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A new Calvet-type calorimeter for excess enthalpies

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Abstract

A new apparatus for the measurement of excess enthalpies of liquid mixtures based on a Calvet microcalorimeter (C-80 Setaram) is described. Vaporization effects in the calorimetric cells are avoided by means of Viton balloons pressurized with nitrogen. Mixing is performed by precision-injection metering pumps connected to the cells by a piping system. The apparatus permits measurements in the range 25-130°C and up to 2.5 MPa for low boiling and highly viscous components. Results are presented for the water-glycerol system at 50° and 80°C.

INTRODUCTION

The Setaram C-80 calorimeter is a Calvet-type heat flux calorimeter [1]. It has a broad applicability due to its operation in isoperibolic as well as scanning mode [2]. Several types of experimental vessels, as described in the manual [3], are available with the standard instrument to realise these possibilities. For the determination of excess enthalpies of liquids, two types of experimental cells can be used: a reversal mixing vessel and a membrane mixing vessel. Although mixing experiments can be performed at elevated pressures (with appropriate cells), the preparation of the samples has to be done at atmospheric pressure and ambient temperature. The separation of the phases by a mobile lid or a membrane excludes mixing experiments of components with large differences in vapour pressure. Furthermore, vaporization effects may cause considerable errors at higher temperatures, as shown by Krug [4].

This paper describes a new concept to overcome these limitations of Calvet-type calorimeters for the measurement of excess enthalpies of liquid mixtures. Thermostated precision-injection metering pumps are used for handling the components. They are connected by a piping system with a

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new H^E-module, which can be inserted as a whole into the C-80 calorimetric block. The mixing process is effected by metering the second component via the reference vessel into the measuring vessel containing the first component. A balloon pressurized with nitrogen prevents vaporization effects. Special care is taken to avoid temperature differences or disturbances of the temperature profile in the thermostated calorimetric unit. Stable thermal conditions are brought about by two heat exchangers situated outside and inside the calorimetric block.

The operational range of the instrument is 25–130°C and 0–2.5 MPa. The duration of one measuring run is about 5000 s. The precision and accuracy of the instrument were tested, as reported elsewhere [5]. In this contribution, results are presented for the system water + glycerol at 50 and 80°C, thereby demonstrating the calorimeter's ability to accommodate highly viscous components.

APPARATUS

The main components of the equipment are the calorimetric unit consisting of the H^E-module and the C-80 calorimeter, the thermostated precision-injection metering pumps, the piping system, and the calorimeter control and data logger connected to a personal computer. A block diagram showing the main components is given in Fig. 1.

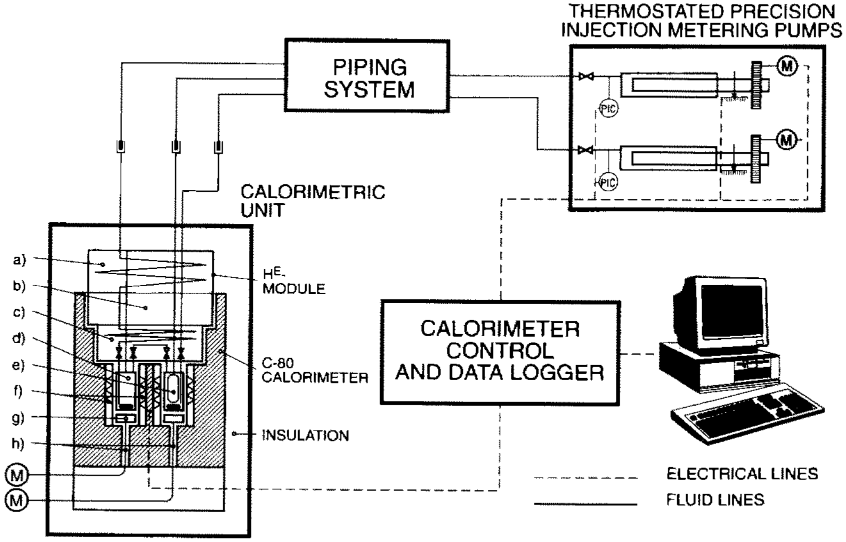

Fig. 1. Block diagram of the apparatus: (a) preheater; (b) insulating lid; (c) inset; (d) reference vessel; (e) measuring vessel; (f) fluxmeter; (g) stirring magnets; (h) flexible shaft.

Calorimetric unit

The calorimetric unit serves to perform the mixing process with the liquids thermostated to about ±0.01°C and to measure the corresponding heat effect. The H^E-module is inserted as a whole into the C-80 calorimeter. An additional insulation of rock wool improves the thermal stability.

The H^E-module consists of the preheater, the insulating lid, the inset and the calorimetric vessels. Figure 1 shows their arrangement. All pipes are 1/8 in stainless steel, except the connections to the calorimetric vessels and between them. Connections to the piping system are the component lines to the metering pumps and the balloon pressurizing systems. These tube joints are Swagelock quick connections.

Components pumped into the calorimeter at the start of a measurement are brought to calorimeter temperature by the preheater, so that disturbances of the block temperature are prevented. The preheater is an electrically heated air thermostat of cylindrical shape made of aluminium and containing a 4-m coil of 1/8 in tube. Its temperature is maintained at the block temperature within ±1°C by a controller (Jumo LAN-N). The insulating lid is part of the insulation of the C-80 calorimeter and separates the preheater and the inset thermally. It is constructed in analogy to the original part [6] with openings for the tubes and the rods of the valves.

The purpose of the inset is two-fold: firstly, the metered component is brought to calorimeter block temperature, and secondly it serves as support for the valves and the tube connections to the calorimetric vessels. It is a cylindrical block of cast aluminium situated directly in the internal chamber [6] of the calorimeter block and is thermally connected with the block. A coil of 1/8 in stainless steel tube, 4 m long, serves as heat exchanger. Openings for tubes and supports for the valves are milled out from this block. In order to minimize the disturbance of the temperature profile, the arrangement of the valves and millings is symmetrical. The temperature is checked by a Pt-100 sensor and a thermometer with a resolution of 0.001°C.

The calorimetric vessels are connected with the inset by three capillaries (1/16 in stainless steel tubes). While both vessels, i.e. the reference vessel and the measuring vessel, are identical, only the experimental vessel contains a balloon. The high pressure vessel provided by Setaram [3] is used directly. Due to the small diameter of the vessels (16.92 mm) and the necessity of providing three inlets for capillaries and a support for the balloon, a special lid was constructed as shown in Fig. 2. The balloon is made of Viton and was manufactured by Angst und Pfister, Zurich. It permits a variation of the cell volume from 1.5 to 7 ml. A Teflon-coated magnet is situated at the bottom of each vessel for stirring.

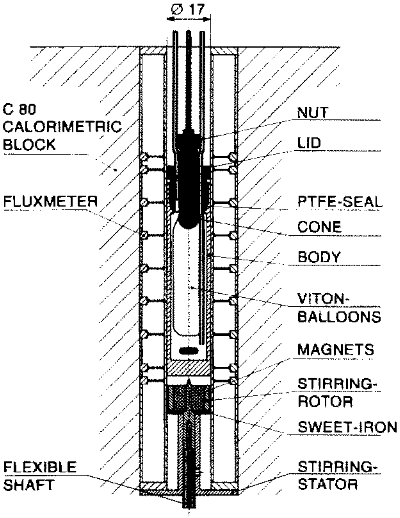

Fig. 2. Calorimetric vessel.

With minor changes, the C-80 calorimeter is used as a thermostat and for heat flux measurements. Magnetic stirrers are installed in the lower part of the fluxmeters and are driven by electric motors situated outside. The load transmission is effected by a flexible shaft. By using calibrated Pt-100 sensors, the temperature measurements in the calorimetric block have now been improved to an accuracy of ±0.01 K. These sensors were calibrated according to DIN IEC751 using a high-accuracy MKT 100 thermometer (AP Paar, Graz) with a resolution of 0.001°C. These temperature measurements indicated fluctuations of the block temperature of ±0.02°C, leading to baseline instabilities. The additional insulation of the calorimeter as mentioned above and the installation of a constant power supply for the thermostat reduced the oscillations to ±0.002°C, which is sufficient for yielding a stable baseline [5].

A detailed description of the various components has been given by Winkler [7] and Miklautsch [8]. The temperature sensors installed in the centre of the calorimetric block and in the inset indicates a temperature gradient within the calorimetric block which depends on the temperature of the thermostat. This causes systematic deviations of the heat effects from the true values, indicated by the fluxmeters, because either a too cold or too hot component is pumped into the reference vessel at the beginning of the measurement. Therefore, a correction has to be applied for the evaluation of the measured effect, which is either determined by blind measurements (determining the heat effect for mixing identical componets) or calculated from the temperature gradient and the specific heat of the corresponding component [8].

Injection-metering pumps

The injection-metering pumps serve to handle the components under pressure and are used for the determination of the metered amounts of the components. They are piston injectors manufactured at Technische Hochschule Darmstadt and correspond exactly to those described by Spiske and Gaube [9].

The liquid is contained in a cylinder and displaced for dosing by a highly polished precision piston. The piston is moved by a spindle; its position is indicated by an optoelectronic digital length gauge (MSA 665, RSF Elektronik) with an accuracy of ±0.0005 mm. The mass of metered substance is given by the product of the length difference, the cross-sectional area of the piston and the density of the liquid. In order to ensure constant liquid density, the piston injector is thermostated within ±0.01°C. Evidently, the pressure of the liquid must remain greater than the balloon pressure in the measuring vessel.

For the system water–glycerol, the pressure in the injector was kept at 0.6 ± 0.025 MPa at the start and the end of dosing by a controller, consisting of a pressure gauge (WIKA Tronic) and a data logger (MPDS 4000, AP Paar). For the evaluation of the injected amounts of the components, their densities at 0.1 MPa were measured with a vibrating tube densimeter (DMA 45 AP Paar).

The maximal volume of displacement in the pumps is 15 ml, which is sufficient for at least two measurements. The inaccuracy of the metered volume is about ±0.003 ml in the mean; the maximum error is about 0.005 ml.

Piping system

The piping system connects the metering pumps to the calorimetric unit. It is used to evacuate the instrument before each experiment, to pressurize the balloon during an experiment, and after each run it is used to clean the system with a suitable solvent and to dry it. The pure liquid components are stored in stainless steel vessels equipped with quick connections. All tubes are stainless steel (1/8 in); valves and connections are from Swagelock. A complete piping scheme is shown in Fig. 3.

Calorimeter control and data logger

The C-80 calorimetric unit is used directly for thermostating and for heat flux measurements, as mentioned above. A Setaram temperature controller and programmer, as well as the A10 amplifier, are also used. Temperature

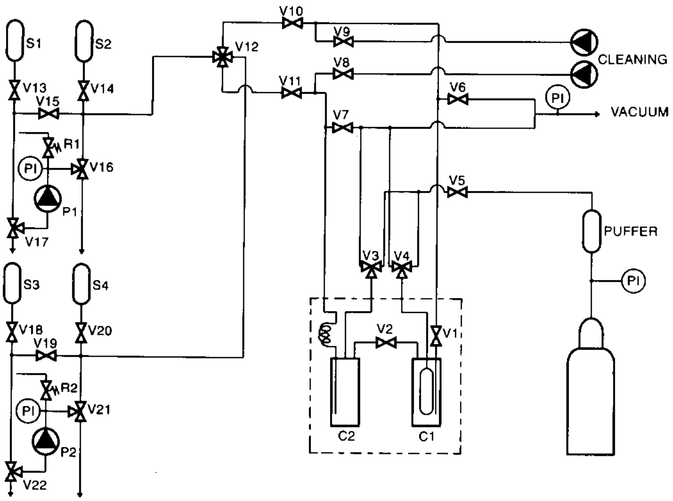

Fig. 3. Piping system: P1, P2, metering pumps; R1, R2, rupture valves; C1, measuring vessel; C2, reference vessel; V1–V22, valves; S1–S4, storage vessels.

fluctuations and baseline instabilities were decreased by using a constant power supply with a floating battery.

All necessary temperature measurements (calorimetric block, inset and injection metering pumps) are performed with high-precision thermometers MKT 100 (AP Paar) with a resolution of 0.001°C, and sensors calibrated according to DIN IEC751 with an inaccuracy of 0.01°C.

The output signal of the amplifier and the MKT 100 are treated and registered in the modular process data system MPDS 4000 (AP Paar), serving as data logger and controller for the injection metering pumps. The analog heat-flux signal from the amplifier is digitalized by a 12-bit analog-to-digital converter integrated in the MPDS 4000 unit. The output signals of the MPDS (heat flux, time, temperatures) are transmitted each second to a personal computer via an RS232 interface, and evaluated there.

EXPERIMENTAL PROCEDURE

The calorimetric unit and the pumps are brought to measuring temperature. Then the pumps are charged with degassed components from storage vessels until stabilization of pump temperature. The required volume of component 1 (1.5–7 ml depending on the desired composition) is metered into the experimental vessel and the balloon is pressurized to a pressure above the vapour pressure of the components and mixture. Component 2 is pumped into the system, filling all pipes, the preheater, the inset, the reference vessel and the capillaries to the last valve (V2, Fig. 2).

Thermal stabilization is indicated by a stable baseline and stable temperatures of the inset and of the calorimetric block. This is usually reached after 3–4 h.

The mixing experiment is then started by opening V2 and metering component 2 into the measuring vessel. After closing V2, both vessels are stirred for one minute. The heat flux curve can be observed in the display. The duration of an experiment is usually about 5000 s. The stability of the baseline is checked before and after the experiment.

The evaluation is performed in the usual manner as described in the literature [1, 2, 6]. The integration is done numerically, following Simpson's rule, with heat flux values taken every second. The sensitivity factor is determined with Joule cells and controlled by measurements of specific heats of the components and synthetic sapphires.

Corrections are applied for the heat effects of stirring and for the temperature gradient in the calorimetric block as described above for the calorimetric unit. The former effect is determined by blind measurements, the latter by numerical calculation and checked by blind measurements.

After each measuring run, the system is cleaned with a suitable solvent (when working on the water–glycerol system, we used i-propanol) and dried with nitrogen. The total time needed for one experimental point is about 1.5 days.

EXPERIMENTAL RESULTS

Test measurements of excess enthalpies were performed for the system *n*-hexane–cyclohexane in the temperature range 25–80°C. Results and error analysis have been published [5]. In general, our values agree with reliable literature data within 1%. The viscosity of *n*-hexane is 0.33 cP and that of cyclohexane 0.88 cP at 25°C [10].

Here, we present the results of our measurements on the system water(1) + glycerol(2) at 50 and 80°C. This system shows very large differences in the viscosities of the pure components. At 25°C, the viscosity of water is 0.90 cP, and that of glycerol is 954 cP.

Demineralized water was doubly distilled in a quartz still, degassed in vacuum and sucked directly into the sample cylinders. The glycerol was a Fluka reagent (No. 49970, water content <0.1%) and was used as received. Due to its hygroscopicity, all manipulations were in a glove bag under dried nitrogen. All measurements were performed with a sample volume of 6–7 ml.

A Redlich–Kister equation of the form

$$H^{\mathrm{E}}_{\mathrm{m,calc}}/(\mathrm{J\,mol^{-1}}) = x_1 x_2 \sum_{i=0}^{n} A_i (x_1 - x_2)^i \qquad (1)$$

TABLE 1

Parameters A_i of eqn. (1), RMSD and mean percent deviations for H^E_m of $[x_1H_2O + x_2C_3H_5(OH)_3]$ at 50 and 80°C and 6 bar

Temperature K	A_0	A_1	A_2	RMSD	Percentage deviation
323.15	−1942.607	−401.739	106.319	8.8	1.9
353.15	−1214.773	−197.676	−974.828	5.3	2.1

was fitted to the experimental excess molar enthalpies H^E_m. For both series of measurements at 50 and 80°C, we set $n = 2$, because a higher degree of the polynomial did not improve the quality of the fit significantly. The parameters A_0, A_1, A_2, the root-mean-square deviations (RMSD) and the mean percent deviations are shown in Table 1.

The experimental excess molar enthalpies H^E_m, the values calculated from eqn. (1) $H^E_{m,calc}$, the differences $H^E_m - H^E_{m,calc}$ and the percent deviations for each composition are listed in Table 2 for 50°C and in Table 3 for 80°C. Figure 4 shows the experimental H^E_m values together with the fitted curves.

The uniform distribution of errors over the whole composition range and the increase in the error with temperature suggests that they are caused by temperature fluctuations of the calorimetric block.

TABLE 2

Excess molar enthalpies and deviations for $[x_1H_2O + x_2C_3H_5(OH)_3]$ at 50°C and 6 bar

x_1	H^E_m/ J mol^{-1}	H^E_{calc}/ J mol^{-1}	$H^E_m - H^E_{m,calc}$/ J mol^{-1}	Percentage deviation
0.0749	−101.8	105.6	+3.8	−3.6
0.1039	−141.3	−145.0	+3.7	−2.5
0.1248	−172.4	−172.7	+0.3	−0.2
0.2014	−279.3	−267.8	−11.5	+4.2
0.2981	−369.1	−368.9	−0.2	0.0
0.4011	−437.1	−446.6	+9.5	−2.1
0.5500	−479.4	−490.5	+11.1	−2.3
0.6003	−508.8	−484.4	−24.4	+5.0
0.6504	−456.4	−467.0	+10.6	−2.3
0.7013	−439.3	−437.3	−2.0	+0.5
0.7502	−398.9	−396.7	−2.2	+0.6
0.7999	−346.0	−343.4	−2.6	+0.7
0.8503	−268.9	−276.4	+7.5	−2.7
0.9002	−198.0	−197.3	−0.7	+0.3
0.9498	−104.8	−105.7	+0.9	−0.9

TABLE 3

Excess molar enthalpies and deviations for $[x_1H_2O + x_2C_3H_5(OH)_3]$ at 80°C and 6 bar

x_1	H^E_m/ J mol^{-1}	H^E_{calc}/ J mol^{-1}	H^E_m–H^E_{calc}/ J mol^{-1}	Percentage deviation
0.0935	−149.2	−143.9	−5.3	+3.6
0.1015	−147.8	−152.9	+5.1	−3.4
0.1931	−230.9	−227.6	−3.3	+1.5
0.1987	−225.1	−230.8	+5.7	−2.5
0.2952	−272.6	−269.9	−2.7	+1.0
0.3184	−277.0	−276.0	−1.0	+0.4
0.3458	−289.0	−282.0	−7.0	+2.5
0.3954	−285.6	−290.7	+5.1	−1.8
0.4403	−294.1	−297.0	+2.9	−1.0
0.4960	−299.3	−303.3	+4.0	−1.3
0.5457	−308.4	−307.7	−0.7	+0.3
0.6468	−314.0	−310.0	−4.0	+1.3
0.6957	−298.6	−305.2	+6.6	−2.1
0.7472	−299.4	−292.9	−6.5	+2.2
0.8228	−263.8	−255.0	−8.8	+3.5
0.8477	−232.5	−235.4	+2.9	−1.2
0.9155	−149.2	−158.8	+9.6	−6.0

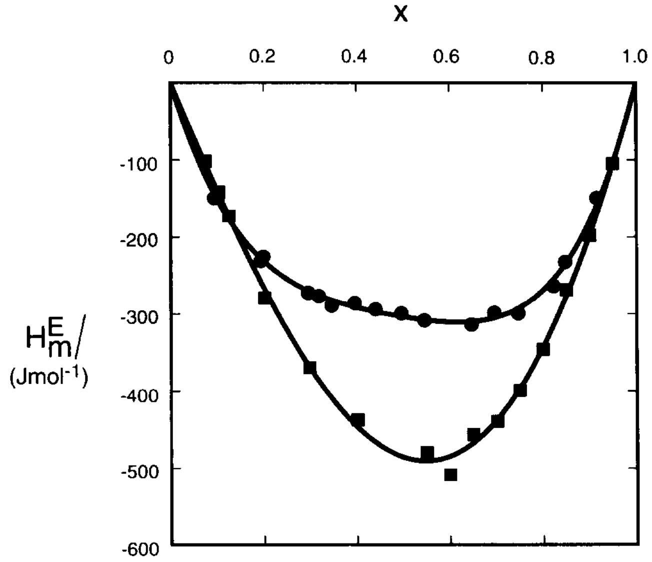

Fig. 4. Excess molar enthalpies H^E_m for $[x_1H_2O + x_2C_3H_5(OH)_3]$ at 50°C (■) and 80°C(●). Continuous curves are calculated from eqn. (1).

CONCLUSIONS

A new apparatus for the determination of excess enthalpies of liquid mixtures bases on a C-80 calorimeter has been developed. The equipment permits measurements of low boiling and highly viscous components in the temperature range 25–130°C at pressures up to 2.5 MPa. The performance of the system is illustrated by the results of the water–glycerol system at 50 and 80°C.

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