J. Chem. Eng. Data **2007,** *52,* 1375−1380

Heat Capacities of Chloroanilines and Chloronitrobenzenes

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Isobaric heat capacities in the liquid and solid phases of chloroanilines and chloronitrobenzenes were measured by using a highly sensitive Tian−Calvet differential scanning calorimeter in the temperature range from 270 K to 350 K. For some of the studied compounds, temperature and enthalpy of fusion were also determined. Data on liquid heat capacities obtained in this work, were merged with available literature data, critically assessed, and correlated as a function of temperature.

Introduction

Chloroanilines are used for the synthesis of highly effective herbicides. Chloronitrobenzenes are important starting materials for manufacturing azo and sulfur dyes; they also find application in the synthesis of fungicides, preservatives, and pharmaceuticals. Chloroanilines and chloronitrobenzenes are important organic contaminants[1] that are dangerous in particular for the aquatic environment and organisms. Despite the importance of these compounds, only limited experimental data on heat capacity are available in the literature.

Heat capacity is a basic thermophysical property which is necessary for energy balances in chemical engineering and process control. Differences between ideal gas and liquid heat capacity can also be used for reliable extrapolation of vapor pressure down to the triple point.[2]

Differential scanning calorimetry was used for measurement of heat capacities of all six compounds (2-chloroaniline, 3-chloroaniline, 4-chloroaniline, 1-chloro-2-nitrobenzene, 1-chloro-3-nitrobenzene, and 1-chloro-4-nitrobenzene) in the temperature range from 270 K to 350 K. Temperature and enthalpy of fusion were also determined for some of the samples.

Experimental Section

Samples of substituted benzenes were of commercial origin (Sigma Aldrich). All compounds were used as received. Their purity is summarized in Table 1. Samples were kept under a dry nitrogen atmosphere when filling the calorimeter cell. At ambient temperature, two of the studied compounds are liquid (2-chloroaniline, 3-chloroaniline) and four are solid (4-chloroaniline, 1-chloro-2-nitrobenzene, 1-chloro-3-nitrobenzene, 1-chloro-4-nitrobenzene).

The Micro DSC III microcalorimeter (Setaram, Caluire, France) was used for the heat capacity and phase transition property determinations in the temperature range from 270 K to 350 K. Thermal effects in the calorimeter are measured by two fluxmeters (one on the measurement vessel side and one on the reference vessel side), each of which measures the thermal power exchanged constantly between the experimental vessel and the calorimetric unit. The Tian−Calvet-type fluxmetric probe envelopes the sample and is therefore capable of measuring almost all the energy exchanges between the vessel and the unit. Background noise is less than 0.2 μW, and temperature stability is better than ± 2 mK (as stated by the Setaram Company). The measurements were carried out in the incremental temperature scanning mode with a number of 10 K steps (heating rate 0.5 $\mathrm{K{\cdot}min^{-1}}$) followed by isothermal delays of 3600 s. Temperature calibration was performed using distilled and demineralized water (Millipore RQ, France), gallium (part of set of calibration substances for temperature and heat calibration of differential scanning calorimeters, H. K. Cammenga, GEFTA), and naphthalene (commercially available naphthalene, Aldrich 99+ % purified by zone refining). Analysis of naphthalene by gas chromatography (Hewlett-Packard 6890 gas chromatograph equipped with column HP5 cross-linked 5 % PHME siloxane, length 30 m, film thickness 0.25 μm, i.d. 0.32 mm, and FID detector) showed no detectable impurities. The synthetic sapphire, NIST Standard reference material No. 720, was used as the reference material. The typical mass of samples was 0.4 g to 1 g. The uncertainty of heat capacity measurements was estimated to be better than ± 1 %.

The measurement vessel was empty in the first run, and it was filled with the reference compound (synthetic sapphire) and with the measured sample in the second and the third runs, respectively. The reference vessel was empty during all three runs. Phase transitions were investigated with heating rates of 0.3 $\mathrm{K{\cdot}min^{-1}}$ (0.1 $\mathrm{K{\cdot}min^{-1}}$ and 0.05 $\mathrm{K{\cdot}min^{-1}}$ were used for 2-chloroaniline). The mass of the samples was around 0.03 g (uncertainty in mass was ± 0.05 mg) for experiments where the phase transition was measured. Peak areas were integrated using the Setaram software package SetSoft 2000. General principles for peak evaluations including determination of temperature of fusion, T_{fus}, and enthalpy of fusion, $\Delta_{\mathrm{fus}}H$, can be found in Höhne et al.[3] The uncertainty of T_{fus} measurements was estimated to be better than ± 0.5 K. A test of our calorimeter carried out by Setaram provided a deviation of $\Delta_{\mathrm{fus}}H$

Table 1. Sample Purity

compound	CAS registry no.	original purity[a] 100w
2-chloroaniline	95-51-2	100[b]
3-chloroaniline	108-42-9	99.6[d]
4-chloroaniline	106-47-8	99.9[b]
1-chloro-2-nitrobenzene	88-73-3	99.9[b]
1-chloro-3-nitrobenzene	121-73-3	99.8[b,c]
1-chloro-4-nitrobenzene	100-00-5	99.9[b]

[a] Results of analyses provided by Sigma Aldrich. [b] GC. [c] HPLC. [d] GLC.

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10.1021/je700080k CCC: $37.00

for naphthalene of 0.2 % from the literature value. Our tests with water and gallium resulted in deviations of $\Delta_{\mathrm{fus}}H$ of better than 1 %.

Heat capacity of the sample was calculated from the following equation

$$C_{p,\mathrm{s}} = \frac{m_{\mathrm{sapp}} C_{p,\mathrm{sapp}} (A_{\mathrm{s}} - A_{\mathrm{B}})}{m_{\mathrm{s}} (A_{\mathrm{sapp}} - A_{\mathrm{B}})} \tag{1}$$

where $C_{p,\mathrm{s}}$ is specific heat capacity of the measured sample; $C_{p,\mathrm{sapp}}$ is specific heat capacity of the reference substance (synthetic sapphire); m_{s} is the mass of the sample; m_{sapp} is the mass of the reference substance; A_{s} is the integrated value of the differential heat flow when the measuring vessel contains the sample; A_{sapp} is the integrated value of the differential heat flow when the measuring vessel contains the reference substance; and A_{B} is the integrated value of differential heat flow in the case of the empty measuring vessel.

The correction for sample vaporization as discussed in Zábranský et al.[4,5] was evaluated for all measured substances. As this correction was smaller than 0.1 % for all samples, i.e., within the uncertainty of measurement, it was not applied.

The experimental data were fitted with the polynomial equation using the weighted least-squares method

$$\frac{C_p}{R} = \sum_{i=0}^{n} A_{i+1} \left(\frac{T}{100}\right)^{i} \quad (R = 8.314472\ \mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}, \text{ see ref 6}) \tag{2}$$

Results and Discussion

Only few heat capacity data of the studied compounds were found in the literature. Zalikin et al.[7] published values of heat capacities for 3-chloroaniline at two temperatures and a mean value of heat capacity in the temperature range from 292 K to 323 K. Lebedeva[8] published several data points for 1-chloro-2-nitrobenzene (from 298 K to 303 K) and 1-chloro-4-nitrobenzene (from 298 K to 353 K). Marchidan[9] published two data points for 1-chloro-4-nitrobenzene, and Bogojawlensky[10] presented an average value in the temperature interval from 318 K to 358 K for 1-chloro-3-nitrobenzene. Tozuka et al.[11] published data from adiabatic calorimetry for 1-chloro-4-nitrobenzene.

Temperature and enthalpy of fusion data available in the literature are summarized in Table 2 along with the data determined in this work.

Table 2. Literature and Experimental Data on Temperature of Fusion, T_{fus}, and Enthalpy of Fusion, $\Delta_{\mathrm{fus}}H^{a}$

compound	T_{fus} (this work) K	$\Delta_{\mathrm{fus}}H$ (this work)[b] kJ·mol^{-1}	T_{fus} (lit.) K	$\Delta_{\mathrm{fus}}H$ (lit.) kJ·mol^{-1}	lit. source
2-chloroaniline	269.2	12.38	259.15[c]		13
	269.5	12.27	269.65[d]		13
			271.05		16
			271.05	11.89	17
			271.37[d]		12
			261.23[c]		12
			260.72[c]		12
			271.21		18
			259.15[e]		14
			273.00		20
			259.1[f]		15
3-chloroaniline			262.80	11.64	17
4-chloroaniline	342.8	20.47	343.65	20.10	17
			345.65	19.97	14
			343−345	19.30	20
			343.50	21.06	15
1-chloro-2-nitrobenzene	305.3	18.11	307.15	17.62	14
			306.00	17.17	20
			305.80	18.21	15
1-chloro-3-nitrobenzene	316.9	19.52	319.15	21.51	14
			317.00	17.58	20
			318.00	18.65	15
1-chloro-4-nitrobenzene	355.1	15.03	354.60	11.85	9
			356.75	17.48	14
			358.00	18.03	21
			356−357	14.24	20
			354.20		11
			356.10	17.95	15

[a] The table does not include all T_{fus} values available in the literature. Only references to papers reporting results of physical chemical properties measurements are presented. [b] Values are reported with one digit more than is justified by the experimental uncertainty. This is to avoid round-off errors in calculations based on these results. [c] α-Modification. [d] β-Modification. [e] Presumably taken from Knoevenagel.[13] [f] Taken from Martin et al.[14] as conveyed by Verevkin and Schick in a private communication.

2-Chloroaniline. Unlike other samples, 2-chloroaniline was measured in the temperature range from 260 K to 350 K. Experimental data (see Table 3 and Figure 1) for eight temperatures in the liquid region and one value in the solid region were obtained. However, due to a problem of reaching a stable crystal phase (see the following text), it was not clear if this value belongs to a completely crystallized sample. Data in the liquid region were fitted using eq 2 (see Table 4 for correlation coefficients and Table 3 for deviations between experimental and fitted data). Experiments to determine temperature of fusion, T_{fus}, and enthalpy of fusion, $\Delta_{\mathrm{fus}}H$, were also carried out. However, it was very difficult to reach a crystal phase when using the Micro DSC III microcalorimeter because its low-temperature limit of measurement is 253 K. In several experiments, we were able to reach an undercooled liquid state only. Literature data on the temperature of fusion are given in Table 2. Aoyama and Morita[12] and Knoevenagel[13] stated that two crystal modifications of 2-chloroaniline, denoted β and α, exist, β the to liquid-phase transition occurring at around 260 K and α to the liquid-phase transition at around 271 K. Some authors[14,15] reported the temperature of a phase transition (not stating if β to liquid or α to liquid) at 260 K; however, it seems that these authors used the value published by Knoevenagel.[13] Other authors[16−20] indicated there was a single phase transition only at around 271 K. In all our experiments, the detected peak consisted of two parts (see Figure 2); the ratio of the area of the two peaks, however, differed significantly for different experiments (the smaller peak was 9 % of the overall peak area in one case, whereas it was 16 % in the second case). We made two experiments where T_{fus} and $\Delta_{\mathrm{fus}}H$ were determined (see Table 2). Our value of T_{fus} is close to that determined in 1907 by Knoevenagel.[13] $\Delta_{\mathrm{fus}}H$ determined in this work (value calculated from the overall peak area) differs by more than 3 % from the value reported in 1921 by Sidgwick and Rubie.[17]

3-Chloroaniline. Heat capacity of 3-chloroaniline was measured from 278 K to 350 K. Data for eight temperatures in the liquid region were obtained (see Table 3 and Figure 3). Experimental liquid heat capacity data were published by Zalikin et al.,[7] who presented only the sample purity of 99 %, but neither the measurement method nor the measurement error was specified. When compared with our data, the two values by Zalikin et al.[7] are 2.1 % and 0.1 % below our fitted data (see Figure 3). We were not capable of determining T_{fus} and $\Delta_{\mathrm{fus}}H$ as it was not possible to reach the crystal phase for the sample of 3-chloroaniline. For values of T_{fus} and $\Delta_{\mathrm{fus}}H$ available in the literature, see Table 2.

4-Chloroaniline. The solid heat capacity of 4-chloroaniline was measured from 278 K to 350 K, and measured data were fitted by the second-degree polynomial (see Tables 3 and 4 and Figure 4). The mean value in the temperature interval from 292

Table 3. Experimental Heat Capacities

$\frac{T^a}{K}$	$\frac{C_p{}^a}{R}$	$\frac{100(C_p - C_p{}^{calcd})}{C_p}$	$\frac{T^a}{K}$	$\frac{C_p{}^a}{R}$	$\frac{100(C_p - C_p{}^{calcd})}{C_p}$	$\frac{T^a}{K}$	$\frac{C_p{}^a}{R}$	$\frac{100(C_p - C_p{}^{calcd})}{C_p}$
				2-Chloroaniline				
258.09^c	18.40		309.14^b	24.23	−0.1	329.56^b	24.71	0.1
278.51^b	23.70	0.1	309.14^b	24.23	−0.1	339.77^b	24.91	−0.0
278.51^b	23.70	0.2	309.14^b	24.20	−0.2	339.77^b	24.94	0.1
288.72^b	23.80	−0.2	319.35^b	24.46	0.0	339.77^b	24.93	0.0
288.72^b	23.83	−0.1	319.35^b	24.46	−0.0	339.77^b	24.91	−0.0
298.93^b	24.12	0.3	319.35^b	24.45	−0.0	349.98^b	25.17	0.0
298.93^b	24.05	0.0	319.35^b	24.47	0.0	349.98^b	25.14	−0.1
298.93^b	24.13	0.4	329.56^b	24.70	0.1	349.98^b	25.15	−0.1
298.93^b	24.06	0.1	329.56^b	24.68	−0.0	349.98^b	25.19	0.1
309.14^b	24.21	−0.1	329.56^b	24.69	0.0	258.10^d	23.37	
				3-Chloroaniline				
278.51^b	24.09	0.1	309.14^b	24.69	−0.1	329.56^b	25.18	0.1
278.51^b	24.04	−0.1	309.14^b	24.68	−0.2	339.77^b	25.39	0.0
288.72^b	24.27	0.0	319.35^b	24.97	0.1	339.77^b	25.35	−0.2
288.72^b	24.24	−0.1	319.35^b	24.94	0.0	339.77^b	25.37	−0.1
298.93^b	24.53	0.1	319.35^b	24.94	0.0	349.98^b	25.67	0.2
298.93^b	24.52	0.1	329.56^b	25.21	0.2	349.98^b	25.62	0.0
298.93^b	24.48	−0.1	329.56^b	25.18	0.1	349.98^b	25.60	0.0
309.14^b	24.72	0.0						
				4-Chloroaniline				
278.51^c	17.14	0.13	298.93^c	18.18	0.1	319.35^c	19.28	0.0
278.51^c	17.11	0.0	298.93^c	18.21	0.2	319.35^c	19.26	−0.1
278.51^c	17.12	0.0	298.93^c	18.19	0.2	319.35^c	19.27	−0.1
288.72^c	17.60	−0.1	309.14^c	18.72	0.0	329.56^c	19.91	0.2
288.72^c	17.59	−0.2	309.14^c	18.70	−0.1	329.56^c	19.90	0.1
288.72^c	17.61	−0.1	309.14^c	18.70	−0.1	329.56^c	19.85	−0.1
				1-Chloro-2-nitrobenzene				
278.51^c	20.76	0.4	288.72^c	22.45	−0.0	329.56^b	25.77	0.0
278.51^c	20.62	−0.3	298.93^c	25.32	−0.5	329.56^b	25.75	−0.0
278.51^c	20.62	−0.3	298.93^c	25.46	0.1	329.56^b	25.78	0.1
278.51^c	20.70	0.1	298.93^c	25.53	0.4	329.56^b	25.79	0.1
278.51^c	20.71	0.1	319.35^b	25.43	−0.2	339.77^b	25.98	−0.2
288.72^c	22.45	0.0	319.35^b	25.46	−0.1	339.77^b	26.05	0.1
288.72^c	22.41	−0.2	319.35^b	25.50	0.1	349.98^b	26.29	−0.0
288.72^c	22.43	−0.1	319.35^b	25.48	0.1	349.98^b	26.32	0.1
288.72^c	22.52	0.3						
				1-Chloro-3-nitrobenzene				
278.51^c	18.63		339.77^b	26.43	0.1	349.98^b	26.74	−0.1
288.72^c	19.26		339.77^b	26.43	0.1	349.98^b	26.74	0.0
298.93^c	20.23		339.77^b	26.39	−0.1	298.93^d	25.11	
298.93^c	20.47		339.77^b	26.40	0.0	298.93^d	25.20	
329.56^b	26.14	0.0	339.77^b	26.41	0.0	309.14^d	25.42	
329.56^b	26.11	−0.1	349.98^b	26.77	0.1	309.14^d	25.47	
329.56^b	26.13	0.0	349.98^b	26.77	0.1	319.35^d	25.81	
329.56^b	26.15	0.1	349.98^b	26.75	0.0	319.35^d	25.78	
329.56^b	26.12	0.0						
				1-Chloro-4-nitrobenzene				
278.51^c	19.39	0.4	309.14^c	21.08	0.8	329.56^c	22.68	−1.0
278.51^c	19.35	0.2	309.14^c	21.07	0.7	329.56^c	22.65	−1.1
288.72^c	19.78	0.5	309.14^c	21.06	0.7	329.56^c	22.68	−1.0
288.72^c	19.72	0.3	309.14^c	21.13	1.0	329.56^c	22.64	−1.1
298.93^c	20.43	1.1	319.35^c	21.64	−0.8	339.77^c	23.93	−1.0
298.93^c	20.43	1.1	319.35^c	21.77	−0.2	339.77^c	24.47	1.2
298.93^c	20.44	1.2	319.35^c	21.74	−0.4	339.77^c	24.47	1.2
298.93^c	20.46	1.2	319.35^c	21.75	−0.3	339.77^c	24.47	1.2
298.93^c	20.42	1.1	319.35^c	21.73	−0.4	339.77^c	24.43	1.1
309.14^c	21.03	0.5	329.56^c	22.48	−1.9			

[a] Values are reported with one digit more than is justified by the experimental uncertainty. This is to avoid round-off errors in calculations based on these results. [b] Liquid. [c] Solid. [d] Undercooled liquid.

K to 323 K was published by Zalikin et al.[7] and deviates from the fitted data by 4.2 %. Temperature of fusion and enthalpy of fusion were also determined (see Table 2). Our value of T_{fus} is lower than all literature values; it differs by 0.7 K from the most recent value by Verevkin and Schick.[15] Our value of $\Delta_{fus}H$ is almost 3 % below the value by Verevkin and Schick.[15]

1-Chloro-2-nitrobenzene. The temperature interval of the calorimeter's measurement range is divided by the solid to liquid-phase transition (see Figure 5). Three values were measured in the solid region. These data were correlated by the second-degree polynomial with the maximum deviation of 0.4 % with the exception of one value which is different by 1.8 %. As this value is very close to the melting region, some premelting phenomena can account for this deviation. This value was not included in the correlation. A mean value in the temperature range from 298 K to 303 K given by Lebedeva[8] is 13 % higher. In the liquid region, four values were obtained and fitted by a polynomial (see Tables 3 and 4). Temperature

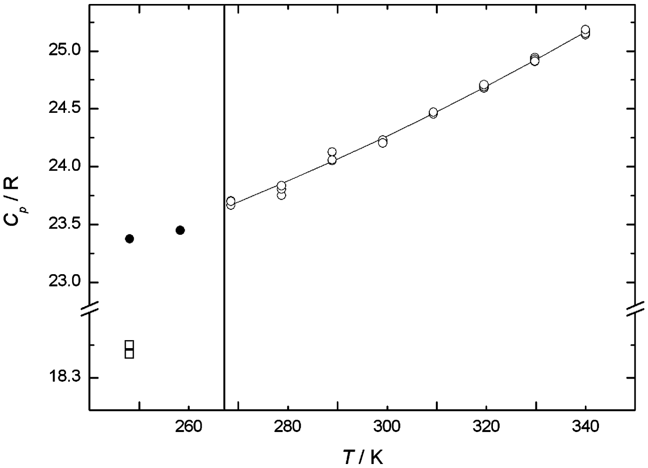

Figure 1. Experimental solid and liquid heat capacities for 2-chloroaniline: ○, this work (liquid phase); ●, this work (undercooled liquid); □, this work (solid phase); line represents fitting equation (eq 2 and Table 4).

Table 4. Parameters of Equation 2 for Liquid and Solid Heat Capacity

	parameters			temperature range		
compound	A_1	A_2	A_3	T_{min}/K	T_{max}/K	s_r[a]
2-chloroaniline (l)	22.8107	−1.11332	0.510408	278.5	350.0	0.033
3-chloroaniline (l)	18.8166	1.63374	0.0888337	278.5	350.0	0.026
4-chloroaniline (s)	10.3303	−0.0790096	0.902846	278.5	329.6	0.036
1-chloro-2-nitrobenzene (s)	439.154	−311.930	58.0502	278.5	298.9	0.089
1-chloro-2-nitrobenzene (l)	11.9663	5.64945	−0.444128	319.4	350.0	0.041
1-chloro-3-nitrobenzene (l)	47.7718	−15.6341	2.75120	329.5	350.0	0.014
1-chloro-3-nitrobenzene (s)	−3.12456	7.87416		278.5	298.9	1.1
1-chloro-4-nitrobenzene (s)	80.4810	−46.4496	8.79299	278.5	339.8	0.19

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

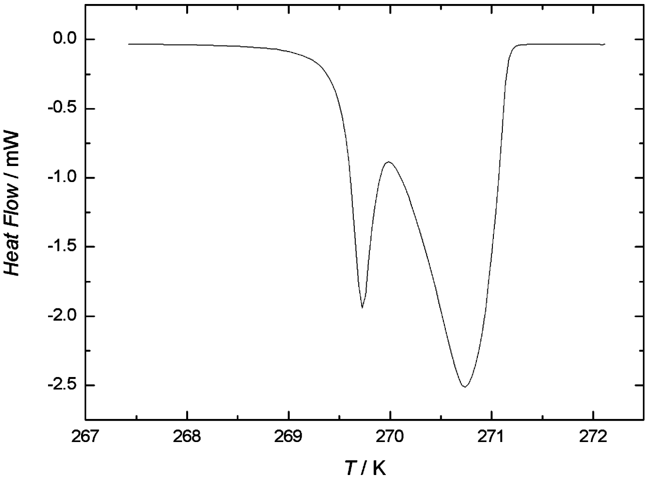

Figure 2. Melting of 2-chloroaniline.

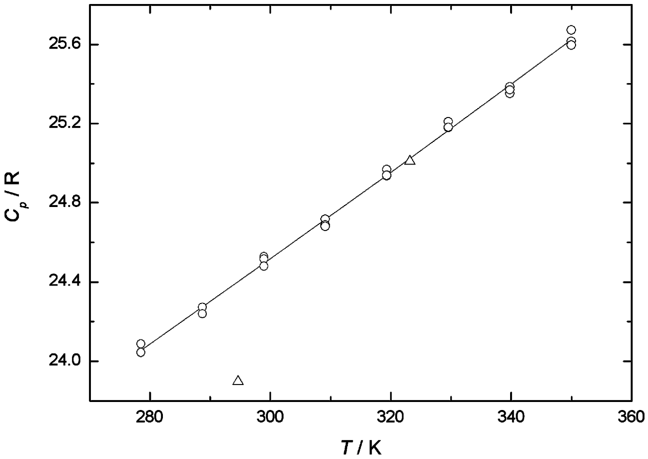

Figure 3. Experimental liquid heat capacities for 3-chloroaniline: ○, this work; Δ, Zalikin;[7] line represents fitting equation (eq 2 and Table 4).

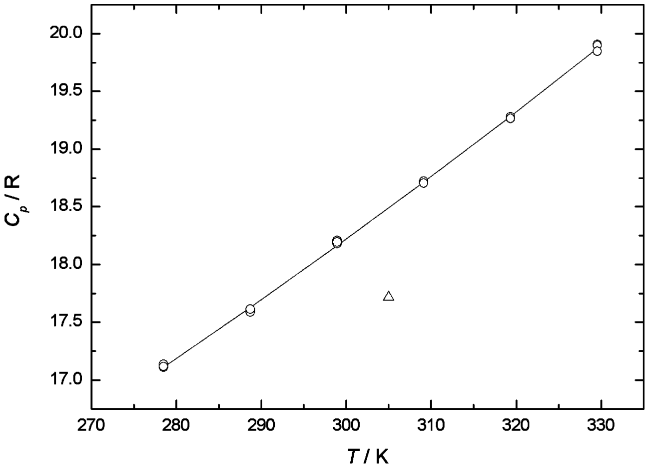

Figure 4. Experimental solid heat capacities for 4-chloroaniline: ○, this work; Δ, Zalikin;[7] line represents fitting equation (eq 2 and Table 4).

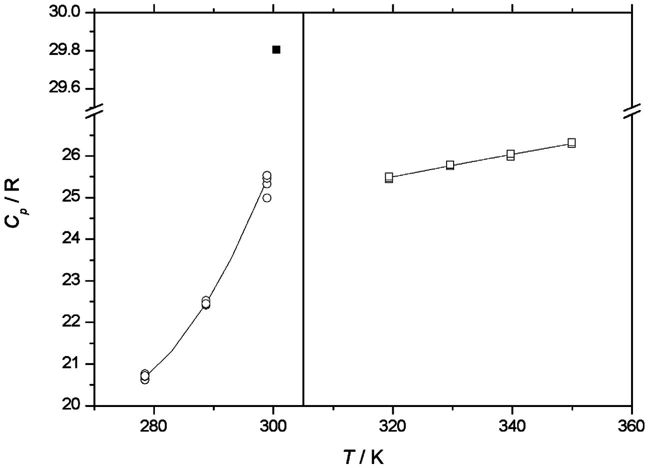

Figure 5. Experimental solid and liquid heat capacities for 1-chloro-2-nitrobenzene: ○, this work (solid phase); □, this work (liquid phase); ■, Lebedeva et al.;[8] line represents fitting equation (eq 2 and Table 4).

of fusion and enthalpy of fusion were also measured. Both T_{fus} and $\Delta_{fus}H$ compare well with the recent data by Verevkin and Schick,[15] the differences being 0.5 K and 0.6 %, respectively (see Table 2).

1-Chloro-3-nitrobenzene. Three values on heat capacity in the liquid region and three values in the solid region were obtained (see Table 3 and Figure 6). For some experiments, heat capacity of the undercooled liquid was measured, as it was not possible to reach the crystal phase. The liquid heat capacity presented by Bogojawlensky[10] is 0.8 % above values from our fitting equation. Temperature of fusion and enthalpy of fusion were measured as well. Our value of T_{fus} is 1.1 K below that reported by Verevkin and Schick,[15] whereas $\Delta_{fus}H$ differs 4 % from the value by the same authors (see Table 2).

1-Chloro-4-nitrobenzene. Solid heat capacities at seven temperatures were measured for 1-chloro-4-nitrobenzene (see

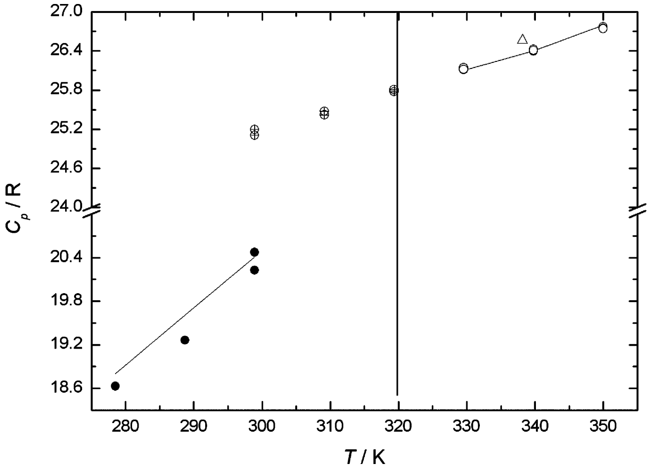

Figure 6. Experimental solid and liquid heat capacities for 1-chloro-3-nitrobenzene: ○, this work (liquid phase); ●, this work (solid phase); ⊕, this work (undercooled liquid); Δ, Bogojawlensky;[10] line represents fitting equation (eq 2 and Table 4).

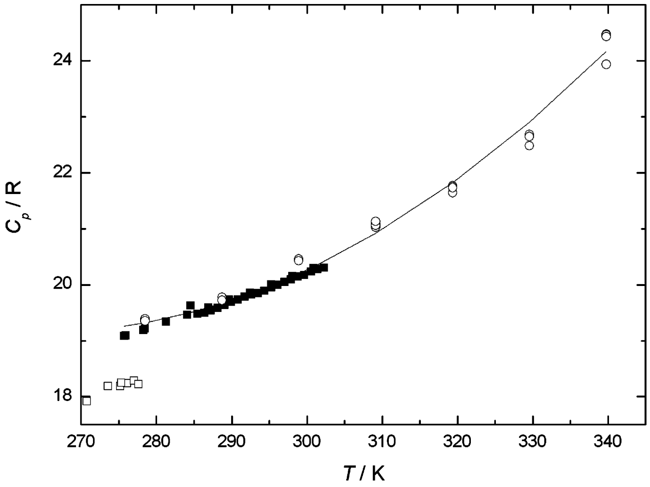

Figure 7. Experimental solid heat capacities for 1-chloro-2-nitrobenzene: ○, this work; □, Tozuka[11] (ordered phase); ■, Tozuka[11] (disordered phase), not displayed (Marchidan et al.);[9] line represents fitting equation (eq 2 and Table 4).

Table 3 and Figure 7). Tozuka et al.[11] measured heat capacities and thermodynamic quantities of the first-order phase transition of 1-chloro-4-nitrobenzene by adiabatic calorimetry in the temperature range from 6 K to 303 K. Tozuka et al. reported the existence of ordered and disordered ("head to tail") phases; for obtaining the ordered phase, either long-term annealing or cooling to very low temperatures was necessary. Phase transition from ordered to disordered phase occurs[11] around 279 K with $\Delta_{\text{trans}}H$ equal to 4.468 kJ·mol^{-1}. This means that heat capacities of the disordered phase were measured. The data by Tozuka et al.[11] for the disordered phase are lower than those obtained in this work (see Figure 7) with the maximum deviation from our fitting equation of around 1 %. Marchidan et al.[9] published a linear correlation equation for the solid heat capacity of 1-chloro-4-nitrobenzene in the temperature range from 298 K to 355 K. However, their equation has an incorrect, negative slope. It is worth noting that data for other compounds published by Marchidan et al.[9] were marked as dubious in the critical compilation by Zábranský et al.[4,5] Temperature of fusion and enthalpy of fusion were also determined (see Table 2). Compared to the work by Tozuka,[11] T_{fus} from this work is 0.9 K higher. Our value of T_{fus} is 1.0 K below the most recent value reported by Verevkin and Schick,[15] and the difference from other literature data varies from 0.5 K to 2.9 K. $\Delta_{\text{fus}}H$ is 20 % lower than the value by Verevkin and Schick,[15] and the difference from other literature data varies from 5 % to 24 %. In general, there is a large scatter of both T_{fus} and $\Delta_{\text{fus}}H$ in the literature and this work data. The presence of some, even though a very small part, of the sample in the *ordered* conformation (despite the fact it was reported by Tozuka et al.[11] to be unstable at room temperature) might have affected results of the measurement.

Conclusion

Heat capacities in the solid and/or liquid phases were measured for three chloroanilines and three chloronitrobenzenes in the temperature range from 270 K to 350 K by a highly sensitive Tian−Calvet Setaram Micro DSCIII calorimeter. Results reported here supplement very limited data available in the literature. Recommended liquid heat capacities were developed by a critical assessment of all the available experimental data and are presented in terms of correlation equation parameters. Liquid heat capacities obtained here will be used to improve existing group contribution estimation methods. New data for T_{fus} and $\Delta_{\text{fus}}H$ were also determined for all compounds except for 3-chloroaniline. Melting of 2-chloroaniline appears to be complex and not fully reproducible. The scatter of literature values of T_{fus} and $\Delta_{\text{fus}}H$ for the 1-chloro-4-nitrobenzene compound is significant with no conclusive and satisfactory explanation.

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Received for review February 9, 2007. Accepted May 3, 2007. This work was supported by the Ministry of Education of the Czech Republic under the grant number MSM 604 613 7307.

JE700080K