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HEAT CAPACITIES OF THREE ISOMERIC CHLOROBENZENES AND OF THREE ISOMERIC CHLOROPHENOLS

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Abstract

Isobaric heat capacities C_p in the liquid and in the solid phase of 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,2,4-trichlorobenzene, 3-chlorophenol and 4-chlorophenol and in the liquid phase of 2-chlorophenol 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): 1,2-dichlorobenzene 208 to 323 K, 1,3-dichlorobenzene 183 to 323 K, 1,2,4-trichlorobenzene 133 to 323 K, 2-chlorophenol from 293 to 353 K, 3-chlorophenol and 4-chlorophenol from 133 to 353 K. The heat capacity data obtained in this work were merged with available experimental data from literature, critically assessed and sets of recommended data were developed by correlating selected data as a function of temperature. Temperature and enthalpy of fusion of two isomeric chlorophenols and of 1,2,4-trichlorobenzene were also determined.

Keywords: chlorobenzenes, chlorophenols, enthalpy of fusion, heat capacity in liquid and solid phase, temperature dependence

Introduction

Heat capacities in liquid phase are required in chemical engineering calculations mainly for establishing enthalpy balances. Even though experimental data are available for a fairly large group of compounds [1, 2] more data are needed for compounds with no data available at all or for extending the temperature range the available data cover or for verifying the presently available literature data. Further, the newly obtained data can be utilized for developing recommended sets of data to be included in

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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 vapour or sublimation pressures, enthalpies of vaporization or enthalpies of sublimation, and differences between heat capacity in the ideal gas state and that in the liquid or solid phase was developed [3] and applied to several families of compounds [4–8] to calculate vapour and/or sublimation pressures over a large temperature range. A similar approach that combines several physical-chemical properties including heat capacity to obtain a reliable description of the vapour-liquid coexistence curve was presented by Weber [9] and by Duarte-Garza and Magee [10].

This work was concerned with measurement of heat capacities in the liquid and solid phases for three isomeric chlorobenzenes and for all three isomeric monochlorophenols. All these compounds belong to different lists of contaminants due to their toxicity and presence in the environment. All compounds do not occur naturally and were released into environment by a human activity.

Experimental

Apparatus and procedure

Two commercial calorimeters made by Setaram (Caluire, France), Micro-DSC II, and DSC 141, were used for measurement of saturation heat capacities. The calorimeters were calibrated with synthetic sapphire (α-Al_2O_3), the NIST Standard Reference Material 720 [11].

The vapour 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]. A detailed calculation of the error due to neglecting sample vaporization in the C80 calorimeter cell of inner volume 9.5 cm^3 was presented by Čenský *et al.* [12] for 2-methylbenzeneamine. It was shown that even in extreme cases when the vapour pressure was almost 10 kPa and 30% of the cell volume was occupied by vapour, the overall error was below 0.1%.

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 lie almost 100 K or more below the normal boiling temperature. The reported saturation heat capacities are identical to isobaric heat capacities C_p.

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 more accurate data than the other calorimeter 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 Micro-DSC II Setaram calorimeter; the amount of the measured substance was about 100 mg. As the crucible is made of aluminium 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 vapour pressure of substances measured in this work was at all experimental temperatures rather low we observed no mass losses during experiments.

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 [13] and of water [14] were also determined for verifying the measurement method and for estimating the uncertainty of the obtained data. Deviation of the mean value from gallium experiments was –0.6%, from the reference value.

Heat capacities in the solid phase were measured using the DSC 141 Setaram calorimeter equipped with a 120 μl crucible made of aluminium 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 [11] and naphthalene [13] 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 g 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.* [15].

Materials

$C_6H_4Cl_2$, 1,2-dichlorobenzene CAS-RN [95-50-1])

Fluka product of stated purity >99%. The sample was purified by a duplicate fractional distillation under reduced pressure of about 1.5 kPa in a packed column and dried over molecular sieves type 4 Å. The final purity was 99.98%.

$C_6H_4Cl_2$, 1,3-dichlorobenzene (CAS-RN [541-73-1])

Aldrich product of stated purity 98%, purified and dried as stated above for 1,2-dichlorobenzene. The final purity was 99.55%.

$C_6H_3Cl_3$, 1,2,4-trichlorobenzene (CAS-RN [120-82-1])

Aldrich product of stated purity 98%. The sample was purified and dried as described above for 1,2-dichlorobenzene. The final purity was 99.87%.

C_6H_5ClO, 2-chlorophenol (CAS-RN [95-57-8])

Aldrich product of stated purity 98%. The sample was purified and dried as described above for 1,2-dichlorobenzene. The final purity was 99.97%.

C_6H_5ClO, 3-chlorophenol (CAS-RN [108-43-0])

Aldrich product of stated purity 98%. The sample was purified by sublimation at a room temperature and under reduced pressure of about 1.5 kPa. The final purity was 99.97%.

C_6H_5ClO, 4-chlorophenol (CAS-RN [106-48-9])

Aldrich product of stated purity 99+%, purified and dried as stated above for 3-chlorophenol. The final purity was 99.81%.

Table 1a Solid and liquid heat capacity of 1,2-dichlorobenzene

T/K	C_p/R	$\Delta C_p/R$	Phase	Calorimeter
208.2	13.27	n.a.[a]	s	DSC 141
213.2	13.59	n.a.	s	DSC 141
218.2	13.93	n.a.	s	DSC 141
223.2	14.28	n.a.	s	DSC 141
228.2	14.64	n.a.	s	DSC 141
233.2	15.02	n.a.	s	DSC 141
238.2	15.40	n.a.	s	DSC 141
243.2	15.80	n.a.	s	DSC 141
248.2	16.21	n.a.	s	DSC 141
263.2	19.80	0.03	l	micro-DSC
283.2	20.17	–0.05	l	micro-DSC
303.2	20.74	0.03	l	micro-DSC
323.2	21.29	0.06	l	micro-DSC

[a] Deviation is not applicable as smoothed data are given in the table

R=8.31451 J K^{-1} mol^{-1}, $\Delta C_p/R=(C_p-C_p^{calc})/R$, where C_p^{calc} was calculated from Eq. (1) using parameters from Table 2

Table 1b Solid and liquid heat capacity of 1,3-dichlorobenzene

T/K	C_p/R	$\Delta C_p/R$	Phase	Calorimeter
183.2	10.98	n.a.[a]	s	DSC 141
188.2	11.17	n.a.	s	DSC 141
193.2	11.40	n.a.	s	DSC 141
198.2	11.65	n.a.	s	DSC 141
203.2	11.93	n.a.	s	DSC 141
208.2	12.24	n.a.	s	DSC 141
213.2	12.57	n.a.	s	DSC 141
218.2	12.94	n.a.	s	DSC 141
223.2	13.33	n.a.	s	DSC 141
228.2	13.75	n.a.	s	DSC 141
233.2	14.20	n.a.	s	DSC 141
263.2	19.71	–0.01	l	micro-DSC
283.2	20.10	–0.03	l	micro-DSC
303.2	20.56	–0.03	l	micro-DSC
323.2	21.18	0.07	l	micro-DSC

[a] Deviation is not applicable as smoothed data are given in the table

R=8.31451 J K^{-1} mol^{-1}, $\Delta C_p/R=(C_p-C_p^{calc})/R$, where C_p^{calc} was calculated from Eq. (1) using parameters from Table 2

Table 1c Solid and liquid heat capacity of 1,2,4-trichlorobenzene

T/K	C_p/R	$\Delta C_p/R$	Phase	Calorimeter
133.2	12.05	n.a.[a]	s	DSC 141
138.2	12.37	n.a.	s	DSC 141
143.2	12.68	n.a.	s	DSC 141
148.2	12.98	n.a.	s	DSC 141
153.2	13.27	n.a.	s	DSC 141
158.2	13.55	n.a.	s	DSC 141
163.2	13.81	n.a.	s	DSC 141
168.2	14.08	n.a.	s	DSC 141
173.2	14.34	n.a.	s	DSC 141
178.2	14.58	n.a.	s	DSC 141
183.2	14.80	n.a.	s	DSC 141
188.2	15.04	n.a.	s	DSC 141
193.2	15.25	n.a.	s	DSC 141
198.2	15.45	n.a.	s	DSC 141
203.2	15.67	n.a.	s	DSC 141

Table 1c Continued

T/K	C_p/R	$\Delta C_p/R$	Phase	Calorimeter
208.2	15.87	n.a.	s	DSC 141
213.2	16.06	n.a.	s	DSC 141
218.2	16.24	n.a.	s	DSC 141
223.2	16.41	n.a.	s	DSC 141
228.2	16.59	n.a.	s	DSC 141
233.2	16.76	n.a.	s	DSC 141
238.2	16.93	n.a.	s	DSC 141
243.2	17.09	n.a.	s	DSC 141
248.2	17.24	n.a.	s	DSC 141
253.2	17.39	n.a.	s	DSC 141
258.2	17.55	n.a.	s	DSC 141
263.2	17.70	n.a.	s	micro-DSC
303.2	24.05	0.11	l	micro-DSC
323.2	23.61	0.08	l	micro-DSC

[a] Deviation is not applicable as smoothed data are given in the table

R=8.31451 J K^{-1} mol^{-1}, $\Delta C_p/R=(C_p-C_p^{calc})/R$, where C_p^{calc} was calculated from Eq. (1) using parameters from Table 2

Table 1d Liquid heat capacity of 2-chlorophenol

T/K	C_p/R	$\Delta C_p/R$	Phase	Calorimeter
293.2	26.15	0.10	l	micro-DSC
303.2	26.18	0.03	l	micro-DSC
313.2	26.19	–0.06	l	micro-DSC
323.2	26.27	–0.09	l	micro-DSC
333.2	26.42	–0.04	l	micro-DSC
343.2	26.59	0.03	l	micro-DSC
353.2	26.73	0.06	l	micro-DSC

R=8.31451 J K^{-1} mol^{-1}, $\Delta C_p/R=(C_p-C_p^{calc})/R$, where C_p^{calc} was calculated from Eq. (1) using parameters from Table 2

Table 1e Solid and liquid heat capacity of 3-chlorophenol

T/K	C_p/R	$\Delta C_p/R$	Phase	Calorimeter
263.2	16.34	–1.65	s	micro-DSC
268.2	16.85	1.52	s	micro-DSC
273.2	17.47	2.18	s	micro-DSC
283.2	19.10	–2.64	s	micro-DSC

Table 1e Continued

T/K	C_p/R	$\Delta C_p/R$	Phase	Calorimeter
288.2	21.31	–1.46	s	micro-DSC
293.2	24.71	2.29	s	micro-DSC
313.2	27.40	0.06	l	micro-DSC
323.2	27.68	–0.14	l	micro-DSC
333.2	27.99	0.08	l	micro-DSC
343.2	28.14	0.03	l	micro-DSC
353.2	28.20	–0.03	l	micro-DSC

R=8.31451 J K^{-1} mol^{-1}, $\Delta C_p/R=(C_p-C_p^{calc})/R$, where C_p^{calc} was calculated from Eq. (1) using parameters from Table 2

Table 1f Solid and liquid heat capacity of 4-chlorophenol

T/K	C_p/R	$\Delta C_p/R$	Phase	Calorimeter
133.2	8.55	1.54	s	DSC 141
138.2	8.72	1.05	s	DSC 141
143.2	8.89	0.51	s	DSC 141
148.2	9.08	0.11	s	DSC 141
153.2	9.28	–0.16	s	DSC 141
158.2	9.48	–0.47	s	DSC 141
163.2	9.69	–0.66	s	DSC 141
168.2	9.93	–0.73	s	DSC 141
173.2	10.16	–0.85	s	DSC 141
178.2	10.41	–0.86	s	DSC 141
183.2	10.67	–0.78	s	DSC 141
188.2	10.93	–0.74	s	DSC 141
193.2	11.19	–0.75	s	DSC 141
198.2	11.47	–0.66	s	DSC 141
203.2	11.77	–0.49	s	DSC 141
208.2	12.04	–0.50	s	DSC 141
213.2	12.35	–0.30	s	DSC 141
218.2	12.66	–0.15	s	DSC 141
223.2	12.97	–0.04	s	DSC 141
228.2	13.28	0.02	s	DSC 141
233.2	13.61	0.16	s	DSC 141
238.2	13.93	0.26	s	DSC 141
243.2	14.26	0.31	s	DSC 141
248.2	14.58	0.33	s	DSC 141

Table 1f Continued

T/K	C_p/R	$\Delta C_p/R$	Phase	Calorimeter
253.2	14.91	0.32	s	DSC 141
258.2	15.25	0.37	s	DSC 141
263.2	15.55	0.20	s	DSC 141
268.2	15.89	0.19	s	DSC 141
273.2	16.23	0.15	s	DSC 141
278.2	16.53	–0.20	s	DSC 141
283.2	16.84	–0.47	s	DSC 141
288.2	17.22	–0.31	s	DSC 141
293.2	17.67	0.16	s	DSC 141
263.2	15.55	0.20	s	micro-DSC
273.2	16.23	0.15	s	micro-DSC
283.2	16.84	–0.47	s	micro-DSC
293.2	17.67	0.16	s	micro-DSC
323.2	27.88	0.01	l	micro-DSC
333.2	28.03	–0.04	l	micro-DSC
343.2	28.22	0.04	l	micro-DSC
353.2	28.37	–0.01	l	micro-DSC

R=8.31451 J K^{-1} mol^{-1}, $\Delta C_p/R=(C_p-C_p^{calc})/R$, where C_p^{calc} was calculated from Eq. (1) using parameters from Table 2

Results

The direct experimental T–C_p values are presented in Tables 1a to 1f. Results from DSC-141 experiments are smoothed data obtained by averaging values of several repetitive experiments.

These data were combined with all other calorimetrically determined heat capacities available in the 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 weighted least-squares method:

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

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

If the selected experimental data in the liquid phase cover the temperature range of at least 100 K then the isobaric data were fitted to another empirical, the so-called quasi-polynomial, equation that allows a meaningful extrapolation to the critical point

$$\frac{C_{\mathrm{p,m}}}{R}=A_1\ln(1-T_{\mathrm{r}})+\frac{A_2}{1-T_{\mathrm{r}}}+A_3+A_4T_{\mathrm{r}} \tag{2}$$

where $T_{\mathrm{r}}=T/T_{\mathrm{c}}$, and T_{c} is the critical temperature. The derivation of Eq. (2) (Zábranský *et al.* [1]) is 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 for the least-squares minimization was used of the form:

$$S=\sum_{\mathrm{i=1}}^{\mathrm{n}}\left(\frac{\Delta C_{\mathrm{i}}}{R}\right)^2(\sigma_{\mathrm{C/R,i}})^{-2} \tag{3}$$

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

$$\sigma_{\mathrm{C/R,i}}=10^{-2}\,\frac{C_{\mathrm{i}}\cdot\sigma_{\mathrm{r}}C}{R} \tag{4}$$

Parameters of Eq. (1) derived from the fit are given in Table 2 along with the relative standard deviation of the fit. Parameters of Eq. (2) are given in Table 3. 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 describe quantitatively the real heat capacity in this region except for the value at the critical point. The flexibility of the quasi-polynomial equation is in general worse than that of the polynomial Eq. (1), even though for the sets of data fitted in this work there is no difference as indicated by the relative standard deviation of the fit s_{r} that is given in Tables 2 and 3.

Temperature and enthalpy of fusion of 1,2,4-trichlorobenzene, 3-chlorophenol, and 4-chlorophenol are given in Table 4.

Discussion

The abundance of literature data for the compounds investigated and the temperature range that the data cover varies. Solid heat capacities determined in this work for 1,2,4-trichlorobenzene, 3-chlorophenol and 4-chlorophenol present the only available data.

Table 2 Parameters of Eq. (1) for isobaric heat capacity

Compound	Phase	Parameters				Temperature range			Uncertainty /
		A_1	A_2	A_3	A_4	T_{min}/K	T_{max}/K	s_r[a]	%
1,2-dichlorobenzene	s	10.2302	–3.50591	2.38406	0	208.2	248.2	0.03	0.5
	l	17.1023	–0.125686	0.433991	0	263.2	377.2	0.2	1.0
1,3-dichlorobenzene	s	23.0289	–16.7968	5.57943	0	183.2	233.2	0.03	3.0
	l	36.2553	–18.1015	5.97816	–0.565233	253.9	377.6	0.2	1.0
1,2,4-trichlorobenzene	s	1.60606	9.70177	–1.36936	0	133.2	263.2	0.2	3.0
	l	16.4160	2.33826	0	0	298.2	469.2	1.4	3.0
2-chlorophenol	l	41.6416	–10.4980	1.77851	0	293.2	353.2	0.1	1.0
3-chlorophenol	s	734.2897	–540.0715	101.5945	0	263.2	293.2	0.6	3.0
	l	–26.2580	30.4931	–4.26736	0	313.2	353.2	0.1	3.0
4-chlorophenol	s	4.64287	1.50448	0.999636	0	133.2	293.2	0.6	3.0
	l	22.5112	1.65996	0	0	323.2	353.2	0.04	3.0

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

Table 3 Parameters of Eq. (2) for isobaric heat capacity

Compound	Phase	Parameters				Temperature range			Uncertainty /
		A_1	A_2	A_3	A_4	T_{min}/K	T_c/K	s_r	%
1,2-dichlorobenzene	l	–4.75784	1.98491	13.2541	2.85114	263.2	698.8	0.2	1.0
1,3-dichlorobenzene	l	–4.07122	2.38356	13.1488	1.73845	253.9	682.2	0.2	1.0
1,2,4-trichlorobenzene	l	86.3520	13.9289	–9.73378	133.835	298.2	734.9	1.2	3.0

For liquid 1,2-dichlorobenzene and 1,3-dichlorobenzene two sources of data were found in the literature. The data measured in an isoperibol drop calorimeter at the beginning of the 20th century by Narbutt [16] agree reasonably well with the data determined by Roháč *et al.* [6] who used a Setaram C80 calorimeter. The latter data cover a somewhat larger temperature interval and extend to higher temperatures.

For solid 1,2-dichlorobenzene and 1,3-dichlorobenzene single values of average heat capacity were published by Narbutt [16] with a stated experimental error of 1%. Value of C_p/R equal to 13.7 at 224.8 K for 1,2-dichlorobenzene and of C_p/R equal to 13.8 at 221.2 K for 1,3-dichlorobenzene are by almost 5% below and above values determined in this work, respectively.

For liquid 1,2,4-trichlorobenzene the present data agree well with the most extensive set of data by Roháč *et al.* [6] and at the lower temperature end also with the data measured by Wilhelm *et al.* [17, 18] in heat of mixing experiments. The data by Petit and Ter Minassian [19] were used in the determination of correlating equations parameters to extend the temperature limit up to temperature higher than the upper temperature limit of the data by Roháč *et al.* [6], even though the data from [19] are rather scattered. The purity of 1,2,4-trichlorobenzene reported by Petit and Ter Minassian [19] was only 98%.

Only for liquid 2-chlorophenol two sources of heat capacity data were found in the literature. Both sets of data were determined in the first half of the previous century. Both the data by Bramley [20] measured in an isothermal drop calorimeter and by Ellyett [21] in an isoperibol calorimeter differ from the present data and were rejected from the correlation. None of the authors [20, 25] presented both an experimental error and purity of the substance. In addition, the slope of the $C_p = f(T)$ curve of the data by Bramley[20] and by Ellyett [21] is different and also differs from the slope of the present data.

Deviation plots showing how experimental heat capacities measured by different authors deviate from the recommended data (Eq. (1) and Table 2) are given in Figs 1 to 4.

Table 4 Temperature and enthalpy of fusion

Compound	T_f/K	$\Delta_f H$/kJ mol^{-1}	Reference
1,2,4-trichlorobenzene	290.5±0.3	17.96±0.06	This work
	289.4	13.6	[22]
	290.4±0.2	15.5	[23]
	290.895	18.2	[24]
3-chlorophenol	304.2±0.5	13.64±0.24	This work
	305.8	14.91	[26]
	306.2	11.79	[25]
4-chlorophenol	315.7±0.5	13.76±0.13	This work
	315.9	14.07	[26]
	316.7	14.71	[25]
	Not reported	14.7	[27]

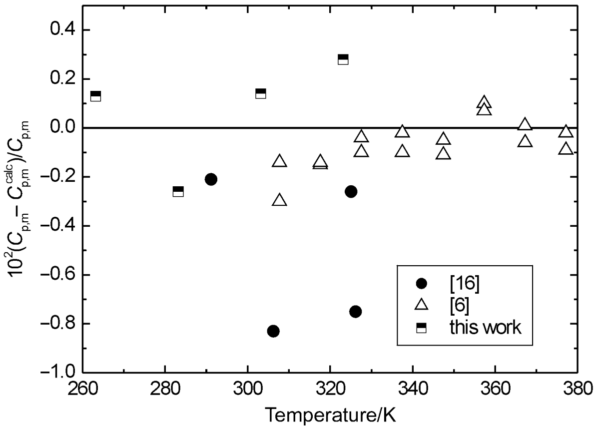

Fig. 1 Deviation plot for heat capacity of liquid 1,2-dichlorobenzene

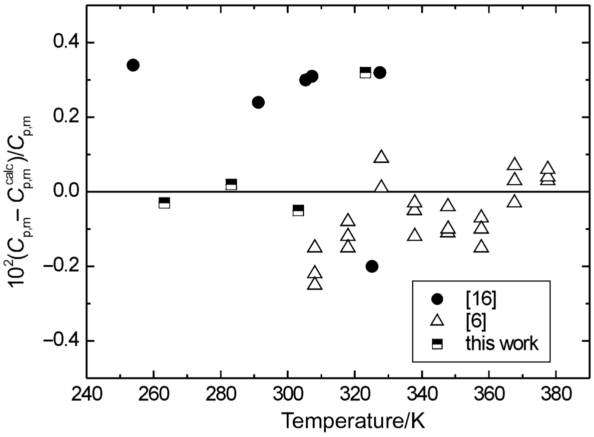

Fig. 2 Deviation plot for heat capacity of liquid 1,3-dichlorobenzene

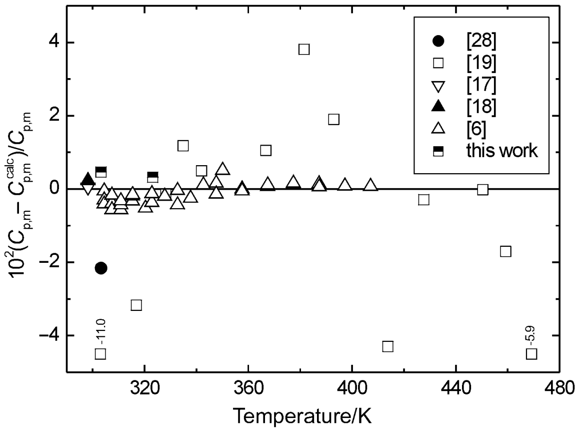

Fig. 3 Deviation plot for heat capacity of liquid 1,2,4-trichlorobenzene

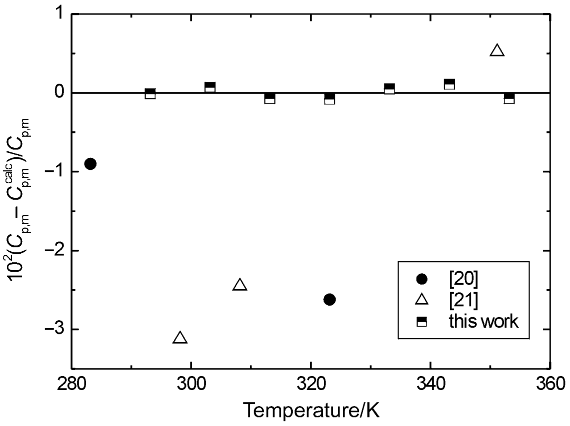

Fig. 4 Deviation plot for heat capacity of liquid 2-chlorophenol

Besides experimental values determined in this work of temperature and enthalpy of fusion for the three compounds studied, 1,2,4-trichlorobenzene, 3-chlorophenol and 4-chlorophenol, some literature data were also found. A comparison of the present and literature data is given in Table 4.

For 1,2,4-trichlorobenzene three non-calorimetric values of enthalpy of fusion are available. Fel'dman *et al.* [22] studied a binary solid-liquid equilibrium of the mixture of trichlorobenzenes and calculated enthalpy of fusion assuming the mixture obeys the ideal solution law. Sears and Hopke [23] reported enthalpy of fusion calculated from vapour pressure above solid and liquid phase. A value obtained from cryoscopy measurement and close to that determined in this work was reported by Munn and Kohler [24].

For 3-chlorophenol and 4-chlorophenol an experimental value of enthalpy of fusion determined by DTA was reported by Martin *et al.* [25]. The compilation by Weast [26] presents values for both isomers but their origin is not specified. Enthalpy of fusion of 4-chlorophenol reported by Luchinskii and Likhacheva [27] was determined from a cooling curve.

Conclusions

Recommended data on heat capacity of solid and liquid 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,2,4-trichlorobenzene, 3-chlorophenol, 4-chlorophenol and of liquid 2-chlorophenol were developed by critical assessment of newly determined and available literature data. Some sets of data published in literature were rejected due to their large systematic deviations. The recommended data are presented in terms of parameters of empirical correlating equations expressing their dependence on temperature.

* * *

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