Two-component phase diagram and the determination of the eutectic composition of dimethyl terephthalate (DMT) and benzoic acid

**Introduction**

The regions in which the various phases of a binary mixture are in equilibrium can be described by a so-called two-component phase diagram in which the temperature is plotted as a function of composition. The term eutectic melting diagram is also used if we are dealing with solid-liquid transitions. There are in fact 12 different basic types of two-component melting diagrams (see for example [1]). In practice, however, we often encounter eutectic systems whose two-component phase diagrams are of the type shown schematically in Figure 1.

**Two-component phase diagrams from DSC measurements**

These types of two-component phase diagrams can be determined by DSC measurements. To do this, samples containing mixtures of the two substances in different ratios are prepared and measured by DSC. Points on the liquidus line are determined.

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**Figure 1:** Below the solidus line both substances exist in separate crystalline forms in the solid state. If the temperature of a mixture of the two components is slowly raised, a portion of the sample melts at the melting point of the eutectic. In this liquid mixture phase, either pure A or pure B in the solid state is also present depending on whether one is on the left or the right side of the eutectic composition. On further heating, the remainder of the solid phase melts until finally the whole sample has completely melted at a temperature corresponding to the initial composition of the mixture \( x_B \). Above the liquidus line there is only one phase (homogeneous melt).

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Fig. 2. DSC curves of different mixtures of DMT and benzoic acid. The benzoic acid content is given in units of mole percent.

Fig. 3. Determination of the eutectic composition of DMT and benzoic acid.

Fig. 4. Two-component phase diagram of DMT and benzoic acid.

by measuring the clear melting points of the different samples and plotting these as a function of the composition of the sample. The clear melting point (the temperature at which melting is complete) corresponds approximately to the temperature of the maximum of the second peak, i.e. the melting peak of the pure (main) component.

These types of measurements can also be used to determine the eutectic composition: the heat of fusion of the eutectic melting peak is plotted against composition and the eutectic composition obtained by extrapolation. This is appreciably more accurate than extrapolating the nonlinear liquidus temperatures. In this way, the melting point of the eutectic (solidus line) and an additional point of the two-component phase diagram have been determined.

Results
This method is illustrated in Figures 2 to 4 using the system dimethyl terephthalate (DMT) and benzoic acid as an example. Figure 2 shows the DSC curves for various mixtures with different ratios of DMT and benzoic acid. As expected, the eutectic always melts at the the same temperature. The heat of fusion of the eutectic peak is however different in each case because of the different sample compositions. The plot of the heats of fusion of the eutectic peaks against sample composition (Fig. 3) yields a value of 72 mol% for the eutectic composition. The two-component phase diagram of DMT and benzoic acid can then be plotted from the melting points of the peaks (see Fig. 4).

Measurement parameters
Module:
DSC 821e, stationary air atmosphere
Temperature program:
70 °C to 160 °C at 5 K/min
Sample weights:
between 4 mg and 8 mg

References