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EXCESS ENTHALPY IN THE METHANOL–WATER SYSTEM AT 278.15, 298.15 AND 323.15 K UNDER PRESSURES OF 0.1, 20 AND 39 MPa. I. DESCRIPTION AND DISCUSSION OF EXPERIMENTAL PROCEDURES

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ABSTRACT

A flow calorimetric system working in large ranges of pressure and temperature is described. Experimental procedures used to determine the excess enthalpy in the methanol–water system under pressures up to 39 MPa in the temperature range 278.15–323.15 K are discussed in detail.

INTRODUCTION

The pressure variable has often been neglected in the thermodynamic investigation of liquids, although already at the beginning of this century Bridgman pointed out its rôle in testing theories of the liquid state [1]. The application of pressure to a liquid will reduce the mean molar separation and hence will increase the cohesion forces between molecules. When performing measurements with changing pressure at constant temperature one can study the interaction energy of electrostatic origin and keep the energy of thermal nature at constant level and vice versa. A perspective for performing such studies was the main reason for us to construct a high-pressure flow calorimeter in which the temperature variable can also be changed in a large range. We have chosen the methanol–water system as the first liquid for such studies. The system methanol–water is interesting from both theoretical and practical points of view. Numerous studies have already been made in the calorimetric investigation of this system, but there are no systematic studies of the influence of both temperature and pressure on the excess enthalpy in the whole composition range.

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In this study we present results of direct calorimetric measurements of excess enthalpy, performed with our high-pressure and elevated temperature flow calorimeter. A detailed description of calorimetric vessels, flow dosing system with active heat exchangers, thermostat and the calorimeter proper is given elsewhere [2,3]. In this paper we present an integral description of the whole measuring system and a discussion of the precision of experimental procedure which were used to find numerical values of excess enthalpy at particular values of composition under given temperature and pressure conditions.

CALORIMETRIC MEASURING SYSTEM

A general scheme of the calorimetric measuring system is given in Fig. 1. The calorimeter proper with thermostat is one of the laboratory model units to the UNIPAN 600 calorimeter [4]. The device is of differential type with 20 iron–constantan thermocouples 1 mounted in series and used as a differential calorimetric detector (sensitivity 1 mV K^{-1}). The wires of

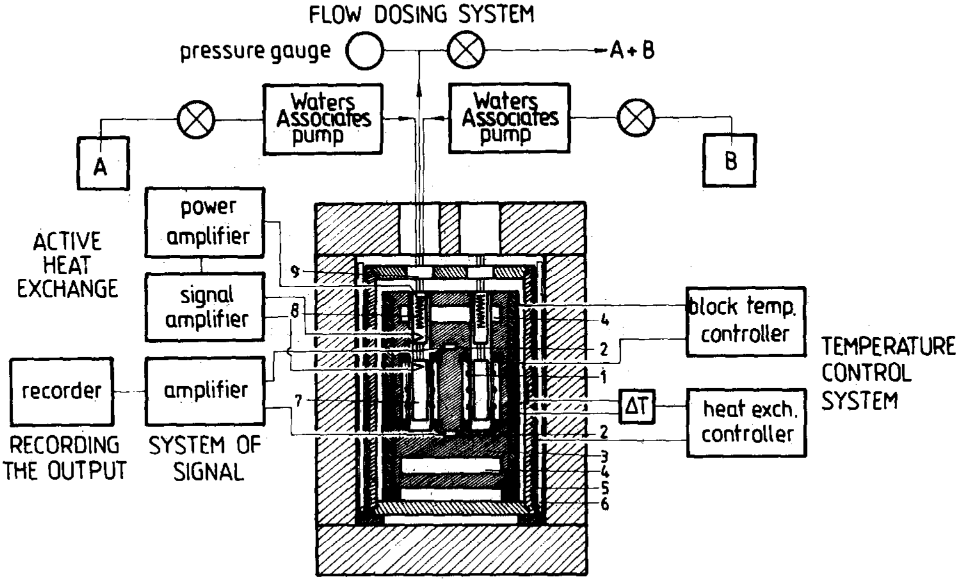

Fig. 1. A scheme of the flow calorimetric system working under pressure up to 39 MPa in a large temperature range. (1) Iron–constantan thermocouples, (2) heat exchangers for the thermocouples, (3) metallic calorimetric block, (4) horizontal air spaces to increase the thermal resistance, (5) heating shield, (6) liquid flow cooler connected to an external cold source, (7) mixing-flow vessel, (8,9) heat exchangers of the calorimetric vessel unit.

thermocouples are placed in heat exchangers 2 situated inside the calorimetric block. This assures that there is no heat flux coming directly through thermocouples from the measuring vessel to the reference vessel and vice versa. The particular thermocouples are placed on the cylindrical vessels in such a manner that each thermocouple junction on the measuring vessel is connected to a homologous junction on the reference vessel placed in a geometrically symmetrical position. This was done in order to compensate possible non-uniformities of the temperature field in the calorimetric block. The signal from the differential detector is amplified and recorded as a calorimetric output signal.

The cylindrical calorimetric block 3 has holes for calorimetric vessels and a heater mounted on its whole lateral surface. Two temperature sensors are placed in the block near its heating surface. To reduce the heat exchange through the bottom and top surfaces of the metallic block, the thermal resistances are increased by horizontal air spaces 4. The calorimetric block is placed coaxially in the heating shield 5 on which a liquid flow cooler 6 connected to an external cold source (FTS System-Flexi-Cool 100-100) is fixed. The heating elements of the block and heating shield are connected through control loops and are controlled by separate controllers. Such a temperature control system ensures temperature stability of the calorimetric block better that 10^{-4} K and good uniformity within the temperature range of 0–450°C. More details are given in [2] and [5].

The calorimetric vessel unit consists of a mixing-flow vessel 7 and two heat exchangers 8 and 9. For the high pressure measurements we have used two versions of the mixing-flow vessels. One, described in detail in [3], is constructed in such a way that the stainless steel capillaries are wound and soldered into the grooves of an internal copper shell. The calibration heater is interwound between the capillaries transporting the liquids. The inner copper shell with capillaries is placed inside an external copper shell, which is placed next to the outer shell made from stainless steel. The outer stainless steel shell, having direct contact with the calorimetric detector, is longer than the inner copper construction in order to avoid or reduce heat losses, possibly undetected by the calorimetric detector. The other version of the mixing-flow vessel is such that the inner copper construction is replaced by a tin–indium alloy. The capillaries with the calibration heater are wound together and then deeped in the hot liquid alloy in a container with proper dimensions and cooled afterwards. Both vessels give comparable results of measurements, but the last version of the vessel is much simpler to make.

The flow dosing system consists of two Waters Associates high pressure pumps, three high pressure needle valves and a Bourdon type pressure gauge. The flow speeds never exceeded 0.3 ml min^{-1}, but even with so low speed we had some problems, particularly concerned with a change of both sensitivity and base line when changing the speed flow or the liquid under investigation. We have explained this by the inadequacy of passive heat exchangers and have constructed an active heat exchanger [2] which works in such a way that the temperature of the liquids coming to the mixing-flow vessel is always equal to the temperature of the vessel. When the dosing system is working with this type of heat exchanger there is no effect on calibration constant neither of flow speed nor of heat capacity of the liquid.

EXPERIMENTAL PROCEDURES

The values of excess enthalpy at particular values of pressure, temperature and composition have been determined with the use of the following formula

$$H^{E}_{P,T}(x) = \frac{kl\left[(1-x)M_{H_2O} + xM_{CH_3OH}\right]}{m} \tag{1}$$

where l (mm) is the recorder deflection from a base line in the stationary state, k (W mm^{-1}) is the calibration constant, x is the molar fraction of methanol in the output mixture, m (g s^{-1}) is the total flow rate, M_{H_2O} and M_{CH_3OH} (g mol) are molecular weights of water and methanol, respectively. The baseline was obtained with only one component flowing through the measuring vessel, the reference vessel was kept as a neutral thermal reference. The molar fraction of methanol in the output mixture was determined from density measurements with a vibrating tube densitometer (Paar) and by using density–composition data of McGlashan and Williamson [6]. The total flow rate was measured with the aid of a balance and a timer. The temperature was measured with a thermocouple, one junction placed in the calorimetric vessel and the other in a reference thermostat, the temperature of which was measured with a quartz thermometer (Hewlett-Packard). The error in temperature measurements did not exceed ±0.02 K. The pressure in the system was measured with a Bourdon gauge providing a resolution of 0.1 MPa.

DISCUSSION

The resolution of measuring the deflection of the recorder was 1 mm when determining the calibration constant electrically. In this case the pumps pumped only one component and the long-term stability was also about 1 mm of the recorder deflection. When determining the calibration constant the deflection recorder in the stationary state was about 600–800 mm. Therefore, the precision of determination of the calibration constant was about 0.15%, because electrical parameters were measured with an error smaller by an order of magnitude than the error of determination of the

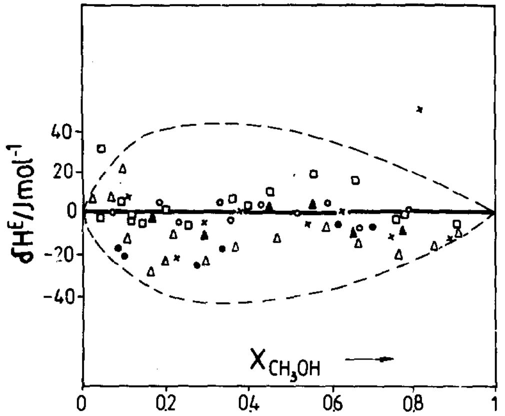

Fig. 2. A comparison of experimental data of H^E in the methanol–water system at 298.15 K and 0.1 MPa obtained in this study and found in the literature. $H^E = H^E_{exp} - H^E_{calc}$ where H^E_{calc} are the values of excess enthalpy calculated with the aid of NRTL formula correlating the experimental data of this study (———); (— — —) is the line of 5% deviations from H^E_{calc}, ○ this work, × Bertrand and Millero [7], ▲ Heintz and Lichtenthaler [8], ● Fenby and Chand [9], □ Lama and Lu [10], ▽ Benjamin and Benson [11].

recorder deflection. When measuring the enthalpy of mixing the resolution in determination of recorder deflection was about 4–5 mm. This arose from inaccuracies of the pumping system resulting in oscillations of the flow, which multiplied by the enthalpy of mixing caused oscillations or fluctuations of the calorimetric output signal. The amplitudes of the recorder deflections were similar to those in the calibration and so the precision of determination of l in eqn. (1) was about 0.65%. Of course, this precision is concerned with the measurements under high pressure, the precision of determination of recorder deflection in measurements under normal pressure was about four times better, because no fluctuations of the calorimetric signal have been observed. The precision in determination of the molar fraction x with a vibrating tube densitometer and by using the McGlashan and Williamson data was about 0.1%. The total flow rate m was determined with a precision of about 0.1% (taking into consideration also evaporation during collection and weighing of the sample). So, the precision of determination of excess enthalpy in the system methanol-water under pressure was better than about 1.1%. A comparison of our data obtained under pressure of 0.1 MPa and at temperature 298.15 K with the data available from the literature is given in Fig. 2. One can see that, probably, the accuracy of our measurements is close to the precision estimated above. Unfortunately, it is difficult to do a similar test for the measurements under higher pressure for the lack of literature data.

The results of measurements of excess enthalpy in the methanol–water system in the pressure range 0.1–39 MPa and in the temperature range

278.15–323.15 K will be presented in a subsequent paper. To do some kind of consistency test our data will be compared with those obtained from different thermodynamic methods available in the literature.

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