binary mixtures the miscibility of the components is very limited in the most of the composition range. For the EEE-SSS system, the SSS-rich mixtures form solid solutions. The components EEE and PPP do not co-crystallize in a solid solution over the whole composition range. However, it was difficult to draw definite conclusions on the miscibility in the EEE-rich mixtures, since they did not crystallize in the most stable polymorph during slow cooling. Regarding the PPP-SSS mixture, the β-polymorph yields a typical eutectic phase diagram with some mixing in the regions close to the pure components. The β-polymorph of the diluted mixtures, formed in the DSC by the re-crystallization of a less stable polymorph, was in the state of solid solutions. On the other hand, the β-polymorph of SSS-rich mixtures, obtained by slow cooling in the adiabatic calorimeter, showed limited miscibility of the components. Apparently, the miscibility of the components is enhanced when the β-polymorph is formed by the re-crystallization. These results demonstrate the impact of the kinetics on the mixing properties of the β-polymorph.

Finally, the solid states of the mentioned TAG mixtures, formed during fast cooling of the melts in the DSC, were discussed. The results show a remarkable difference between the samples containing the unsaturated EEE component and the PPP-SSS mixture. In the latter sample, the α-polymorph was easily obtained for high cooling rates, whereas for the mixtures containing EEE only part of the sample crystallized in the α-form. An explanation of this behaviour could be that the mixing in the α-polymorph is not ideal for the EEE containing samples, due to the significant structural differences in the molecular shapes of the saturated and the unsaturated TAG component.