Journal of Thermal Analysis and Calorimetry, Vol. 63 (2001) 879–899

HEAT CAPACITIES OF HYDROXY AND AMINODERIVATIVES OF BENZENE

M. Čenský[1], *M. Lipovská*[1], *H.-G. Schmidt*[2], *V. Rů ička*[1]* *and G. Wolf*[2]

[1]Department of Physical Chemistry, Institute of Chemical Technology, Technická 5,
166 28 Prague 6, Czech Republic
[2]Institute of Physical Chemistry, Faculty of Chemistry and Physics, Technical University –
Bergakademie Freiberg, Leipziger Strasse 29, D-09596 Freiberg/Sachsen, Germany

(Received June 13, 2000; in revised form October 10, 2000)

Abstract

Heat capacities in the liquid phase C^l of methylbenzeneamines and heat capacities in the solid phase C^s of benzenediols and of 4-methylbenzeneamine were measured by commercial Setaram heat conduction and power compensated calorimeters. Results obtained cover the following temperature range (depending on the compound and state of aggregation): 2-methylbenzeneamine 313 to 371 K, 3-methylbenzeneamine 263 to 371 K, 4-methylbenzeneamine 133 to 353 K, 1,2-benzenediol 153 to 353 K, 1,3-benzenediol 173 to 353 K, 1,4-benzenediol 133 to 403 K. The heat capacity data obtained in this work were merged with experimental data from literature, critically assessed and sets of recommended data were developed by correlating selected data as a function of temperature.

Keywords: benzenediols, heat capacity in liquid and solid phase, methylbenzeneamines, temperature dependence

Introduction

Heat capacities in liquid phase are required for enthalpy balances in chemical engineering calculations. Even though experimental data are available for a fairly large group of compounds [1], more data are needed either for extending the temperature range the available data cover or for verifying the presently available literature data. Furthermore, the newly obtained data can be utilized for developing recommended sets of data to be included in databases of critically evaluated data and/or used for extending the estimation methods, in particular those based on the group-contribution approach.

Heat capacities in both liquid and solid phases can be employed in simultaneously correlating several related physical-chemical properties by the use of thermodynamic relationships. A method of simultaneous correlation of vapor or sublima-

---

* Author for correspondence: E-mail: vlastimil.ruzicka@vscht.cz

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

tion pressures, enthalpies of vaporization or sublimation, and differences between heat capacity in the ideal gas state and that in the liquid or solid phase was developed [2] and applied to several families of compounds [3–5] to calculate vapor and/or sublimation pressures over a large temperature range.

Experimental

Apparatus and procedure

Three commercial calorimeters made by Setaram (Caluire, France), C80, Micro-DSC II, and DSC 141, were used for measurement of saturation heat capacities defined as

$$C_{\mathrm{sat}}=T\left(\frac{\partial S}{\partial T}\right)_{\mathrm{sat}} \tag{1}$$

All three calorimeters were calibrated with synthetic sapphire (α-Al_2O_3), the NIST Standard Reference Material 720.

The vapor pressure of all studied substances was below 5 kPa at all experimental temperatures; it was thus not necessary to apply any correction for sample vaporization. This correction was discussed by Zábranský *et al.* [1] and the following equation was derived

$$C_{\mathrm{sat}}=\frac{C_{\mathrm{t}}}{N}+T\left(\frac{\partial p}{\partial T}\right)_{\mathrm{sat}}\left(\frac{\partial V_{\mathrm{m}}^{1}}{\partial T}\right)_{\mathrm{sat}}-T\left(\frac{V}{N}-V_{\mathrm{m}}^{1}\right)\left(\frac{\partial^{2} p}{\partial T^{2}}\right)_{\mathrm{sat}} \tag{2}$$

where C_{t} is the heat capacity of a two-phase vapor-liquid equilibrium system, V is the total volume of the calorimetric cell, N is the total number of moles of the measured substance in the cell. The correction on the right hand side of this relationship can be calculated from the vapor pressure equation and pVT properties of the liquid. The temperature variation of the second and third terms of the Eq. (2) is illustrated for 2-methylbenzeneamine and for the C80 calorimeter cell (volume 9.5 cm^3) in Table 1. The first two lines correspond to real experimental conditions in this work, the last two lines represent extreme cases. It is seen that the correction even in extreme cases never exceeds 0.1%. The correction was calculated assuming the calorimetric cell was filled under vacuum. As in this work the cell was filled under air, the correction will be even smaller and can therefore be neglected.

The temperature dependence of heat capacity for all studied substances was close to linear. Thus, the average heat capacity over the individual temperature step could be considered as true heat capacity relating to the mean temperature of the interval. All experimental heat capacities determined in this work are at about 100 K below the normal boiling temperature. The reported saturation heat capacities are identical to isobaric heat capacities defined as

$$C_{\mathrm{p}}=T\left(\frac{\partial S}{\partial T}\right)_{\mathrm{p}}=\left(\frac{\partial H}{\partial T}\right)_{\mathrm{p}} \tag{3}$$

The C80 Setaram heat conduction calorimeter is capable of measuring from ambient temperature up to 573 K but requires a fairly large quantity of a measured substance (about 5 g minimum). The Micro-DSC II Setaram heat conduction calorimeter, when utilized for measuring heat capacities, covers temperature range from 258 to 358 K and requires about 0.5 g of a measured substance. It provides the most accurate data among the calorimeters used in this work. The power compensated calorimeter Setaram DSC 141, which offers a very large measuring temperature range, was in this work employed from 133 K up to ambient temperature. The crucible containing the measured substance is rather small compared with that of the two other calorimeters; the amount of the measured substance was about 100 mg. As the crucible is made of aluminum, it cannot be sealed satisfactorily. This may lead to substance loss during measurement thus deteriorating the reliability and uncertainty of the obtained data. As the vapor pressure of substances measured in this work was at all experimental temperatures rather low, we observed no mass losses during experiments.

Table 1 Correction for sample vaporization for 2-methylbenzeneamine
$V_{vap}=100(V-NV_m)/V$ denotes the percentage of the cell volume occupied by the vapor,
corrI=$T(\partial p/\partial T)_{sat}(\partial V/\partial T)_{sat}$, corrII=$-T(V/N-V_m)(\partial^2 p/\partial T^2)_{sat}$,
correction=$100(C_{sat}-C_t/N)/C_{sat}$ denotes the overall percentage difference between C_{sat} and C_t/N

T/K	p/kPa	V_{vap}/%	C_{sat}/	CorrI/	CorrII/	Correction/
				J K^{-1} mol^{-1}		%
313.10	0.12	16.0	221.4	0.0002	–0.0033	–0.001
371.10	3.18	11.6	235.0	0.0058	–0.0317	–0.010
298.15	0.04	30.0	218.5	0.0001	–0.0030	–0.001
398.15	9.87	30.0	242.2	0.0178	–0.2445	–0.090

Heat capacities in the liquid phase were measured with a C-80 Setaram calorimeter equipped with standard cells having the inner volume of 9.5 cm^3 reduced by a raised bottom. Experiments were carried out in a continuous mode where temperature was steadily increased with a heating rate of 2.5 mK s^{-1}. The time integrals of the differential thermopile signal for the filled and empty sample cells provided heat flow differences. Heat capacity was then obtained from the ratio of the heat flow differences and the derivative of temperature with respect to time [6]. In our previous experiments we estimated the uncertainty of data measured by C80 calorimeter to be ±1% by making test experiments with synthetic sapphire and with several compounds of well-known heat capacity values. Due to thermal instability of the studied compounds we raised the uncertainty of results in this work to ±2%.

Heat capacities in the solid and liquid phases were measured with a Micro-DSC II Setaram calorimeter equipped with standard cells made of Hastelloy with inner volume of 1 cm^3. A discontinuous step heating method was employed with reference discrete temperatures ranging from 263 to 353 K, with an equidistant step of 10 K. In a typical experiment, the temperature was increased in steps of 2 K with a heating rate of 5 mK s^{-1} with an isothermal delay of 2000 s. The uncertainty of heat capacity measurements estimated from calibration and test experiments with several compounds is ±0.5% of the measured value.

Enthalpy and temperature of fusion were measured with a Micro-DSC II Setaram calorimeter. Measurements were repeated with a varied heating rate of 3.3, 5, and 8.3 mK s^{-1}. In addition to heat flow calibration with a synthetic sapphire, enthalpy of fusion of pure gallium and of water were also determined to verify the measurement method and to estimate the uncertainty of the data obtained. Deviation of the mean value from gallium experiments was –0.6%, from the reference value. Gallium was recommended by Sabbah *et al.* [7] as a standard reference material for calorimetry and thermal analysis.

Heat capacities in the solid phase were measured using the DSC 141 Setaram calorimeter equipped with a 120 μl crucible made of aluminum with a disk-shaped cover. A continuous method with a reference was employed and disks of synthetic sapphire were used as a standard. Several test experiments with powdered α-Al_2O_3 and naphthalene were carried out to determine the best working conditions. It was concluded that a low heating rate of 50 mK s^{-1} and a sample mass from 50 to 80 mg would lead to uncertainty in the measured heat capacity values of 3 and 5% in the temperature ranges 203 to 293 K and 133 to 203 K, respectively. Dry nitrogen from a gas cylinder was used as a sweeping gas. Working conditions adopted in this work are in accordance with recommendations of de Barros *et al.* [8].

Materials

C_7H_9N, *2-methylbenzeneamine*

Fluka product of stated purity >99.5%, original purity measured by GC 99.97%.

C_7H_9N, *3-methylbenzeneamine*

Fluka product of stated purity >99%, original purity measured by GC 99.7%.

C_7H_9N, *4-methylbenzeneamine*

Fluka product of stated purity >99%, original purity measured by GC 99.7%.

$C_6H_6O_2$, *1,2-benzenediol*

Fluka product of stated purity >99%, original purity measured by GC 99.95%.

$C_6H_6O_2$, *1,3-benzenediol*

Fluka product of stated purity >99%, original purity measured by GC 99.8%.

$C_6H_6O_2$, 1,4-benzenediol

Fluka product of stated purity >99%, original purity measured by GC 100% (amount of impurities below detection limit of the GC method).

All chemicals were used without further purification.

Results

The direct experimental T–$C_{p,m}$ values are presented in Tables 2a to 2g. Results from DSC-141 experiments are smoothed data obtained by averaging values of several repetitive experiments.

Table 2a Liquid heat capacity of 2-methylbenzeneamine

T/K	C_p/R	$\Delta C_p/R$	Calorimeter
313.1	26.66	0.03	C80
313.2	26.64	0.02	C80
318.1	26.77	0.02	C80
318.2	26.79	0.04	C80
323.1	26.92	0.04	C80
323.2	26.90	0.02	C80
328.1	27.05	0.04	C80
328.2	27.03	0.02	C80
333.2	27.15	0.00	C80
333.2	27.17	0.03	C80
338.1	27.28	–0.01	C80
338.2	27.30	0.02	C80
343.1	27.41	–0.01	C80
343.2	27.43	0.01	C80
348.2	27.56	–0.01	C80
348.2	27.55	–0.01	C80
353.2	27.69	–0.02	C80
353.2	27.68	–0.04	C80
358.1	27.82	–0.04	C80
358.2	27.79	–0.07	C80
363.1	27.94	–0.07	C80
363.1	27.91	–0.11	C80
368.2	28.06	–0.12	C80
368.2	28.01	–0.16	C80
371.1	28.12	–0.15	C80

R=8.31451 J K^{-1} mol^{-1}, $\Delta C_p/R=(C_p-C_p^{calc})/R$

Table 2b Liquid heat capacity of 3-methylbenzeneamine

T/K	C_p/R	$\Delta C_p/R$	Calorimeter
313.2	26.42	–0.28	C80
313.2	26.42	–0.28	C80
318.2	26.57	–0.25	C80
318.2	26.58	–0.25	C80
323.2	26.72	–0.23	C80
323.2	26.73	–0.23	C80
328.2	26.87	–0.21	C80
328.2	26.88	–0.21	C80
333.2	27.02	–0.19	C80
333.2	27.02	–0.19	C80
338.2	27.17	–0.17	C80
338.2	27.17	–0.17	C80
343.2	27.32	–0.15	C80
343.2	27.31	–0.16	C80
348.2	27.47	–0.12	C80
348.2	27.46	–0.13	C80
353.2	27.63	–0.10	C80
353.2	27.62	–0.11	C80
358.2	27.78	–0.07	C80
358.2	27.77	–0.09	C80
363.2	27.93	–0.05	C80
363.2	27.92	–0.06	C80
368.1	28.08	–0.03	C80
368.1	28.08	–0.03	C80
371.2	28.17	–0.02	C80
371.2	28.17	–0.02	C80
263.2	25.43	0.01	micro-DSC
273.2	25.69	0.02	micro-DSC
283.2	25.93	0.00	micro-DSC
293.2	26.19	0.00	micro-DSC
303.2	26.46	0.02	micro-DSC
313.2	26.75	0.06	micro-DSC
323.2	27.00	0.05	micro-DSC
333.2	27.26	0.05	micro-DSC
343.2	27.53	0.06	micro-DSC
353.2	27.79	0.06	micro-DSC

R=8.31451 J K^{-1} mol^{-1}, $\Delta C_p/R=(C_p-C_p^{calc})/R$

Table 2c Liquid heat capacity of 4-methylbenzeneamine

T/K	C_p/R	$\Delta C_p/R$	Calorimeter
328.3	26.91	–0.13	C80
328.6	26.92	–0.12	C80
333.2	27.06	–0.12	C80
333.2	27.07	–0.11	C80
338.2	27.22	–0.11	C80
338.2	27.21	–0.11	C80
343.1	27.36	–0.11	C80
343.2	27.36	–0.11	C80
348.1	27.49	–0.12	C80
348.1	27.50	–0.11	C80
353.1	27.61	–0.15	C80
353.1	27.62	–0.13	C80
323.2	26.88	0.00	micro-DSC
333.2	27.21	0.03	micro-DSC
343.2	27.57	0.10	micro-DSC
353.2	27.77	0.02	micro-DSC

R=8.31451 J K^{-1} mol^{-1}, $\Delta C_p/R=(C_p-C_p^{calc})/R$

Table 2d Solid heat capacity of 4-methylbenzeneamine

T/K	C_p/R	$\Delta C_p/R$	Calorimeter
133.2	9.24	0.06	DSC 141
138.2	9.54	0.02	DSC 141
143.2	9.83	–0.01	DSC 141
148.2	10.13	–0.03	DSC 141
153.2	10.44	–0.04	DSC 141
158.2	10.75	–0.04	DSC 141
163.2	11.04	–0.05	DSC 141
168.2	11.35	–0.04	DSC 141
173.2	11.66	–0.03	DSC 141
178.2	11.97	–0.02	DSC 141
183.2	12.27	–0.02	DSC 141
188.2	12.58	–0.01	DSC 141
193.2	12.89	0.01	DSC 141
198.2	13.18	0.01	DSC 141
203.2	13.49	0.03	DSC 141
208.2	13.79	0.03	DSC 141
213.2	14.10	0.04	DSC 141

Table 2d Continued

T/K	C_p/R	$\Delta C_p/R$	Calorimeter
218.2	14.40	0.04	DSC 141
223.2	14.69	0.04	DSC 141
228.2	15.00	0.05	DSC 141
233.2	15.30	0.05	DSC 141
238.2	15.59	0.04	DSC 141
243.2	15.89	0.02	DSC 141
248.2	16.20	0.02	DSC 141
253.2	16.50	–0.01	DSC 141
258.2	16.81	–0.02	DSC 141
263.2	17.11	–0.04	DSC 141
268.2	17.42	–0.07	DSC 141
273.2	17.73	–0.10	DSC 141
278.2	18.06	–0.13	DSC 141
283.2	18.38	–0.17	DSC 141
288.2	18.71	–0.20	DSC 141
293.2	19.05	–0.23	DSC 141
263.2	17.13	–0.03	micro-DSC
273.2	17.85	0.01	micro-DSC
283.2	18.58	0.04	micro-DSC
293.2	19.28	0.00	micro-DSC
303.2	20.05	0.00	micro-DSC

R=8.31451 J K^{-1} mol^{-1}, $\Delta C_p/R=(C_p-C_p^{calc})/R$

Table 2e Solid heat capacity of 1,2-benzenediol

T/K	C_p/R	$\Delta C_p/R$	Calorimeter
313.2	17.80	0.40	C80
313.2	17.77	0.37	C80
318.1	18.04	0.37	C80
318.1	18.07	0.40	C80
323.1	18.30	0.35	C80
323.2	18.34	0.39	C80
328.2	18.57	0.33	C80
328.2	18.62	0.38	C80
333.2	18.82	0.31	C80
333.2	18.89	0.38	C80
338.2	19.09	0.30	C80
338.2	19.17	0.37	C80

Table 2e Continued

T/K	C_p/R	$\Delta C_p/R$	Calorimeter
343.2	19.37	0.29	C80
343.2	19.46	0.39	C80
348.2	19.66	0.30	C80
348.2	19.78	0.42	C80
263.2	14.66	0.00	micro-DSC
273.2	15.19	–0.01	micro-DSC
283.2	15.73	–0.01	micro-DSC
293.2	16.21	–0.08	micro-DSC
303.2	16.82	–0.03	micro-DSC
313.2	17.30	–0.10	micro-DSC
323.2	17.83	–0.13	micro-DSC
333.2	18.38	–0.13	micro-DSC
343.2	19.03	–0.04	micro-DSC
353.2	19.75	0.11	micro-DSC
153.2	8.79	–0.10	DSC 141
158.2	9.07	–0.08	DSC 141
163.2	9.35	–0.05	DSC 141
168.2	9.64	–0.02	DSC 141
173.2	9.92	0.00	DSC 141
178.2	10.20	0.02	DSC 141
183.2	10.46	0.03	DSC 141
188.2	10.74	0.05	DSC 141
193.2	11.02	0.07	DSC 141
198.2	11.28	0.07	DSC 141
203.2	11.56	0.09	DSC 141
208.2	11.83	0.09	DSC 141
213.2	12.09	0.10	DSC 141
218.2	12.36	0.10	DSC 141
223.2	12.62	0.10	DSC 141
228.2	12.89	0.10	DSC 141
233.2	13.15	0.10	DSC 141
243.2	13.67	0.08	DSC 141
248.2	13.92	0.07	DSC 141
253.2	14.17	0.05	DSC 141
258.2	14.42	0.03	DSC 141
263.2	14.67	0.01	DSC 141
268.2	14.92	–0.01	DSC 141

Table 2e Continued

T/K	C_p/R	$\Delta C_p/R$	Calorimeter
273.2	15.18	–0.03	DSC 141
278.2	15.43	–0.05	DSC 141
283.2	15.67	–0.08	DSC 141
288.2	15.92	–0.10	DSC 141
293.2	16.16	–0.14	DSC 141

R=8.31451 J K^{-1} mol^{-1}, $\Delta C_p/R=(C_p-C_p^{calc})/R$

Table 2f Solid heat capacity of 1,3-benzenediol

T/K	C_p/R	$\Delta C_p/R$	Calorimeter
188.2	10.33	–0.20	DSC 141
193.2	10.61	–0.20	DSC 141
198.2	10.91	–0.18	DSC 141
203.2	11.20	–0.17	DSC 141
208.2	11.51	–0.15	DSC 141
213.2	11.83	–0.11	DSC 141
218.2	12.14	–0.08	DSC 141
223.2	12.46	–0.04	DSC 141
228.2	12.78	0.00	DSC 141
233.2	13.10	0.03	DSC 141
238.2	13.43	0.08	DSC 141
243.2	13.75	0.12	DSC 141
248.2	14.08	0.17	DSC 141
253.2	14.40	0.20	DSC 141
258.2	14.71	0.24	DSC 141
263.2	15.02	0.26	DSC 141
268.2	15.32	0.29	DSC 141
273.2	15.61	0.30	DSC 141
278.2	15.90	0.31	DSC 141
283.2	16.17	0.29	DSC 141
288.2	16.43	0.27	DSC 141
293.2	16.67	0.23	DSC 141
263.2	15.00	0.25	micro-DSC
273.2	15.51	0.19	micro-DSC
283.2	15.98	0.10	micro-DSC
293.2	16.58	0.14	micro-DSC
303.2	17.07	0.06	micro-DSC
313.2	17.61	0.04	micro-DSC

Table 2f Continued

T/K	C_p/R	$\Delta C_p/R$	Calorimeter
323.2	18.10	–0.03	micro-DSC
333.2	18.61	–0.09	micro-DSC
343.2	19.24	–0.02	micro-DSC
353.2	19.71	–0.12	micro-DSC

R=8.31451 J K^{-1} mol^{-1}, $\Delta C_p/R=(C_p-C_p^{calc})/R$

Table 2g Solid heat capacity of 1,4-benzenediol

T/K	C_p/R	$\Delta C_p/R$	Calorimeter
313.2	17.35	0.14	C80
313.2	17.37	0.15	C80
313.2	17.35	0.13	C80
323.1	17.90	0.15	C80
323.1	17.90	0.16	C80
323.2	17.90	0.15	C80
333.1	18.40	0.12	C80
333.2	18.41	0.13	C80
333.2	18.39	0.11	C80
343.2	18.88	0.08	C80
343.2	18.83	0.03	C80
343.2	18.85	0.05	C80
353.1	19.28	–0.05	C80
353.2	19.36	0.03	C80
353.2	19.26	–0.07	C80
363.1	19.84	0.00	C80
363.1	19.67	–0.18	C80
363.2	19.70	–0.14	C80
373.2	20.33	–0.04	C80
373.2	20.10	–0.27	C80
373.2	20.16	–0.21	C80
383.1	20.68	–0.21	C80
383.2	20.82	–0.07	C80
383.2	20.63	–0.26	C80
393.1	21.34	–0.07	C80
393.1	21.29	–0.12	C80
393.2	21.31	–0.10	C80
403.1	21.87	–0.06	C80
403.1	22.08	0.16	C80

Table 2g Continued

T/K	C_p/R	$\Delta C_p/R$	Calorimeter
403.2	22.17	0.24	C80
410.7	22.37	0.06	C80
412.5	22.99	0.58	C80
412.7	22.97	0.55	C80
133.2	7.83	0.38	DSC 141
138.2	8.03	0.30	DSC 141
143.2	8.25	0.25	DSC 141
148.2	8.46	0.18	DSC 141
153.2	8.70	0.15	DSC 141
158.2	8.94	0.11	DSC 141
163.2	9.18	0.07	DSC 141
168.2	9.43	0.05	DSC 141
173.2	9.68	0.02	DSC 141
178.2	9.93	0.00	DSC 141
183.2	10.20	–0.01	DSC 141
188.2	10.46	–0.02	DSC 141
193.2	10.74	–0.02	DSC 141
198.2	11.01	–0.02	DSC 141
203.2	11.28	–0.02	DSC 141
208.2	11.56	–0.01	DSC 141
213.2	11.84	–0.01	DSC 141
218.2	12.12	0.00	DSC 141
223.2	12.40	0.01	DSC 141
228.2	12.67	0.01	DSC 141
233.2	12.95	0.02	DSC 141
238.2	13.23	0.03	DSC 141
243.2	13.51	0.03	DSC 141
248.2	13.77	0.03	DSC 141
253.2	14.05	0.04	DSC 141
258.2	14.32	0.03	DSC 141
263.2	14.58	0.03	DSC 141
268.2	14.85	0.03	DSC 141
273.2	15.10	0.01	DSC 141
278.2	15.35	–0.01	DSC 141
283.2	15.60	–0.02	DSC 141
288.2	15.84	–0.05	DSC 141
293.2	16.08	–0.08	DSC 141

Table 2g Continued

T/K	C_p/R	$\Delta C_p/R$	Calorimeter
263.2	14.59	0.04	micro-DSC
273.2	15.11	0.02	micro-DSC
283.2	15.67	0.05	micro-DSC
293.2	16.18	0.03	micro-DSC
303.2	16.73	0.04	micro-DSC
313.2	17.28	0.06	micro-DSC
323.2	17.79	0.04	micro-DSC
333.2	18.35	0.08	micro-DSC
343.2	18.91	0.11	micro-DSC
353.2	19.41	0.09	micro-DSC

R=8.31451 J K^{-1} mol^{-1}, $\Delta C_p/R=(C_p-C_p^{\mathrm{calc}})/R$

These data were combined with all other calorimetrically determined heat capacities available in literature. All available sources were critically assessed. The important part of the selection process was the simultaneous correlation of all experimental data which served to test the consistency and helped to reveal systematic errors. The following criteria were observed in the selection process: a) accuracy of the experimental technique claimed by the author, b) laboratory performance history, c) consistency of the data with values from other laboratories (if available), d) substance purity, e) calorimeter type, f) time of data origin, g) scatter of the data. It is not possible to apply the above selection criteria in a rigorous manner following strictly the outlined policy. In some cases, the error of measurement claimed by the author is too optimistic and it may even be unrealistic. In addition, evaluating the reputation of various laboratories is a relatively subjective process.

The selected data were fitted with the polynomial equation using the weighed least-squares method:

$$\frac{C_{\mathrm{p,m}}}{R}=\sum_{\mathrm{i}=0}^{\mathrm{n}}A_{\mathrm{i}+1}\left(\frac{T}{100}\right)^{\mathrm{i}} \tag{4}$$

(R=8.31451 J K^{-1} mol^{-1}).

Considering the width of the temperature range of experimental values for 2-methylbenzeneamine the data were correlated by cubic splines in three uneven subintervals. In this case the correlation is constrained to yield the identical C, dC/dT and d^2C/dT^2 values at the two knots (temperatures splitting the overall temperature range of experimental values into subintervals). The lower and upper subintervals are relatively short (about 145 and 100 K) and correspond to highly accurate low temperature adiabatic data and scattered values near the critical temperature, respectively. Results of the correlation by cubic splines are presented in terms of parameters of Eq. (3) with n=3. More detailed information regarding temperature correlation of C with cubic splines can be found in the monograph by Zábranský *et al.* [1].

Table 3 Parameters of Eq. (4)

Compound	Phase	Parameters				Temperature range			Uncertainty/ %
		A_1	A_2	A_3	A_4	T_{min}/K	T_{max}/K	s_r^*	
2-methylbenzeneamine C_p	l	33.7573	–9.28054	2.96374	–0.232246	235.2	400.0		0.5
	l	21.5471	–0.122886	0.674323	–0.0414613	400.0	600.0		2
	l	–3084.81	1553.06	–258.189	14.3398	600.0	700.0	1.0	5
2-methylbenzeneamine C_{sat}	l	34.0373	–9.55395	3.05112	–0.241372	235.2	400.0		0.5
	l	22.1827	–0.663034	0.828389	–0.0561445	400.0	600.0		2
	l	–1960.95	990.903	–164.433	9.12502	600.0	700.0	0.9	5
3-methylbenzeneamine	l	18.6574	2.56735	0	0	241.6	371.1	0.6	3
4-methylbenzeneamine	s	–3.35984	13.2898	–3.74281	0.629054	133.1	303.1	0.4	3
4-methylbenzeneamine	l	17.5264	2.89715	0	0	323.0	363.0	0.7	3
1,2-benzenediol	s	1.45689	4.63316	0.146083	0	110.3	353.1	1.2	3
1,3-benzenediol	s	–0.0664483	5.63222	0	0	110.3	353.1	2.4	3
1,4-benzenediol	s	–0.0872530	5.75447	–0.0729345	0	110.3	430.0	1.5	3

$^*s_r=10^2\left(\sum_{i=1}^{n}\left[\frac{\{C_m-C_m(\text{calc})\}/C_m}{n-m}\right]_i^2\right)^{\frac{1}{2}}$, where n is the number of fitted data points, and m is the number of independent adjustable parameters

Table 4 Parameters of Eq. (5)

Compound	Phase	Parameters				Temperature range			Uncertainty/ %
		A_1	A_2	A_3	A_4	T_{min}/K	T_{max}/K	s_r	
2-methylbenzeneamine	l	–3.42010	0.250085	19.1691	11.6931	235.2	716.5	1.0	5
3-methylbenzeneamine	l	–4.57704	2.31487	18.7336	2.26247	241.6	709.0	0.4	5

If the selected experimental data in the liquid phase cover the temperature range of at least 50 K, the isobaric data were fitted to another empirical, the so-called quasi-polynomial, equation that allows a meaningful extrapolation to the critical point is:

$$\frac{C_{\mathrm{p,m}}}{R}=A_1\ln(1-T_{\mathrm{r}})+\frac{A_2}{1-T_{\mathrm{r}}}+A_3+A_4T_{\mathrm{r}} \tag{5}$$

where $T_{\mathrm{r}}=T/T_{\mathrm{c}}$, and T_{c} is the critical temperature. The derivation of Eq. (5) (Zábranský *et al.* [1]) was based on the assumption that the heat capacity is always an increasing function of temperature and that it is unbounded at the critical point. An objective function of the form was used:

$$S=\sum_{i=1}^{n}\left(\frac{\Delta C_{\mathrm{i}}}{R}\right)^2(\sigma_{\mathrm{C/R,i}})^{-2} \tag{6}$$

where the variance $\sigma_{\mathrm{C/R,i}}$ was estimated for each value on the basis of the assumed experimental error of the set of data used in the correlation. The input information was the percentage error of the experimental data $\sigma_{\mathrm{r}}C$ given by the author for the whole data set. The variance of the *i*-th data point was expressed as

$$\sigma_{\mathrm{C/R,i}}=10^{-2}\frac{C_{\mathrm{i}}\sigma_{\mathrm{r}}C}{R} \tag{7}$$

Parameters of Eq. (4) derived from the fit are given in Table 3 along with the relative standard deviation of the fit. Parameters of Eq. (5) are given in Table 4. It should be emphasized that extrapolation above the upper temperature limit of the experimental data by the quasi-polynomial equation is correct only in a qualitative manner. No guarantee can be given that the extrapolation will quantitatively describe the real heat capacity in this region except for the value at the critical point. The flexibility of the quasi-polynomial equation is generally worse than that of the polynomial Eq. (4), even though for the sets of data fitted in this work there is almost no difference as indicated by the relative standard deviation of the fit s_{r} that is given in Tables 3 and 4.

When the heat capacity data extend above the normal boiling temperature, differences between the isobaric and saturation heat capacities become significant. If accurate heat capacities are available, the data are converted to either type and correlated separately (Zábranský *et al.* [1]). This was the case for 2-methylbenzeneamine. The parameters for both heat capacity types are presented in Table 3.

Temperature and enthalpy of fusion of 4-methylbenzeneamine are given in Table 5.

Table 5 Temperature and enthalpy of fusion of 4-methylbenzeneamine

T_{f}/K	$\Delta_{\mathrm{f}}H$/kJ mol^{-1}
317±0.5	17.19±0.14

Discussion

The abundance of literature data for the compounds investigated and the temperature range that the data cover varies. For 2-methylbenzeneamine the data are the most abundant covering the entire liquid-vapor temperature range. For all remaining compounds, data are usually available from one or two literature sources. Bret-Dibat and Lichanot [9] determined heat capacities for benzenediols in solid phase using the Setaram DSC 111G microcalorimeter. Andrews' *et al.* [10] results for solid and liquid benzenediols were presented as temperature dependence of enthalpy, and were converted into heat capacity data. Andrews [11] published raw heat capacity data for solid benzenediols. Ueberreiter and Orthmann [12] determined heat capacities of solid benzenediols and presented them as a function of temperature in terms of parameters of a linear equation. Lange [13] measured heat capacity of 1,4-benzenediol over a wide temperature range from 28 to 274 K. Meva'a and Lichanot [14] measured heat capacities of liquid methylbezeneamines. The data cover a temperature range only for 4-methylbenzeneamine. For 2-methylbenzeneamine and for 3-methylbenzeneamine only a single data point was published. Steele *et al.* [15] determined heat capacity of liquid 2-methylbenzeneamine in a wide temperature range using two techniques, low temperature adiabatic calorimetry and DSC. For 2-methylbenzeneamine there are also average and isobaric heat capacity data by von Reis [16], Schiff [17] and Louguinine [18] but this was from the end of the 19th and the beginning of the 20th century. Despite the time of their origin the data are good. The data by Guseinov *et al.* [19] for 2-methylbenzeneamine and 3-methylbenzeneamine are apparently subject to large systematic errors as they deviate from other data by around –30%. The data for 2-methylbenzeneamine and 3-methylbenzeneamine by Kolosovskii and Udovenko [20] and for 2-methylbenzeneamine by Radulescu and Jula [21], both obtained by a simple experimental technique, are reported at a single room temperature.

Benzenediols are unstable when heated. Jedelský *et al.* [22] observed a significant decomposition of benzenediols in aqueous solutions at temperatures above 473 K. We observed in our C80 experiments a change in color of the measured compound from colorless to slightly grayish even at lower temperatures. This means the measured compounds may be contaminated after completion of our experiment performed with the C80 calorimeter. For this reason we raised the uncertainty of our C80 experiments to ±2%.

Reliability of our C80 data was evaluated by comparing them with other literature data obtained by different experimental techniques. For liquid 2-methylbenzeneamine our data agree within their experimental error with results of Steele *et al.* [15]. We consider their data, in particular in the lower temperature range from 235 to 441 K, the most accurate and the most reliable. A similar agreement with the data of Meva'a and Lichanot [14], being also within the experimental error, was observed for 4-methylbenzeneamine.

For benzenediols, the solid heat capacities obtained by Bret-Dibat and Lichanot [9] seem dubious. For all three isomers their data exhibit a temperature slope differing both from the data measured in our work and from the Andrews' data [11]. Except for

1,4-benzenediol we also rejected the Andrews' *et al.* data [10], which lie in the upper temperature range of all available data. The data by Andrews *et al.* [10] are scattered along our recommended data more than corresponds to their stated experimental error. We rejected the data for 1,4-benzenediol by Lange [13] as their slope differs from the selected data at the upper temperature limit. The data by the same author determined below 110 K were both rather scattered along the fitted line and beyond the interest of this work. The data by Ueberreiter and Orthmann [12] were included in the correlation for 1,3-benzenediol and 1,4-benzenediol. The slope of the data for 1,2-benzenediol differed from our recommended data; therefore, we rejected these data.

Deviation plots showing how experimental heat capacities measured by different authors deviate from the fitted data (Eq. (4) and Table 3) are given in Figs 1 to 6.

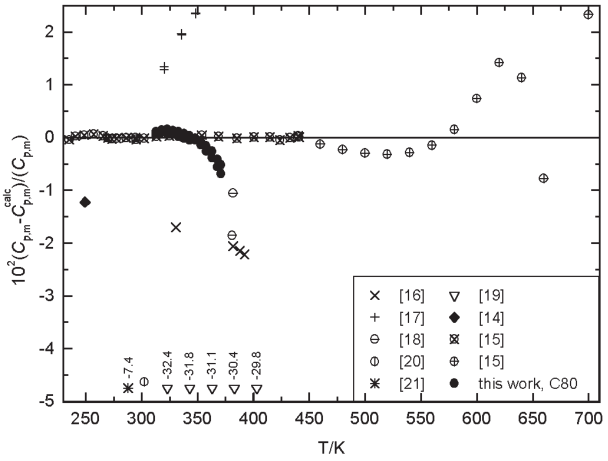

Fig. 1 Deviation plot for heat capacity of liquid 2-methylbenzeneamine

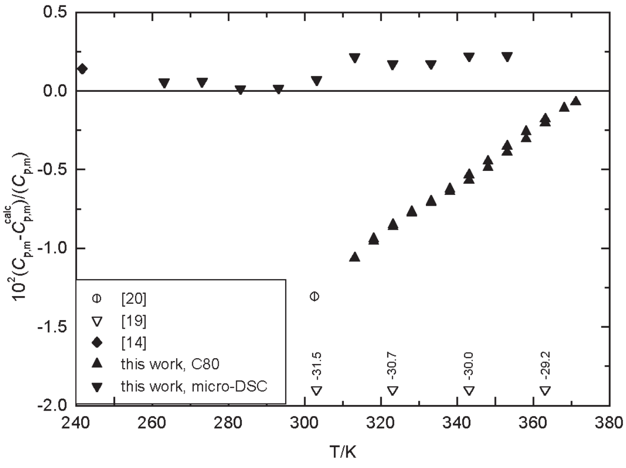

Fig. 2 Deviation plot for heat capacity of liquid 3-methylbenzeneamine

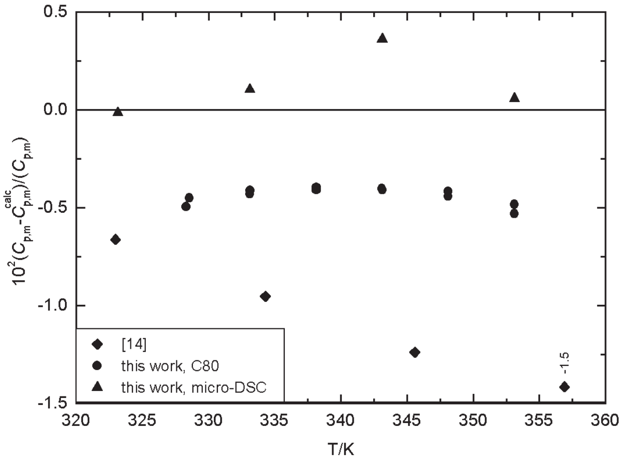

Fig. 3 Deviation plot for heat capacity of liquid 4-methylbenzeneamine

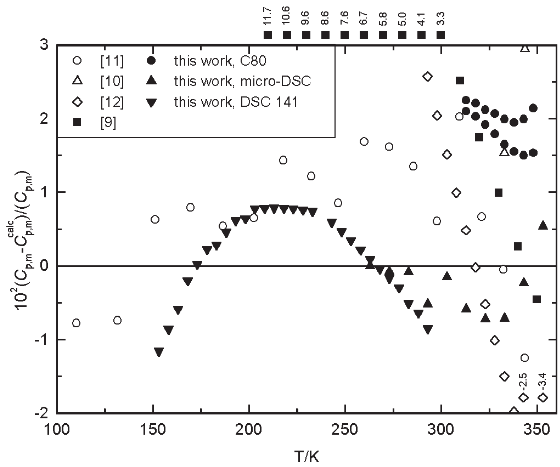

Fig. 4 Deviation plot for heat capacity of solid 1,2-benzenediol

In general, the solid heat capacities of isomeric benzenediols and the liquid heat capacities of two isomeric methylbenzeneamines were assigned the overall uncertainty of 3% derived from mutual scatter of data measured by different authors. Only for 2-methylbenzeneamine, where data were fitted by cubic splines in three subintervals we distinguished between different accuracies of experimental techniques. This was accomplished by assigning unlike uncertainty in each subinterval.

Our DSC-141 experiments with 1,2-benzenediol revealed a thermal event between 233 and 243 K without a significant change in heat capacity compared to the measurement accuracy. This event may be attributed to a possible solid-solid phase transition. However, more accurate experimental technique is required to provide evidence of the transition. A solid-solid phase transition was reported for 1,3-benzene-

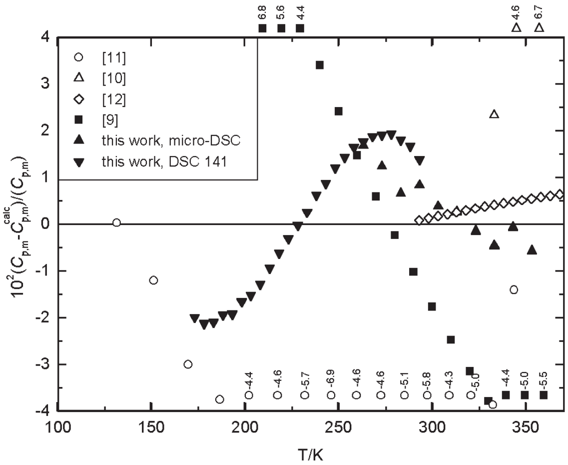

Fig. 5 Deviation plot for heat capacity of solid 1,3-benzenediol

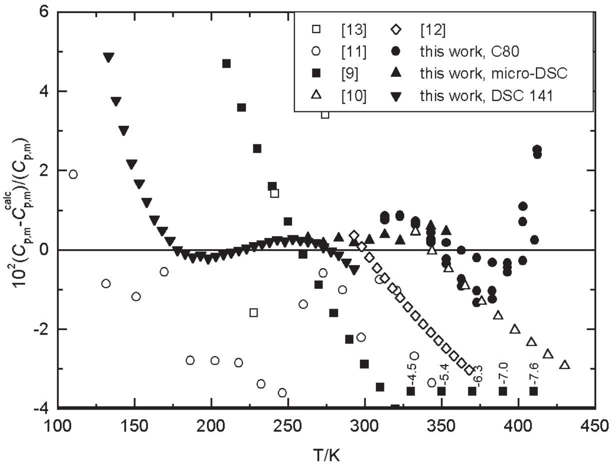

Fig. 6 Deviation plot for heat capacity of solid 1,4-benzenediol

diol by Bret-Dibat and Lichanot [9] at temperature of 366.75 K and by Ebisuzaki *et al.* [23] at temperature of 369 K. An evidence of a similar thermal event with onset temperature of 370.7 K was provided in our DSC141 experiment. 1,4-Benzenediol is known to form three crystalline modifications, denoted as α, β, γ, [24] under atmospheric pressure with phase α being stable at room temperature. However, we found no data on phase transition temperatures in the literature. Recently, a transition of phase α into phase δ occurring under elevated pressure was reported [25].

Conclusions

Recommended data on heat capacity of liquid methylbenzeneamines and solid benzenediols and 4-methylbenzeneamine were developed by critical assessment of newly determined and literature data. The recommended data are presented in terms of parameters of an empirical correlating equation expressing their dependence on temperature. Several sets of data published in the literature were rejected due to their large systematic deviations from the selected data.

* * *

M. Lipovská acknowledges the financial support of Deutscher Akademischer Austauschdienst, which made her stay possible at the Bergakademie Freiberg. This work was supported by the Ministry of Education of the Czech Republic under the grant number CB MSM 223400008.

References

1 M. Zábranský, V. Růžička, V. Majer and E. S. Domalski, Heat Capacity of Liquids. Critical Review and Recommended Values, J. Phys. Chem. Ref. Data Monograph number 6, American Chemical Society, Washington D.C. 1996.
2 K. Růžička and V. Majer, J. Phys. Chem. Ref. Data, 23 (1994) 1.
3 V. Růžička, M. Zábranský, K. Růžička and V. Majer, Thermochim. Acta, 245 (1994) 121.
4 K. Růžička, I. Mokbel, V. Majer, V. Růžička, J. Jose and M. Zábranský, Fluid Phase Equilib., 148 (1998) 107.
5 V. Roháč, V. Růžička, K. Růžička, M. Poledníček, K. Aim, J. Jose and M. Zábranský, Fluid Phase Equilib., 157 (1999) 121.
6 G. Höhne, W. Hemminger and H.-J. Flammersheim, Differential Scanning Calorimetry. An Introduction for Practitioners, Springer Verlag, Berlin 1996, p. 222.
7 R. Sabbah, Thermochim. Acta, 331 (1999) 93.
8 T. M. V. R. de Barros, R. C. Santos, A. C. Fernandes and M. E. Minas da Piedade, Thermochim. Acta, 269/270 (1995) 51.
9 P. Bret-Dibat and A. Lichanot, Thermochim. Acta, 147 (1989) 261.
10 D. H. Andrews, G. Lynn and J. Johnston, J. Am. Chem. Soc., 48 (1926) 1274.
11 D. H. Andrews, J. Am. Chem. Soc., 48 (1926) 1287.
12 K. Ueberreiter and H.-J. Orthmann, Z. Naturforsch. A, 5 (1950) 101.
13 F. Lange, Z. Phys. Chem., 110 (1924) 343.
14 L. M. Meva'a and A. Lichanot, Thermochim. Acta, 158 (1990) 335.
15 W. V. Steele, R. D. Chirico, A. Nguyen and S. E. Knipmeyer, J. Chem. Thermodyn., 26 (1994) 515.
16 M. A. von Reis, Ann. Phys. (Leipzig), [3] 13 (1881) 447.
17 R. Schiff, Z. Phys. Chem. Stoechiom. Verwandtschaftslehre, 1 (1887) 376.
18 W. Louguinine, Ann. Chim. Phys., [7] 27 (1902) 105.
19 S. O. Guseinov, A. A. Mirzaliev and Sh. G. Shakhmuradov, Izv. Vyssh. Ucheb. Zaved., Neft Gaz, 31 (1988) 13.
20 N. A. Kolosovskii and V. V. Udovenko, Zh. Obshch. Khim., 4 (1934) 1027.
21 D. Radulescu and O. Jula, Z. Phys. Chem., Abt. B, 26 (1934) 390.

22 J. Jedelský, L. Hnědkovský and I. Cibulka, J. Chem. Thermodyn., 31 (1999) 27.
23 Y. Ebisuzaki, L. H. Askari and A. M. Bryan, J. Chem. Phys., 87 (1987) 6659.
24 W. A. Caspari, J. Chem. Soc., (1927) 1093.
25 M. Naoki, T. Yoshizawa, N. Fukushima, M. Ogiso and M. Yoshino, J. Phys. Chem. B, 103 (1999) 6309.