HEAT CAPACITIES OF LIQUID 2,3,6-TRIMETHYLPYRIDINE, 2,4,6-TRIMETHYLPYRIDINE AND 3-METHOXYPROPIONITRILE WITHIN THE RANGE OF TEMPERATURES OF 300 TO 328 K

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Molar heat capacities of 2,3,6-trimethylpyridine, 2,4,6-trimethylpyridine and 3-methoxypropionitrile in the liquid state were measured at the constant atmospheric pressure in the temperature interval of 300·60 to 328·35 K. The static type of adiabatic calorimeter was used for the measurements.

Unlike dimethylpyridines, where heat capacities were measured[1] for all six existing isomers from their melting points to normal boiling points, it is not known from the accessible literature that the heat capacities for any of trimethylpyridine isomers (collidines) would be measured. Therefore, two of them, viz. 2,3,6-trimethylpyridine and 2,4,6-trimethylpyridine were measured in this work; for a similar reason, heat capacities of 3-methoxypropionitrile, used as the stationary phase in gas chromatography, were measured, too.

EXPERIMENTAL

Apparatus: The measurements were carried out using the static type of adiabatic calorimeter which is of the design and control unit described earlier[2]. The apparatus pertains to the series of calorimeters designed in our laboratory which work in case of measuring heats of vaporization or mixing[3] in the isothermal regime whereas in case of measuring heat capacities[4,5], the regime approaching the adiabatic regime is employed. Between the warmer calorimetric vessel and the colder controlling thermostatted wall, the controlled and well-known heat flow takes place which is taken into the correction for heat losses. Velíšek[6], in his classification of calorimeters, suggested to use term isodiathermal and Nölting[7] called an analogously functioning equipment of his own design diabatic calorimeter. No one of these terms, however, has been accepted in the literature.

The scheme of the calorimeter is given in Fig. 1. Calorimetric vessel (Fig. 2) is sheathed into shell 1 on which electrical heatings and resistance thermometers are coiled up. The controlling thermostatted wall 2 is surrounded by thermostat 3 and outer protective jacket 4 on which heatings and resistance thermometers are coiled up, too. The bridge connection of resistance thermometers and further electrical connections are identical with the description in paper[2].

The use of a microcomputer for controlling the calorimeter and data collection[8] is a novelty. The calibration of platinum resistance thermometer for measuring temperatures and temperature differences was carried out in terms of a standard platinum thermometer and resistance bridge — model F 26 of Automatic Systems Laboratories.

The calorimeter design required even a new design of calorimetric vessel (Fig. 2). For substances exhibiting saturated vapour pressures higher than 100 kPa and for accurate measurements, it is necessary to measure without air presence. For this purpose serves vessel *a* (Fig. 2*a*) which can be evacuated and filled without the air access by means of a transparent packing and a simple filling device. In such a vessel, heat capacity of one-component two-phase system of vapour and liquid is measured which can be converted to the heat capacity along the saturation line C_s (refs[9,10]). For substances with low saturated vapour pressure where the presence of small amount of air does not matter, vessel *b* is designed (Fig. 2*b*) which does not make it possible to be evacuated. Both the vessels are of volume about 10 cm^3 and are made of brass. Their inner built-in part is made of silver sheet and serves to ensure the heat distribution into the whole sample volume.

Measuring procedure: The first-rate task is the filling of calorimetric vessel in such a way that the size of vapour space should be as small as possible during the measurement. Therefore it is necessary to know the data on the temperature expansion of the substance measured in the

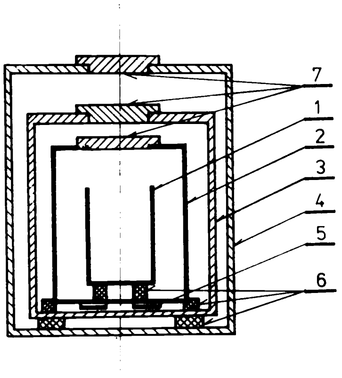

FIG. 1

Scheme of calorimeter: 1 shell of calorimetric system, 2 controlling thermostatted wall, 3 thermostat, 4 outer protective jacket, 5 resistances of control bridges, 6 Teflon supports, 7 covers

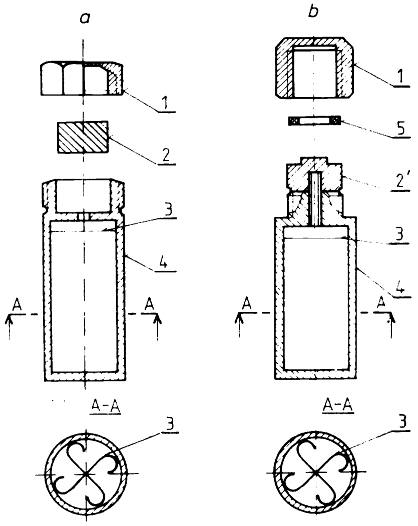

FIG. 2

Sketch of calorimetric vessels for measuring heat capacities of liquids: *a* construction making it possible to evacuate the vessel; *b* vessel designed for measuring at constant pressure. 1 Vessel closure, 2 transparent packing, 2′ Teflon packing, 3 built-in part, 4 vessel body, 5 press washer temperature range in which the measurement takes place. They are usually determined on measuring the densities of liquid substances.

In this work, the substances were measured which enabled us to fill up the vessel to the volume of 9·5 cm^3. The resulting vapour space is small. Since the saturated vapour pressure of substance measured is as well low in the chosen temperature interval (normal boiling points lie around 443 K), it was not necessary to introduce corrections for the vapour space. For these reasons it is also possible to identify the values of heat capacities along the saturation line with isobaric heat capacity C_p.

The measurement itself consists of three phases: In the initial and final phase, the heat loss flow is measured from the calorimetric vessel to surroundings for the adjustable temperature difference between the vessel and controlling thermostatted wall. The temperature difference amounts to 0·001—0·003 K. The experiment is controlled in such a way that the loss flow in the

TABLE I

Experimental values of molar heat capacity C_p as a function of temperature

T, K	C_p, J K^{-1} mol^{-1}		
	2,3,6-trimethylpyridine	2,4,6-trimethylpyridine	3-methoxypropionitrile
300·60	220·0	215·1	180·6
305·48	221·2	216·2	180·5
310·26	222·7	218·6	180·8
314·94	224·0	220·7	181·0
319·51	225·7	222·4	181·4
323·98	227·6	225·0	181·7
328·35	229·0	227·1	182·3

TABLE II

Constants of Eq. (*1*) for the temperature dependence of molar heat capacity C_p in the temperature interval of 300—328 K

Constants	2,3,6-Trimethylpyridine	2,4,6-Trimethylpyridine	3-Methoxypropionitrile
A_0	410·64	81·418	391·56
A_1	−1·5171	0·44263	−1·4014
$A_2 . 10^3$	2·9366		2·3268
s^a	0·148	0·439	0·076

[a] Standard deviation.

initial and final period should be the same and lie within 0·5—1 J for 25 min. In the main phase lasting about 15 min, the heat of about 400 J is supplied into the vessel, which results in temperature increase about $\Delta T = 4 \cdot 5$ K. The temperature increase was always the same for all three samples and the same are also mean temperature $T = T_i + \Delta T/2$ to which the measured heat capacities are related (T_i is the initial temperatures of measurement).

The molar heat capacity of liquid substance was calculated from the relation

$$C_p = \left(\frac{Q - Q_z}{\Delta T} - C_n \right) \frac{M}{m}, \qquad (1)$$

where Q is the heat supplied into the calorimetric vessel with sample which increases temperature by ΔT, Q_z represents the correction for the heat loss flow converted to the main period time, C_n is the heat capacity of empty calorimetric vessel, M the molar mass and m the sample mass.

The heat capacity of empty calorimetric vessel was determined by means of heptane[11]. The calorimeter was tested by measuring heat capacity of benzene and methanol. From the comparison with the tabulated data of heat capacities[11] and from the error analysis results the experimental error of the apparatus is about 0·3%.

Substances used: All three measured substances are chromatographic standards prepared in the Institute of Physical Chemistry, Polish Academy of Science, Warsaw. The purity given by them is for both trimethylpyridines better than 99·9 mole % (GLC) and for 3-methoxypropionitrile 99·96 mole % (GLC). Heptane, used for calibrating the apparatus, was described formerly[5].

RESULTS

The measured molar heat capacities at constant atmospheric pressure are given in Table I for all three substances. Table II presents the constants of polynomial expansion of dependence of heat capacity C_p on temperature T:

$$C_p = \sum_{j=0}^{m} A_j T^j \qquad (2)$$

and standard deviation s. The degree of polynomial, m, was determined in terms of the statistical criterion, so-called F-test[12].

A higher value of standard deviation for 2,4,6-trimethylpyridine follows from the greater scatter of measured values C_p and from the used linear expansion (2) which is less flexible. However, with this, nor for one measured point exceeded the value of $[(C_p)_{exp} - (C_p)_{calc}]\, 100/(C_p)_{exp}$ the estimated accuracy of measurement, i.e., 0·3%. Subscripts exp and calc represent the experimental and calculated quantity.

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