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A METHOD TO DETERMINE MIXING ENTHALPIES BY DSC

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Abstract

A method has been developed that utilizes a special custom-made mixing device and HPLC micro liter syringe to perform mixing experiments of liquid systems directly in open measuring cells of differential scanning calorimeters. The present paper describes how to determine mixing enthalpies from time scans of the isothermal heat flux during an exothermal or endothermal process. Using ethylene glycol and the slightly volatile component water to calibrate the mixing calorimeter, the mixing enthalpy of the binary system poly(ethylene glycol) 400/water could be determined with sufficient precision compared to the results of measurements with a conventional flow calorimeter.

Keywords: DIC, DSC, heat capacity, mixing enthalpy, PEG, water

Introduction

Differential scanning calorimetry (DSC) is a versatile measuring technique to determine temperatures and heat flows during phase transformations and other transitions in materials, such as glass transition, 'cold' crystallization, phase changes like melting or crystallization [1–3], and many others. In the past years the number of thermodynamic data has increased with continuous improvements and developments in this type of calorimeters. The temperature-modulated DSC is only one example for the development of this well-known technique [4–6]. Typically, in a differential scanning calorimeter temperature scans of the differential heat flux into the sample and reference cells at different heating or cooling rates are performed.

Another method of DSC, referred to as differential isothermal calorimetry (DIC), is based on the differential heat flux into the sample and reference cells in an isothermal mode [7, 8], and is mainly used for measurements of vaporization and enthalpies of chemical reactions under isothermal and isobaric conditions. In addition to that, DIC may serve to measure mixing enthalpies because mixing enthalpies cannot be quantitatively determined from binary phase diagrams, such as liquidus curves or other equilibrium curves [9].

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The evaluation and interpretation of DIC measurements is often simpler than those of the conventional DSC curves [10–13]. Due to the isothermal mode, heat capacity changes are not involved and the baseline remains absolutely constant (horizontal). Even after exothermal and endothermal processes, once the heat flux is zero, the signal reaches the constant baseline again.

The new mixing device for the measuring head of the DSC apparatus allows to add small amounts of liquids into the DSC measuring cell with a microliter syringe, and to monitor the differential isothermal heat flux as a function of time in order to compensate, for instance, for the temperature of the injected liquid. By injecting another liquid into a liquid submitted in the measuring cell, the mixing enthalpy can directly be measured because of extremely small paths of diffusion due to the small amounts of matter of about 5–10 mg. Thus a stirring of the systems is not required. Any exothermal or endothermal mixing effect superimposing on other thermal processes that may take place after the injection can, too, be determined with DIC.

Needless to say, DIC may be used to determine specific heat capacities of liquid components or mixtures by measuring the energy for temperature compensation and correlating this energy to the mass and temperature of the injected liquid [14]. And, with a DIC apparatus reaction enthalpies of components and e.g. polymerisation enthalpies of systems can be measured after adding, for instance, a suitable starter. It is remarkable that the masses used here are in the order of a few milligrams as opposed to other conventional calorimeters. This is of importance if only such small masses of a substance are available.

The DSC mixing device and experimental procedures

Mixing device

The DSC-2C from Perkin Elmer is equipped with both a low-temperature device and the new custom-made mixing device, which will be described below. A Personal Computer controls the DSC and continuously monitors the differential heat flux in either scanning (DSC) or isothermal mode (DIC). To prevent water from condensing on the DSC measuring head caused by the low temperature device, the DSC is equipped with a glove box and purged with dry nitrogen. This allows to directly perform mixing experiments in an open DSC pan using HPLC microliter syringes.

Figure 1 shows a sketch of the custom-made mixing device for the DSC. The device is mounted on a solid plate of stainless steel (f) above the DSC measuring head. Since the mixing experiment requires the DSC mixing pan to be quickly taken out of the DSC cell, the syringe holder (c) has been designed to be movable in two directions: vertically using an electric motor to precisely adjust the position of the syringe above the DSC pan, and horizontally, as shown by the unidirectional double arrow in Fig. 1b, to allow visual access to the mixing pan.

The syringe holder (c) is made of solid aluminum and contains a hole, the dimensions of which are precisely adapted to the shape and dimensions of the HPLC microliter syringe. The temperature of the syringe holder (c), which is insulated with

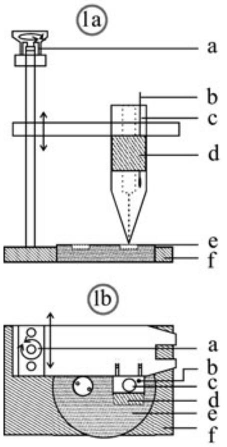

Fig. 1 Mixing device for the DSC. 1a – Side view; 1b – Top view; a – height-adjustable vertical axis, b – PT-100 resistor, c – temperature-adjustable syringe holder, d – Peltier elements, e – DSC measuring head and f – base plate firmly attached to the DSC to avoid movements of the mixing device during the operations

insulating tape, can be adjusted by two Peltier elements (d). These elements are located behind and in front of the holder to avoid temperature distribution in the aluminum holder. The temperature of the holder is measured and controlled by a PT-100 resistor (b) and adjustable within temperatures from –5 to 50°C with an accuracy of ±0.5°C. The estimation of error connected with the temperature difference between a liquid in the calorimeter and a liquid in the syringe due to ±0.5 K corresponds to 2.1 J g^{-1} which has been ignored. In principal the temperature regulation may be improved thus reducing this error. The syringe should be placed as close as possible to the surface of the liquid in the pan, which will be mixed with the liquid in the syringe, to eliminate any dissipation of kinetic energy of the liquid added.

Experimental procedures

The following is a description of the procedure how to measure mixing enthalpies with the new calorimeter.

The DSC aluminum pan is weighed and partially filled with approximately 8 mg of the first liquid component. The temperature of the DSC and the syringe holder is preset to e.g. 25°C. The second liquid is filled into the syringe with an absolute injection volume of 10 μL and annealed in the syringe holder for 15 min.

After starting the isothermal experiment by recording heat flux *vs*. time at 25°C, the other component in the syringe holder is injected into the DSC pan. This causes either an exothermal or endothermal reaction depending on the mixing enthalpy of the binary system.

After the mixing experiment is over, which usually takes no longer than 4 min (without annealing time), the syringe holder is moved upwards and put aside to allow free visual access to the DSC mixing pan. The pan filled with the mixed solution is taken out of the DSC apparatus to determine mass and concentration of that solution.

The mass of the mixed solution is determined by reweighing the DSC pan, which has been placed in a small tight glass vessel, thus preventing the evaporation of the slightly volatile component (water) during the weighing procedure. The concentration of the solution can be measured using an Abbé refractometer or any other suitable method to determine the composition of the mixture. With the known mass of the mixture and its composition after the mixing process at hand, the measured mixing enthalpy can be converted to the specific integral mixing enthalpy.

As mass and concentration of all mixtures are determined after the mixing process it is necessary to pay attention that the time between the end of the mixing and the end of determination of the mass and concentration is the same for every sample, although this time lasts 1.5 min. It could be shown that during the reweighing process of the mixtures no significant evaporation of water occurred. Measuring the evaporation rate of pure water and water from a liquid mixture on a microgram balance showed in both cases an evaporation velocity of 0.13 mg min^{-1}. The error in the mass determination of ca. 16 mg solution is 1.5% and could be neglected as well as the error in concentration of a component being 0.7%. The transport of the mixture from the balance to the glass plate of the refractometer takes only a few seconds in which no further evaporation is important.

The concentrations of the measured systems were determined by use of an Abbé refractometer calibrated to the system ethylene glycol/water which shows a linear relationship between the refractive index and composition:

$$n_{\mathrm{D}}^{20}(\text{sol})=w_1 n_{\mathrm{D}}^{20}(\text{water})+w_2 n_{\mathrm{D}}^{20}(\text{ethylene glycol}) \qquad (1)$$

where w_1 and w_2 are the mass fractions of water and ethylene glycol. n_{D}^{20}(water) and n_{D}^{20}(ethylene glycol) are the refractive indices of the pure components, and n_{D}^{20}(sol) is the refractive index of the solution of water and ethylene glycol.

In the present paper ethylene glycol/water is used to calibrate the mixing calorimeter since its large exothermal mixing enthalpies are known from the literature [15] and the concentrations of those liquid mixtures, which are not volatile at 25°C, may readily be correlated to their refractive indices. Poly(ethylene glycol) 400/water serves as sample system whose mixing enthalpies are measured with the new mixing device.

Results and discussion

Figure 2 is a DIC scan of the isothermal heat flux during an injection of 5 mg pure water in an empty DSC pan at a temperature of 25°C. Upon injecting water, the DIC curve instantaneously shows an endothermic step which, after adjusting the temperature within 20 s, turns into a steady state. This steady state is caused by a continuous isothermal evaporation of the pure water over a period of about 1000 s.

Enthalpy of evaporation has to be continuously fed to the DSC pan to keep the temperature constant at 25°C. Otherwise the temperature of the DSC pan would drop.

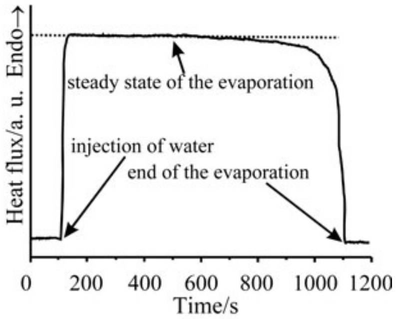

Fig. 2 DIC diagram for a water injection into an empty DSC pan and the following evaporation of water

The heat flux of the DSC more or less remains constant while water is being evaporated. Little deviations from the steady state result from slight changes in the surface of the water droplet. At the end of the evaporation, the surface of the droplet and, thus, the entailed heat flux decreases very fast so that the baseline reaches the value of the heat flux measured before the injection of the water and becomes horizontal again. The area between the DIC signal and the baseline is proportional to the total enthalpy of evaporation and the sample mass.

Next, the calorimeter needs to be calibrated by injecting pure water into ethylene glycol at 25°C. First, a droplet of ethylene glycol is placed into a weighed DSC pan. Then, pure water is filled into the syringe located in the syringe holder of the mixing device and kept for 15 min at a syringe temperature of 25°C for temperature equalization. Approximately 30 to 40 s after the DIC scan has started, water is injected into the DSC pan and added to the ethylene glycol. The amount of the injected water was set to get a final concentration of the mixture in the range $0.4<w_2<0.6$ where the exothermal mixing enthalpy of the system is maximum (w_2 is the mass fraction of ethylene glycol).

Figure 3 represents the calibration mixing experiment of ethylene glycol and water showing isothermal heat flux *vs*. time. In this experiment ethylene glycol was placed in the pan and water was added by means of the syringe. Overall, the heat flux increases within 82 s due to the evaporation of water and leads to a baseline shift, with respect to the baseline before the injection of water, where the DIC signal becomes stationary. It is remarkable that the mixing is achieved in such short time without stirring the system. This is due to the extremely small amounts of the masses used and thus guaranteeing very short diffusion paths. Apart from that, the negative mixing enthalpy of the system ethylene glycol/water superimposes on the signal of evaporation. The heat of evaporation is strictly the heat of transferring the water in the solution to the pure water vapor. The heat of transfer contains the reverse mixing enthalpy besides the heat of evaporation [16]. The heat of mixing is very small in comparison to the heat of evaporation so that the mixing enthalpy can be neglected and the heat of transfer is in good agreement represented by the heat of evaporation. For this reason, using the DIC curve of Fig. 2 as baseline, shown here as dotted line and established for the injection of pure water in an empty DSC pan, allows to determine the mixing enthalpy of the underlying binary system from the hatched (grey) area between the measured heat flux (solid line) and constructed baseline (dotted line).

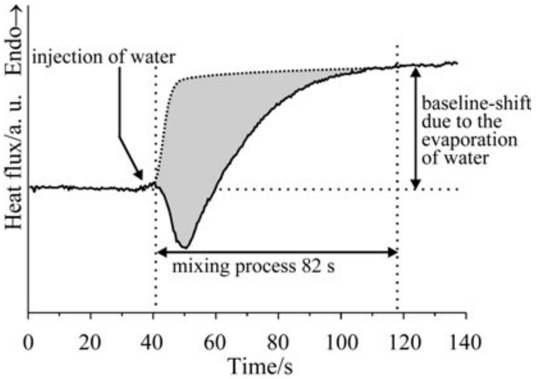

Fig. 3 DIC diagram for the injection and mixing of water into a DSC pan already filled with ethylene glycol. The exothermal mixing enthalpy is represented by the grey area

Figure 4 sketches the inverse experiment which was carried out to double-check the mixing enthalpy measured in Fig. 3. For this reason, ethylene glycol was filled into the syringe and added to water in the DSC pan. The baseline is nearly horizontal before and after the mixing process of ethylene glycol and water representing a constant value of the heat flux due to the continuous evaporation of water out of the DSC pan. The evaporation of the water out of the mixed solution shows the same heat flux as for the evaporation of pure water before the injection of ethylene glycol. The determination of the exothermal mixing enthalpy is easier in this case than in the previous experiment because of the missing step in the baseline. The baseline is constructed linearly between the beginning and end of the mixing signal, and the mixing enthalpy can be calculated directly from the area under the baseline. If in other systems the baseline is not horizontal because of a different evaporation velocity the baseline

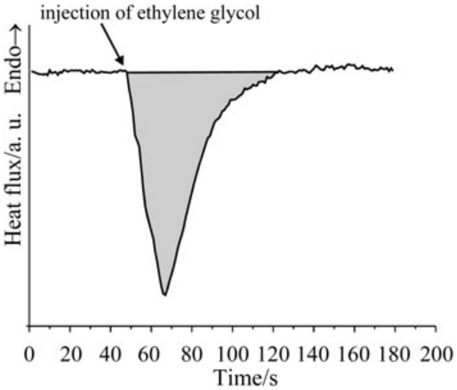

Fig. 4 DIC diagram for the injection and mixing of ethylene glycol into a DSC pan already filled with water. The exothermal mixing enthalpy is represented by the gray area

should be constructed like the step in the baseline of DSC measurements of melting diagrams e.g. [1, 3, 9].

It is surprising that the evaporation rate of the pure water is nearly the same as the evaporation rate of the same mass of water out of the mixtures. This already mentioned effect serves discussion. Normally the evaporation rate should be decreasing with higher ethylene glycol concentrations caused by the reduced vapor pressure in these mixtures. Because of the larger surface in the mixtures the evaporation rate of the water increases. Finally the two effects appear to compensate each other resulting in the same evaporation rate shown in Fig. 4. Many other effects also contribute to the evaporation rate of droplets but are of minor importance in this paper [17].

Drawing a comparison between the mixing enthalpies obtained from Figs 3 and 4, both results match with one another with an accuracy of ±3 J g^{-1}.

The measurements show that a few properties of the measured systems are required. The measured enthalpy of the system at nearly the same amounts of both components should be larger than ±30 J g^{-1}. This property is responsible for the limited measurable concentration range of the systems. In the highly diluted region of the systems the mixing enthalpies are too small to be detected with this method because the absolute error in the enthalpy determination is too high. It is mandatory that both components should be only slightly volatile. If the components are volatile the error in the mass and concentration determination increases and the absolute error increases additionally. If the concentration is determined by use of an Abbé refractometer it is necessary that the refraction indices of the two components are different and the dependence of the refractive index on the concentration is known.

After the mixing calorimeter was calibrated by means of the mixing enthalpies of the system ethylene glycol/water, the mixing enthalpies of the system PEG 400/water were investigated. In addition to that, a flow microcalorimeter, model LKB 2107 – 121, was used, too, for a cross-check of the results.

Figure 5 shows the mixing enthalpies of the systems ethylene glycol/water and PEG 300/water which were taken from the literature [15, 18] along with the mixing enthalpies of the system PEG 400/water [19]. The stars represent the mixing enthalpies determined by the DSC mixing calorimeter. The dashed dotted curve represents the mixing enthalpy of the system PEG 400/water measured with the LKB flow calorimeter [19, 21]. The mixing enthalpies of the systems PEG 300/water and PEG 400/water *vs.* mass fraction of the oligomers are slightly asymmetrical with an extremum at nearly w_2=0.55.

As can be seen from Fig. 5, the mixing enthalpies established with the new DSC mixing device match that of the flow calorimeter with an accuracy of 3 J g^{-1}. Repeated measurements of the described systems show also an average error of ±3 J g^{-1}.

Because of this accuracy, with this DIC calorimeter mixing enthalpies can be measured most accurately at middle concentrations (in this system ca. 40–60% by mass), where the mixing enthalpy is maximum, assuming nearly symmetrical mixing enthalpy diagrams. This fact is given in the investigated binary systems. At high and low concentrations, therefore, the mixing enthalpies are too small to be precisely determined by this instrument.

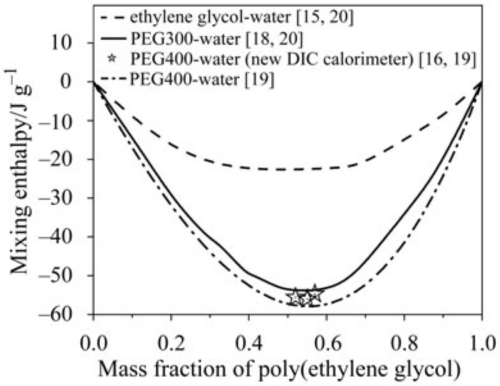

Fig. 5 Specific mixing enthalpies of the binary systems ethylene glycol/water [15, 20] and PEG 300/water [18, 20] and PEG 400/water [16, 19] obtained by the new DIC calorimeter and LKB mixing calorimeter

Evidently, the mixing enthalpy of the system PEG 400/water is more exothermal than that of the system PEG 300/water and that of ethylene glycol/water. A comparison of the mixing enthalpies of water with ethylene glycol, di(ethylene glycol) and tri(ethylene glycol) [15] shows a trend towards increasing exothermal mixing enthalpies with increasing chain length of the poly(ethylene glycol) in the binary systems in the middle concentration range.

Conclusions

The present paper introduces a special custom-made mixing device for differential scanning calorimeters (DSC) and serves to directly measure mixing enthalpies of liquid mixtures in the DSC while differential isothermal calorimetric (DIC) heat flux-time scans are being performed.

As opposed to conventional flow calorimeters, such as the flow microcalorimeter from LKB, this mixing device requires much smaller liquid volumes, typically at milligram or microliter levels, which significantly reduce the sample consumption (by a factor in the range of 60 to 100). The diffusion distances are extremely short thus mixing processes take place quite rapidly (in about 80 s) without needing a stirring to achieve mixing. The accuracy of this new device is slightly lower than that of conventional mixing calorimeters. It turns out that the specific mixing enthalpies of the system PEG 400/water may be determined with an accuracy of about ±3 J g^{-1}. For this reason, it is highly recommended to only measure mixing enthalpies in the middle of the concentration range of a binary system where the mixing effect is maximum.

The method is limited to the mixing of liquid substances with low volatility. Overall, the new mixing device with its simplicity in design and construction, indicates a useful and promising alternative for determining mixing enthalpies by means of differential scanning calorimetry (DSC) with reasonable accuracy. Additionally it is possible to determine heat capacities or reaction enthalpies by use of this new method.

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References

1 W. Hemminger and G. Höhne, Calorimetry: Fundamentals and practice, VCH, Weinheim 1984.
2 G. W. H. Höhne, W. Hemminger and H.-J. Flammersheim, Differential scanning calorimetry, Springer, Berlin 1996.
3 W. F. Hemminger and H. K. Cammenga, Methoden der thermischen Analyse, Springer, Berlin 1989.
4 J. E. K. Schawe, Thermochim. Acta, 271 (1996) 127.
5 M. Reading, A. Luget and R. Wilson, Thermochim. Acta, 238 (1994) 295.
6 M. Reading, Trends Polym. Sci., 8 (1993) 248.
7 W. Smith, Thermochim. Acta, 313 (1998) 27.
8 W. Smith, Thermochim. Acta, 112 (1987) 289.
9 A. Müller, Dissertation, Duisburg 1998.
10 A. Müller and W. Borchard, J. Phys. Chem., 101 (1997) 4283.
11 A. Müller and W. Borchard, J. Phys. Chem., 101 (1997) 4297.
12 A. Müller and W. Borchard, J. Phys. Chem., 101 (1997) 4307.
13 G. V. Kotelnikov, S. P. Moiseyeva, E. V. Mezhburd and V. P. Krayev, J. Therm. Anal. Cal., 68 (2002) 803.
14 W. Oelsen, K. H. Rieskamp and O. Oelsen, Archiv für das Hüttenwesen, 26 (1955) 253.
15 H. G. Könnecke, H. Steinert and E. Leibnitz, Z. Phys. Chem., 208 (1957) 147.
16 W. Borchard and P. Jablonski, Dechema Forschungsbericht, 2000, p. 157.
17 A. Tomlinson, Ch. Chylewski and W. Simon, Tetrahedron, 19 (1963) 949.
18 G. Cunninghame and G. N. Malcolm, J. Phys. Chem., 65 (1961) 1454.
19 P. Jablonski, Dissertation, Duisburg 2002.
20 Landolt Börnstein, New series, Vol. IV: Physical Chemistry; IV/2; Heats of Mixing and Solution.
21 P. Jablonski, D. Eagland and W. Borchard, in preparation.