Metastability in solid solution growth

Marija Matovic[a,*], J.C. van Miltenburg[a], Jan Los[b]

[a]*Chemical Thermodynamics Group, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands*
[b]*RIM Laboratory of Solid State Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands*

Abstract

Crystallization of binary mixtures of 1,4-dichlorobenzene and 1,4-dibromobenzene is examined in an adiabatic calorimeter. First heated to 380 K under adiabatic conditions and thus transformed into a binary melt, the mixture was slowly cooled to 250 K. The experimental cooling curves (the recorded change of mixture's temperature with time) obtained for the various compositions of the issued mixture, served for the specification of enthalpy change of the mixture during crystallization. In order to demonstrate the importance of the kinetics during an even slow crystallization process, the experimental data will be interpreted in terms of a kinetic model as opposed to the traditionally used equilibrium approach. We will show that kinetic model can serve for the derivation of excess parameters that characterize the degree of mixing in the phases.
© 2004 Elsevier B.V. All rights reserved.

1. Introduction

The formation of a solid phase from a multi-component liquid mixture is still not completely described and understood, thus being the subject of many investigations. The equilibrium approach does not describe the solidification as a kinetic process nor it is able to characterize properly the formed crystalline state. Regarding the equilibrium access to this problem, for a given composition of a mixed system, at fixed pressure and temperature, the composition of the equilibrated phases is determined by the minimum of their Gibbs free energies. This approach excludes any deviations from the homogeneous state of phases that can arise from the kinetics of the crystallization process and very slow diffusion rates in the solid phase.

The first step toward an approach beyond total equilibrium is to assume local equilibrium between the liquid phase and the surface of the solid during crystallization. Clearly, the assumption may be valid only for low cooling rates and thus for slow

*Corresponding author. Fax: +31 30 253 3946.

E-mail address: m.matovic@chem.uu.nl (M. Matovic).

solidification processes. However, as shown in this work, this assumption will still lead to a non-homogeneous solid phase containing the composition gradients in its volume. In other words, if we neglect completely the very slow diffusion rates in solid phase, the final state within a reasonable timescale will not be the equilibrium state.

Both in the equilibrium and kinetic picture, the final state of a solid phase will depend on the degree of mixing of components present in each phase. In that sense, the crucial property of a mixture is its excess energy, giving the deviation from ideal mixing of the components in the phase. A system of any composition with high miscibility of components exhibits lower excess energy and will form solid solution, while for an eutectic mixture miscibility in the solid phase is limited corresponding to higher excess energy. Usually, the kinetics favours mixing as it was shown in Ref. [1]. Here, we explore the possibility of finding the excess parameters from a kinetic modeling of a crystallization process in an adiabatic calorimeter.

2. Experimental procedure

The subject of our investigation is the binary mixture of 1,4-dichlorobenzene and 1,4-dibromo-benzene whose behaviour during heating and melting in an adiabatic calorimeter was previously examined [2]. For the calculation of an isobaric phase diagram, a computational method [3] that fits the experimental liquidus points was used and is based on the concept of the Equal-G Curve [4], yielding the difference between the excess energies of the mixed phases. As an input, the method requires the thermodynamic properties of the pure substances and the excess energy for at least one of the phases. The excess energies for the liquid and the solid phase of the binary mixture of our interest, experimentally determined in Ref. [2], were employed in the computation of the equilibrium phase diagram for issued components, which demonstrates their high miscibility in the liquid as well as in the solid phase. However, the experimental data were interpreted within the equilibrium approach while, here, we propose a kinetic interpretation of the data obtained during the cooling of the mixture under controlled conditions.

Cooling and heating of the issued mixture were performed in the adiabatic calorimeter VII [5] by regulating the temperatures of a wire heater and shields to relevant values with respect to the vessel temperature (Fig. 1). The vessel containing a mechanical mixture (ca. 5 g) of a known
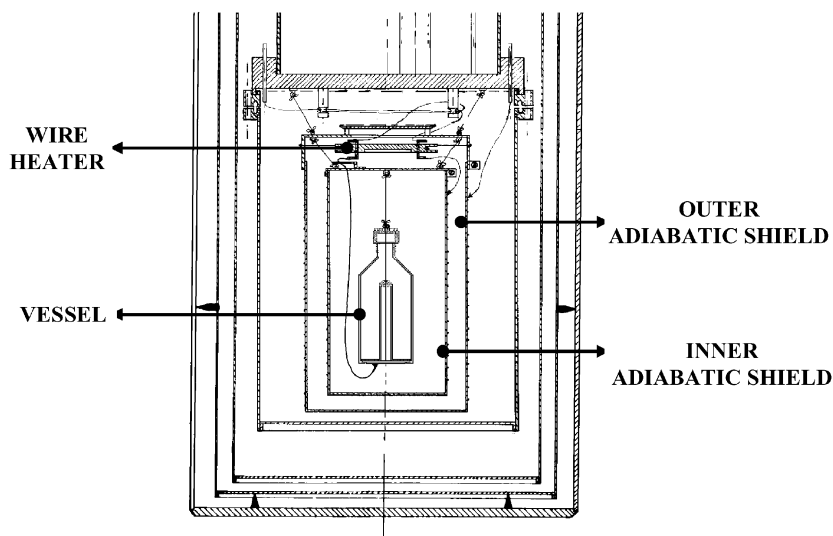

Fig. 1. Sketch of the sample container in the adiabatic calorimeter.

composition is first heated to 380 K and thus the mixture is slowly brought to the liquid phase. The measuring protocol, introduced in Ref. [6], is applied upon the controlled adiabatic heating and it allows determination of the heat capacity of vessel and its contents.

By setting the temperature of the system's surroundings, consisting of the wire heater and two adiabatic shields, to appropriate values, the cooling of the homogeneous melt is performed under an average cooling rate of $\sim 0.1\,\mathrm{K/min}$. The solid material, formed during such a slow cooling, was afterwards melted in the heating mode of the calorimeter, providing the heat capacity of vessel and mixture as a function of temperature.

In the cooling mode of the calorimeter, the heat transfer from the system to its surroundings is the only heat flow that causes the enthalpy change of the system

$$dH_{\mathrm{system}} = d(H_{\mathrm{vessel}} + H_{\mathrm{mixture}}) = \dot{Q}_{\mathrm{cool}}\,dt, \qquad (1)$$

where H_{system}, H_{vessel} and H_{mixture} are the enthalpies of system, vessel and mixture, respectively.

The cooling power of the apparatus ($\dot{Q}_{\mathrm{cool}}$) as a function of system's temperature is obtained from the values of system's heat capacity ($c_{\mathrm{p,sys}}$) measured in the heating mode and the recorded temperature change of the system during its cooling (dT_{sys}/dt), by using the following expression but only for the temperature domains where the mixture is either completely in the solid or in the liquid phase, actually where the heat capacities during heating and cooling should be equal:

$$\dot{Q}_{\mathrm{cool}} = c_{\mathrm{p,sys}} \frac{dT_{\mathrm{sys}}}{dt}. \qquad (2)$$

Since the heat is withdrawn from the system to the shields by mechanism of radiation and by conduction via the wire heater, the calculated values (Eq. (2)) are fitted in an expression that is a sum of radiation and conduction heat terms:

$$\begin{aligned}(\dot{Q}_{\mathrm{cool}})_{\mathrm{fit}} &= \dot{Q}_{\mathrm{radiation}} + \dot{Q}_{\mathrm{conduction}} \\ &= q_1(T_{\mathrm{sys}}^4 - \Delta T^4) + (q_2 + q_3 T_{\mathrm{sys}}), \qquad (3)\end{aligned}$$

where ΔT is the difference in temperatures of the system and the inner adiabatic shield, being set to 10 K during the cooling experiments.

Eventually, Eq. (1) reproduces the enthalpy path of the system (vessel and mixture) during cooling under the given conditions. From an experiment done previously in order to calibrate the calorimeter, the enthalpy path of the empty vessel is known for the temperature range of our interest. Now, we can specify the enthalpy path for each mixture as a product of controlled cooling by applying the simple relation

$$H_{\mathrm{mixture}}(T) = H_{\mathrm{system}}(T) - H_{\mathrm{vessel}}(T). \qquad (4)$$

3. Experimental results and qualitative interpretation

The enthalpy, as a function of temperature obtained from the cooling data for mixtures of different compositions, are presented in Fig. 2, together with the corresponding enthalpy paths obtained from heating. Obviously, the kinks in the cooling curves, indicated as points 0 and 1, are typical for the cooling process of all investigated mixtures. Their temperature values, being dependent on the composition of mixture, are presented in Table 1.

The registered rise of temperature from point 0 indicates the onset of crystallization by nucleation and subsequent fast crystal growth. Apparently, point 0 corresponds to a thermodynamically unstable state of liquid phase. At this point, the temperature of the liquid mixture of a particular composition z is far below the equilibrium
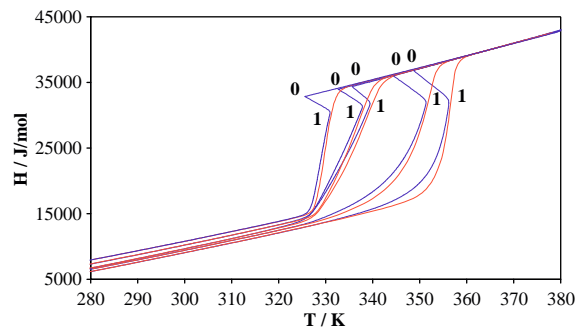

Fig. 2. Enthalpy path for mixtures of different compositions obtained upon heating (dashed line) and cooling (solid line) of the mixtures in the adiabatic calorimeter.

Table 1
Experimental values of nucleation and equilibrium temperature

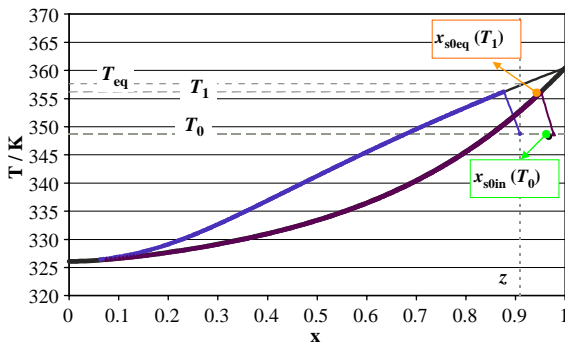| Mixture	n/mol	x_2	T_0/K	T_1/K
1	0.02944	0.2937	325.537	330.932
2	0.02667	0.4791	332.641	337.808
3	0.02077	0.5338	335.622	339.435
4	0.02300	0.7976	344.306	351.329
5	0.02055	0.9089	348.653	356.193

Fig. 3. Crystallization path for the mixture of overall composition z schematically presented in the phase diagram from Ref. [2].

temperature, T_{eq} (see Fig. 3), i.e. the liquid phase is highly undercooled and thus supersaturated [7].

Let us now refer to a cooling trajectory for the melt of overall composition z, constructed in the already determined phase diagram [2] by employing the corresponding values of T_0 and T_1 (Fig. 3). The relatively high heat flow, evolved along path 0–1 due to the fast initial crystallization, causes the temperature increase of the system under adiabatic conditions. Therefore, the undercooling decreases until the point 1 is reached. For the onward crystallization from T_1, accompanied by the registered gradual temperature fall, it may be assumed that the remaining liquid is in near equilibrium with the surface of solid phase, i.e. the solidification front. In other words, for this second part of crystallization where the growth of solid phase is apparently slower than along path 0–1, we assume the composition of the liquid phase is changing along the equilibrium liquidus while, correspondingly, the composition of solid that grows on the surface follows the equilibrium solidus on further cooling of the system (see Fig. 3). Clearly, neglecting the diffusion in the

solid phase, in the end the solid phase will be inhomogeneous with the last-grown solid portion being richer in 1,4-dichlorobenzene as compared to the first-grown part of solid. On behalf of the latter, the investigation of mixed crystals of the issued components by Raman effect [8] illustrates their distribution along the length and diameter of the single crystal, showing that the concentration of 1,4-dichlorobenzene increases in direction from the centre to the periphery of the crystal.

The above qualitative analysis provides the basis for a quantitative kinetic approach as opposed to the traditionally used equilibrium approach, which assumes overall equilibrium at each moment during the cooling process.

4. Kinetic model. Determination of excess parameters

From the experimental values of the enthalpy of the mixture, obtained from the cooling experiment, we can evaluate the Gibbs free energy of the mixture at each temperature by

$$G_{mix}^{exp}(T) = H_{mix}^{exp}(T) - TS_{mix}^{exp}(T), \tag{5}$$

where $S_{mix}^{exp}(T)$ follows from the thermodynamic integration, assuming that the process takes place reversibly:

$$S_{mix}^{exp}(T) = S_{mix}^{exp}(T_1) + \int_{T_1}^{T} \frac{c_{pmix}^{exp}}{T}\,\mathrm{d}T. \tag{6}$$

At a given temperature of an isobaric crystallization from a melt, the Gibbs free energy of mixture is calculated from

$$G_{mix}^{calc}(T) = lG_{liq}^{calc}(T) + sG_{sol}^{calc}(T), \tag{7}$$

where l and s are the molar amounts of liquid and solid phase, respectively.

The calculated Gibbs free energies of the liquid phase, G_{liq}^{calc}, and that of the solid phase, G_{sol}^{calc}, depending on their compositions (x_{liq}^{eq}, $x_{sol,av}$) and the excess properties (G_{liq}^{exc}, G_{sol}^{exc}), are given by

$$G_{liq}^{calc}(T) = (1 - x_{liq}^{eq})G_1^{liq} + x_{liq}^{eq}G_2^{liq} + G_{liq}^{exc}, \tag{8}$$

$$G_{sol}^{calc}(T) = (1 - x_{sol,av})G_1^{sol} + x_{sol,av}G_2^{sol} + G_{sol}^{exc}. \tag{9}$$

In the latter equations, G_1^{liq} and G_2^{liq} stand for the Gibbs free energies of pure components 1 and 2 in the liquid phase, while G_1^{sol} and G_2^{sol} are their free energies in the solid phase. According to our previous assumptions, on a relevant timescale, only the surface of the formed solid phase is in (near) equilibrium with the remaining liquid phase, while the composition gradients in the solid bulk pursue to exist.

The excess energy of a phase, being not significantly dependent on the temperature, typifies the mixing behaviour of components in the phase and is commonly expressed as an expansive function of the component's mole fraction x in a binary mixture [9]

$$G_P^{\text{exc}} = x(1-x) \sum_i A_i (1-2x)^{i-1}, \quad i = 1, 2, \ldots .$$
(10)

Our aim is to obtain parameters A_i by fitting the experimental data in a kinetic model in line with the above assumptions regarding the mechanisms of solid formation. This model is based on constrains imposed by energy balance (Eq. (1)) which, during crystallization of the mixture when the heat is released due to the phase transition, can be written as

$$c_{\text{p,vessel}} \, \text{d}T + c_{\text{p,mixture}} \, \text{d}T + \text{d}H_{\text{trans}} = \dot{Q}_{\text{cool}} \, \text{d}t.$$
(11)

Additionally, at each time during crystallization the mass balance has to be obeyed:

$$(1-s)x_{\text{liq}} + sx_{\text{sol,av}} = z,$$
(12)

where z is the overall composition of the mixture.

All the required thermodynamic properties of the two components in question are taken from Ref. [2]. Furthermore, the excess free energy of the liquid phase is taken as equal to zero, which can be accomplished by an appropriate choice of the zero level of energy. Note that the relevant quantity for the phase behaviour is the difference in the excess free energy for the liquid and solid phase, which is not affected by a shift of the origin.

For our calculation of the evolution of the enthalpy of the mixture during crystallization, we first have to determine the amount of solid phase formed along path 0–1 and its average composi-

tion. This initial crystallization occurs at conditions not close to equilibrium, and therefore the segregation during this part of the crystallization may deviate from the equilibrium segregation. In other words, the composition of the growing solid phase is generally not lying on the equilibrium solidus in a phase diagram, but its determination requires a non-equilibrium approach that enables the calculation of the so-called kinetic phase diagram [10]. Here we adopt the approach described in Ref. [1], which is based on linear non-equilibrium thermodynamics, to calculate the composition of the first-grown solid phase $x_{s0\text{in}}$ at T_0 (see Fig. 3). Nevertheless, in accordance with our assumption given above, we know that the solid phase that is growing at T_1 is in (near) equilibrium with the remaining liquid phase, and thus has the corresponding equilibrium composition $x_{s0\text{eq}}$. Therefore, the composition of the initial solid portion ($x_{s0\text{av}}$), formed between T_0 and T_1, is taken as the average value of $x_{s0\text{in}}$ and $x_{s0\text{eq}}$. The results of modeling path 0–1 for all investigated mixtures are presented in Table 2.

From T_1, the calculated enthalpy is fitted to the experimental cooling path consistently with the given energy and mass balance equations. As a result, we obtain two dimensionless excess energy parameters g_{12} and g_{21} for each mixture, which characterize the excess free energy of the final solid phase $G_{\text{sol}}^{\text{exc}}$ of overall composition z, by

$$G_{\text{sol}}^{\text{exc}} = RT_{\text{av}}x(1-x)(g_{21}(1-x) + g_{12}x),$$
(13)

where T_{av} is the average value of the melting temperatures of the two components.

The values of the obtained excess parameters and the excess free energy of the solid phase calculated from Eq. (13) are given in Table 3 for

Table 2
Results from model applied to the crystallization path 0–1

x_2	s_0	$x_{s0\text{av}}$	$x_{s0\text{eq}}$	$x_{\text{liq,eq}}$
0.2937	0.1892	0.41564	0.41557	0.28115
0.4791	0.1973	0.67400	0.67307	0.45822
0.5338	0.1809	0.74326	0.74111	0.51235
0.7976	0.2794	0.90559	0.90003	0.75902
0.9089	0.3240	0.95870	0.95483	0.88151

the overall compositions of the investigated mixture.

For clarity, we present in Fig. 4 the results only for the mixture of overall composition $z = 0.7976$, while the same observations reported below in the text apply to all investigated compositions of the given mixture. Namely, the enthalpy curve that fits best the experimental cooling path, in the temperature range from the relevant T_1 to the fixed temperature where the mixture is completely in the solid phase, is shown in Fig. 4. Moreover, the calculated path corresponds to a certain set of excess parameters obtained from the fitting procedure. For the known values of excess parameters, the kinetic model calculates the enthalpy of the mixture of a given overall composition during crystallization, with respect to the relevant energy and mass balance (Eqs. (11) and (12)). The integration of the mixture's enthalpy from the appropriate T_1 is done by following the equilibrium compositions of the phases at each temperature, but assuming that the solidification front is in equilibrium with the remaining liquid, as

opposed to the assumption that the equilibrium between the bulks of the phases is reached. To illustrate the reliability of the kinetic modeling, the cooling paths obtained from the kinetic and equilibrium approach for the known excess parameters, as determined in Ref. [2], are also given in Fig. 4. Note that the kinetic enthalpy path, even not being produced with our excess parameters, shows quite a satisfactory agreement with the experimental cooling path, while the equilibrium approach obviously cannot describe the crystallization process properly.

So, despite our assumption that the evolution of the solid phase from T_1 happened in the conditions close to equilibrium, the total equilibrium was not reached, since low values of diffusion coefficient in the solid phase [11] do not allow the whole bulk of solid to become homogeneous on a relevant timescale. Consequently, the final product of an even slow crystallization process, as demonstrated here, is a metastable state of the solid phase, containing composition gradients.

The affirmation of the kinetic approach suggests that it is justifiable to use the proposed kinetic model for providing the excess parameters needed for the calculation of the phase diagram. In other words, we can come to the phase diagram without relying on unjustified assumption that the system is in equilibrium during crystallization of a liquid mixture as compared to traditional methods for their determination. For that purpose, we derive the excess parameters A_i by fitting the values of excess free energy of the solid phase (Table 3) in the two-parameter and three-parameter expansive form (Eq. (9)). The calculated phase diagrams are presented in Fig. 5 together with one from Ref. [2].

The similarity in shapes of our and equilibrium phase diagram [2], both obtained by using two excess parameters, suggests almost the same phase behaviour during the formation of mixed crystals. In that sense, it seems that both approaches will always lead to the similar excess properties of the final solid phase. The latter could be valid only for enough slow crystallization processes, which in our case can be taken as a possibility, for we determine the excess property of the solid phase formed under low cooling rates. However, the more quality fit of excess free energies is achieved by

Table 3
Excess parameters and the excess Gibbs energy of solid phase

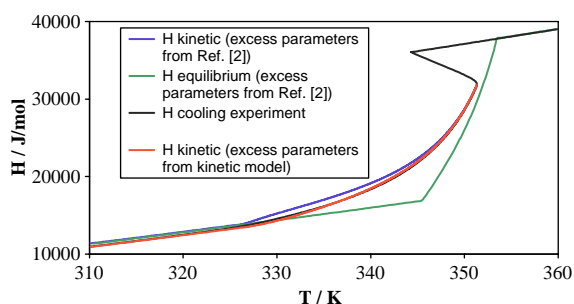| x_2	g_{12}	g_{21}	g_{sol}^{exc}
0.2937	0.5169	0.5362	0.1101
0.4791	0.6045	0.5811	0.1478
0.5338	0.7393	0.6947	0.1788
0.7976	0.5226	0.4139	0.0808
0.9089	0.4954	0.0528	0.0377

Fig. 4. Enthalpy paths during cooling of the mixture of overall composition $z = 0.7976$, obtained from the kinetic and equilibrium approach by using appropriate excess parameters.
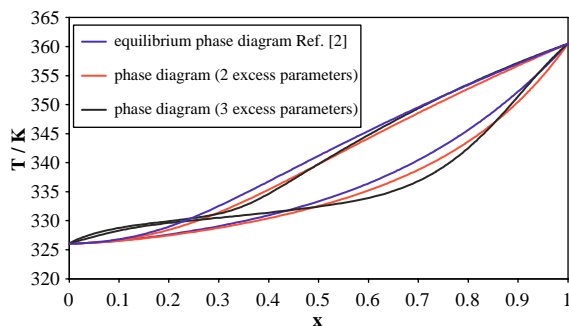
Fig. 5. Comparison of the phase diagrams obtained by excess parameters from the equilibrium [2] and the kinetic approach.

using the three-parameter expansion that approves the validity of the corresponding phase diagram. The significant deviation in the shape of the three-parameter phase diagram comparing to the other two, that occurs for the compositions of the mixtures corresponding to higher concentration of 1,4-dichlorobenzene, still requires more experimental data in the relevant composition range. That would lead to the more accurate determination of the excess parameters, while there are also indications that the fitting procedure could be more adequately performed. Furthermore, one should be careful when using only two excess parameters for the determination of the phase diagram, since by doing so it is possible that some limitations are brought into the complete under-

standing of the phase behaviour and thus the accuracy of the computed phase diagram is doubtful.

References

[1] J.H. Los, et al., Metastable states in multicomponent liquid–solid systems I: a kinetic crystallization model, J. Phys. Chem. B (2002) 106.

[2] P.R. van der Linde, Molecular mixed crystals from thermodynamic point of view, Thesis, Utrecht University, 1992.

[3] J.A. Bouwstra, Thermodynamic and structural investigations of binary systems, Thesis, Utrecht University, 1985.

[4] H.A.J. Oonk, Phase Theory: The Thermodynamics of Heterogeneous Equilibria, Elsevier, Amsterdam, 1981.

[5] J.C. van Miltenburg, H.A.J. Oonk, Heat capacities and derived thermodynamic functions of 1-Octadecanol, 1-Nonadecanol, 1-Eicosanol and 1-Docosanol between 10 K and 370 K, J. Chem. Eng. Data 46 (2001) 90–97.

[6] J.C. van Miltenburg, A.C.G. van Genderen, G.J.K. van den Berg, Design improvements in adiabatic calorimetry—the heat capacity of cholesterol between 10 and 425 K, Thermochim. Acta 383 (1998) 13–19.

[7] P.G. Debenedeti, Metastable Liquids—Concept and Principles, Princeton University Press, Princeton, NJ, 1996.

[8] M.A. Korshunov, Distribution of component molecules in *p*-dibromobenzene–*p*-dichlorobenzene solid solutions from Raman effect data, Crystallography Reports 48 (2003) 3.

[9] O. Redlich, A.T. Kister, Ind. Eng. Chem. 40 (1948) 345.

[10] Z. Chvoj, J. Sestak, A. Triska, Kinetic Phase Diagrams, Elsevier, Amsterdam, 1991.

[11] P.A. Reynolds, Disorder in the crystal structures of paradichlorobenzene, Molecular Phys. 29 (2) (1975) 519–529.