Journal of Thermal Analysis and Calorimetry, Vol. 70 (2002) 455–466

HEAT CAPACITIES OF SOME PHTHALATE ESTERS

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(Received January 7, 2002)

Abstract

Isobaric heat capacities C_p in the liquid phase of dimethyl phthalate, diethyl phthalate, dibutyl phthalate, bis(2-ethylhexyl) phthalate, and benzyl butyl phthalate were measured by commercial SETARAM heat conduction calorimeters. Results obtained cover the following temperature range: dimethyl phthalate 283 to 323 K, diethyl phthalate 306 to 370 K, dibutyl phthalate 313 to 447 K, bis(2-ethylhexyl) phthalate from 313 to 462 K, benzyl butyl phthalate from 313 to 383 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.

Keywords: heat capacities, in liquid phase, phthalate esters, 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 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 subli-

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1418–2874/2002/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

mation 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 phase for five phthalate esters (esters of 1,2-benzenedicarboxylic acid). Phthalate esters are used as plasticizers in polymeric materials to increase their processability and flexibility. As phthalate esters are not chemically bound to the polymeric matrix, they can be released from plastic products and consequently enter into the environment. Today's concern in human exposure to phthalate esters is mainly due to their leaching into drinking water from plastic containers.

Experimental

Apparatus and procedure

Two commercial calorimeters made by SETARAM (Caluire, France), C80 and Micro-DSC II were used for measurement of saturation heat capacities. Both 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 1 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 more than 150 K below the known normal boiling temperature (for bis(2-ethylhexyl) phthalate and benzyl butyl phthalate we found no data for normal boiling temperature in literature). The reported saturation heat capacities are identical to isobaric heat capacities C_p.

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 more accurate heat capacity data than the C80 calorimeter.

Heat capacities were measured with a C80 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 [13]. 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.

Heat capacities were also 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 K 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.

Materials

$C_{10}H_{10}O_4$, dimethyl phthalate (CAS-RN [131-11-3]).

Aldrich product of stated purity 99%. The sample was purified by a duplicate fractional distillation under reduced pressure of about 800 Pa in a 1.2 m packed column and dried over molecular sieves type 4A. The final purity determined by g.c. was 99.95 mass%.

$C_{12}H_{14}O_4$, diethyl phthalate (CAS-RN [84-66-2]).

Aldrich product of stated purity 99%, purified and dried as stated above for dimethyl phthalate. The final purity was 99.53 mass%.

$C_{16}H_{22}O_4$, Dibutyl phthalate (CAS-RN [84-74-2]).

Aldrich product of stated purity 99%, purified and dried as stated above for dimethyl phthalate. The final purity was 99.97 mass%.

$C_{19}H_{20}O_4$, Benzyl butyl phthalate (CAS-RN [85-68-7]).

Aldrich product of stated purity 98%, purified and dried as stated above for dimethyl phthalate. The final purity was 99.82 mass%.

$C_{24}H_{38}$, Bis(2-ethylhexyl) phthalate (CAS-RN [117-81-7]).

Sigma product of stated purity 99%, purified and dried as stated above for dimethyl phthalate. The final purity was 99.64 mass%.

Results

The direct experimental T-C_p values are presented in Tables 1a to 1e.

Table 1a Liquid heat capacity of dimethyl phthalate

T/K	C_p/R	$\Delta C_p/R$	Calorimeter
283.2	36.85	0.08	micro-DSC
303.2	37.60	0.07	micro-DSC
323.2	38.51	0.17	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 1b Liquid heat capacity of diethyl phthalate

T/K	C_p/R	$\Delta C_p/R$	Calorimeter
283.2	43.35	0.15	micro-DSC
303.2	44.40	0.06	micro-DSC
323.2	45.63	0.10	micro-DSC
305.6	44.37[a]	–0.11	C80
310.6	44.66[a]	–0.11	C80
315.5	45.01[a]	–0.06	C80
320.5	45.23[a]	–0.14	C80
325.5	45.49[a]	–0.18	C80
330.4	45.84[a]	–0.14	C80
335.4	46.11[a]	–0.18	C80
340.4	46.46[a]	–0.14	C80
345.3	46.80[a]	–0.11	C80
350.3	47.07[a]	–0.17	C80
355.3	47.39[a]	–0.17	C80
360.2	47.66[a]	–0.23	C80
365.2	48.06[a]	–0.16	C80
370.2	48.46[a]	–0.09	C80

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

[a] Average values of heat capacities from six independent experimental runs carried out on C80 calorimeter at the same temperature are given in the table

The data determined in this work 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 weighted least-squares method:

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

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

Considering the width of the temperature range of experimental values for dibutyl phthalate and bis(2-ethylhexyl) phthalate the data were correlated by cubic splines in two subintervals. In this case the correlation is constrained to yield the identical C, dC/dT and d^2C/dT^2 values at the knot (temperature splitting the overall temperature range of experimental values into subintervals). Results of the correlation by cubic splines are presented in terms of parameters of Eq. (1) 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].

For the first three phthalates, dimethyl, diethyl and dibutyl, where the selected experimental data cover a wide temperature range and where a reliable estimate of critical temperature could be obtained the data were fitted to another empirical, the so-called quasi-polynomial, equation that allows a meaningful extrapolation “to the critical point”

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

where T_r=T/T_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

Table 1c Liquid heat capacity of dibutyl phthalate

T/K	C_p/R	$\Delta C_p/R$	Calorimeter
312.8	58.79	0.29	C80
312.8	58.82	0.32	C80
322.7	59.65	0.32	C80
322.8	59.62	0.29	C80
328.0	59.96	0.19	C80
332.7	60.38	0.21	C80
332.7	60.48	0.32	C80
337.9	60.73	0.12	C80
342.6	61.33	0.33	C80
342.6	61.35	0.34	C80
347.9	61.75	0.29	C80
352.5	62.18	0.32	C80
352.5	62.19	0.33	C80
357.8	62.69	0.38	C80
362.5	63.02	0.30	C80
362.5	63.08	0.37	C80
367.7	63.55	0.38	C80
372.4	63.83	0.24	C80
372.4	63.81	0.22	C80
377.6	64.47	0.43	C80
377.7	64.45	0.39	C80
377.8	64.28	0.21	C80
387.5	65.24	0.30	C80
387.7	65.32	0.37	C80
397.6	66.30	0.43	C80
407.6	67.06	0.27	C80
417.5	67.86	0.12	C80
427.5	68.87	0.16	C80
437.4	69.54	–0.16	C80
447.3	70.38	–0.35	C80

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

$$\sigma_{C/R,i} = 10^{-2} \frac{C_i \sigma_r C}{R} \tag{4}$$

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 either no or a small difference between the two equations as indicated by the relative standard deviation of the fit S_r that is given in Tables 2 and 3.

Table 1d Liquid heat capacity of benzyl butyl phthalate

T/K	C_p/R	$\Delta C_p/R$	Calorimeter
313.1	61.35	–0.11	C80
313.2	61.48	0.02	C80
323.1	62.36	–0.03	C80
323.1	62.35	–0.05	C80
323.1	62.52	0.12	C80
333.0	63.40	0.08	C80
333.1	63.23	–0.10	C80
333.1	63.30	–0.03	C80
343.0	64.41	0.15	C80
343.0	64.30	0.04	C80
343.0	64.27	0.00	C80
352.9	65.17	–0.03	C80
352.9	65.20	0.00	C80
362.9	66.06	–0.06	C80
362.9	66.17	0.04	C80
362.9	66.20	0.08	C80
372.8	67.16	0.10	C80
372.8	66.86	–0.20	C80
382.7	68.03	0.04	C80
382.7	67.95	–0.04	C80

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 Liquid heat capacity of bis(2-ethylhexyl) phthalate

T/K	C_p/R	$\Delta C_p/R$	Calorimeter
313.0	86.98	0.39	C80
313.1	86.79	0.19	C80
313.2	87.07	0.46	C80
323.0	88.24	0.31	C80
323.0	88.17	0.23	C80
323.1	88.29	0.35	C80
332.9	89.58	0.29	C80
333.0	89.59	0.28	C80
333.1	89.62	0.31	C80
342.9	91.04	0.35	C80
342.9	91.26	0.56	C80
343.0	91.12	0.41	C80
352.8	92.53	0.43	C80
352.8	92.64	0.53	C80
362.7	93.90	0.36	C80
362.8	93.90	0.36	C80
372.6	95.41	0.44	C80
372.7	95.53	0.55	C80
382.6	96.84	0.42	C80
382.6	96.91	0.49	C80
387.5	97.61	0.47	C80
392.5	98.22	0.35	C80
397.4	99.05	0.46	C80
402.4	99.64	0.33	C80
407.3	100.22	0.19	C80
412.3	101.06	0.30	C80
417.2	101.37	–0.10	C80
422.2	102.46	0.27	C80
427.1	102.84	–0.06	C80
432.1	103.79	0.18	C80
437.1	104.13	–0.18	C80
442.0	105.11	0.10	C80
447.0	105.52	–0.18	C80
452.0	106.43	0.04	C80
461.9	107.37	–0.37	C80

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

Compound	Parameters				Temperature range		S_r^a	Uncertainty/ %
	A_1	A_2	A_3	A_4	T_{min}/K	T_{max}/K		
Dimethyl phthalate	32.6009	–0.604958	0.736242	0	283.2	447.2	0.4	1.0
Diethyl phthalate	33.4046	1.40920	0.724886	0	273.2	370.2	0.2	1.0
Dibutyl phthalate	109.651	–71.7062	27.6630	–3.18754	179.2	290.0	0.4	0.5
	24.3773	16.5077	–2.75563	0.308848	290.0	447.3		1.0
Benzyl butyl phthalate	32.0501	9.39194	0	0	313.1	382.7	0.1	1.0
Bis(2-ethylhexyl) phthalate	127.061	–61.6255	22.7638	–2.30250	190.0	300.0	0.3	0.5
	85.2931	–19.8572	8.84107	–0.755525	300.0	461.9		1.0

[a] $S_r = 10^2 \left(\sum_{i=1}^{n} \left[\frac{\{C_m - C_m(calc)\}/C_m}{n-m} \right]_i^2 \right)^{\frac{1}{2}}$, 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 liquid isobaric heat capacity

Compound	Parameters				Temperature range		S_r	Uncertainty/ %
	A_1	A_2	A_3	A_4	T_{min}/K	T_c/K		
Dimethyl phthalate	9.36281	1.97672	25.0700	11.0868	283.2	765.0	0.4	1.0
Diethyl phthalate	–12.9396	4.61362	26.4527	9.07277	273.2	760.2	0.3	1.0
Dibutyl phthalate	–10.2711	15.6931	26.4437	1.68061	200.0	790.0	0.8	1.0

Discussion

For four phthalate esters investigated in this work some liquid heat capacity data were found in literature.

For dimethyl phthalate all available heat capacity data were critically assessed and recommended values were presented by Roháč *et al.* [7]. In this work we give only the data measured by using the Micro-DSC Setaram calorimeter. These data were already included in the evaluation and correlation of selected data by Roháč *et al.* [7]. Parameters of correlating equations in Tables 2 and 3 are identical to those given in [7] and are presented here only for the sake of lucidity.

For diethyl phthalate very precise data were determined by Chang *et al.* [14] who used low temperature adiabatic calorimeter. The data obtained in this work agree within the error of measurement with the data of Chang *et al.* [14] and extend them by about 20 K to higher temperatures. A single value at 298 K determined by Fuchs [15] is obviously dubious as it differs from other data by more than 2%, even though the author claims error of measurement of 0.5% (Fig. 1).

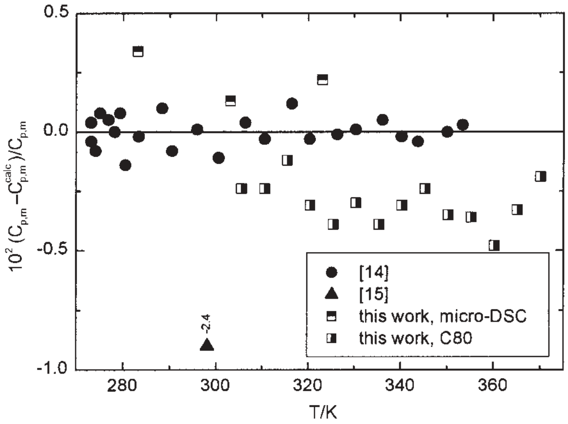

Fig. 1 Deviation plot for heat capacity of liquid diethyl phthalate

For dibutyl phthalate (Fig. 2) and for bis(2-ethylhexyl) phthalate (Fig. 3) there are two sets of data coming from the same laboratory, the Chemistry Institute of Lobachevski State University, Gorki (now Nizhny Novgorod), Russia. Martynenko *et al.* [16] and Rabinovich *et al.* [17] measured heat capacities in an adiabatic calorimeter in a wide temperature range. By analyzing the temperature dependence of heat capacity, Martynenko *et al.* concluded dibutyl phthalate and bis(2-ethylhexyl) phthalate do not crystallize. They determined temperature of phase transition between the glassy and liquid states. Rabinovich *et al.* [17] denote their data above this temperature as liquid despite the fact Fordyce and Meyer [18] determined for dibutyl phthalate the melting temperature of 238.2 K. We included in our correlation heat capacities presented by Martynenko *et al.* [16] and Rabinovich *et al.* [17] above the re-

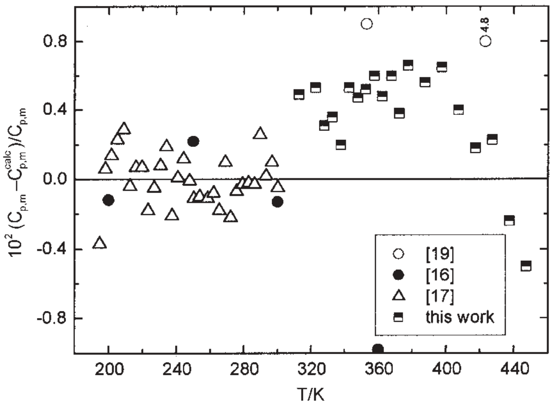

Fig. 2 Deviation plot for heat capacity of liquid dibutyl phthalate

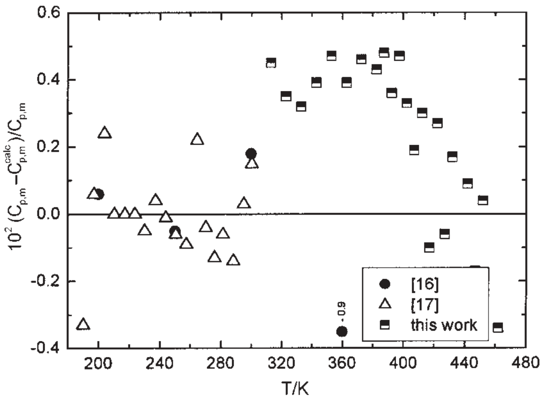

Fig. 3 Deviation plot for heat capacity of liquid bis(2-ethylhexyl) phthalate

spective temperature of phase transition between the glassy and liquid states. The data obtained in this work extend those from [16, 17] into higher temperatures. All data agree within the claimed error of measurement. The data by Berman *et al.* [19] for dibutyl phthalate are apparently dubious.

Conclusions

Recommended data on heat capacity of liquid dimethyl phthalate, diethyl phthalate, dibutyl phthalate, bis(2-ethylhexyl) phthalate, and benzyl butyl phthalate 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.

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

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