Measurement of Heat Capacities for 12 Organic Substances by Tian−Calvet Calorimetry

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Heat capacities for 1,2-dimethoxybenzene, 2,5,8,11-triethylene glycol dimethyl ether, *N*-ethyl-2-pyrrolidone, isopentyl acetate, 2-ethylhexanal, toluene, 1-phenylethanol, propyl acetate, octyl acetate, dimethyl sulfoxide, diethyl phthalate, and diethyl carbonate were measured with the "three-step" method using a Tian−Calvet batch calorimeter. The measurements of saturated liquid heat capacity have an approximate uncertainty of ±0.5% and cover a temperature range between 310 K and 420 K. Furthermore, the experimental results were compared with three group contribution methods for liquid heat capacities.

Introduction

To complete the Dortmund Data Bank, which contains nearly all worldwide available phase equilibrium data and excess properties, work on pure component properties was started in 1992 at the University of Oldenburg. The main objectives of the project, sponsored by the German Federal Ministry for Research and Technology (BMBF), are, in addition to the basic aim of collecting and correlating the data, the testing and further development of estimation methods for pure component properties with a view to the development of software tools for CAMD. Although the Department of Industrial Chemistry at the University of Oldenburg has built up the world's largest factual data bank for pure component properties, it is still required to measure data for compounds with missing or questionable values or for which data are available only for a limited temperature range.

The aim of this work is to measure heat capacities with the help of a SETARAM Tian−Calvet calorimeter using the "three-step" method. Furthermore, a comparison of the experimental data with calculated values of the group contribution methods for isobaric heat capacities developed by Ruzicka and Domalski,[1,2] Missenard,[3] and Luria and Benson[4] was performed. Additionally, the reproducibility of the Tian−Calvet calorimeter for the measurement of heat capacities was checked.

Experimental Section

The measurements reported here were performed using a Tian−Calvet heat flow batch calorimeter from SETARAM (model BT2.15), applicable in a temperature range from 77 K to 473 K. The principle of the measurement method has been described in detail by Calvet and Prat.[5] The calorimeter consists of two thermal fluxmeters, each constructed by a series of 480 thermocouples surrounding a cylindrical cavity. The fluxmeters are arranged symmetrically around the two cells in an aluminum block located in the cavity. The signal delivered by the power difference of the two fluxmeters is proportional to the heat effects occurring in the cells. The temperature of the calorimeter block can be regulated using liquid nitrogen and electrical heating and is monitored using a Pt 100 resistance thermometer located between the two cells. Only the temperature of the calorimeter block is recorded. It is not possible to measure the temperature of the sample in the cell directly. For heat capacity measurements the temperature of the calorimeter block is varied linearly with time. This means that there is a temperature difference between the calorimeter block and the sample during the measurement. To consider this, the melting points of heptane and benzoic acid were measured using three different temperature programs with heating rates of 0.15, 0.3, and 0.5 K·min^{-1} (in total six "melting" points).

The parameters of the following equation were fitted to the differences ΔT_m between the measured and published melting temperatures ($T_m = 182.57$ K for heptane[6] and $T_m = 395.49$ K for benzoic acid[7]) and the corresponding heating rates Z:

$$T_{corr} = b_0 + b_1 \Delta T_m + b_2 Z + b_3 Z^2 \tag{1}$$

T_{corr} is the corrected temperature. The temperature is computer controlled, and the signals (temperature and heat flux) are automatically recorded.

The cells used (volume = 8.5 cm^3) are made of stainless steel with aluminum or Teflon seals. The two cells were placed in the calorimeter, one charged with the sample and the other cell empty. To determine the mass of the samples a SATORIUS A 200 S balance with an accuracy of ±0.2 mg was used. As the cells were not totally filled with the sample, the measured heat capacities c_{sat} are measured at saturated pressure. At low vapor pressure, as in this case, the heat of vaporization can be neglected. Therefore, it is not necessary to distinguish between isobaric heat capacities C_p at the saturation curve and c_{sat} below $0.9T_b$ (normal boiling point) because the differences are smaller than the uncertainty of high-precision measurements.[8]

The temperature program of the three-step method (performed between 20 °C and 160 °C) keeps the temperature of the cells constant for 4 h at 20 °C before the temperature is increased to 160 °C with a heating rate of 0.15 K·min^{-1}. This procedure corresponds to Figure 1.

The temperature program has to be repeated with empty cells and with the reference sample (because of the reference sample no electrical calibration is required). In our investigation, sapphire was used as reference substance,

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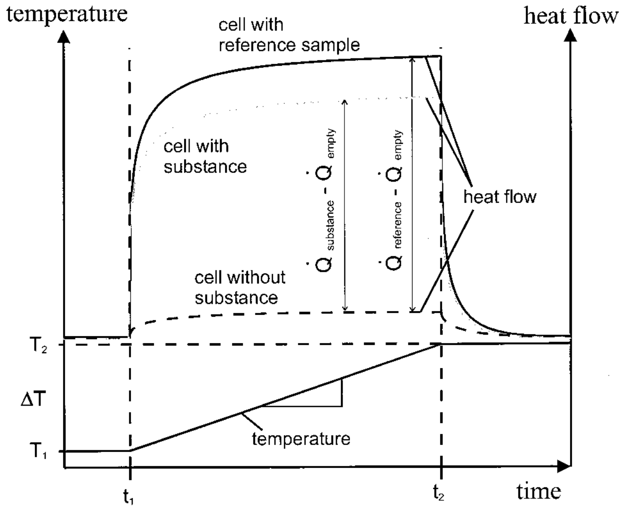

Figure 1. Three-step method for determination of heat capacities (the course of temperature is not true to scale).

because a large number of reliable heat capacity data are available for it. For each run (temperature, heat flow, and time) 5000 heat-flow data points are recorded. It is not possible to calculate heat capacities from each data point because a large number of data points are necessary to get reliable baselines at the start and the end of a measurement and to reach equilibrium during the temperature increase. Therefore, only 1500 data points can be used for calculating the heat capacities with the following equation:[7]

$$c_{\mathrm{probe}} = \frac{\dot{Q}_{\mathrm{sample}} - \dot{Q}_{\mathrm{empty}}}{\dot{Q}_{\mathrm{ref}} - \dot{Q}_{\mathrm{empty}}} \times \frac{n_{\mathrm{ref}}}{n_{\mathrm{sample}}} \times c_{\mathrm{ref}} \qquad (2)$$

n describes the number of moles of sample (n_{sample}) or of the reference sample (n_{ref}).

Heat capacities for 1,2-dimethoxybenzene ($C_8H_{10}O_2$, 138.17 g/mol, CAS Registry No. 91-16-7), 2,5,8,11-triethylene glycol dimethyl ether ($C_8H_{18}O_4$, 178.23 g/mol, CAS Registry No. 112-49-2), *N*-ethyl-2-pyrrolidone ($C_6H_{11}NO$, 113.159 g/mol, CAS Registry No. 2687-91-4), isopentyl acetate ($C_7H_{14}O_2$, 130,19 g/mol, CAS Registry No. 123-92-2), 2-ethylhexanal ($C_8H_{16}O$, 128.214 g/mol, CAS Registry No. 123-05-7), toluene (C_7H_8, 92.14 g/mol, CAS Registry No. 108-88-3), 1-phenylethanol ($C_8H_{10}O$, 122.17 g/mol, CAS Registry No. 98-85-1), propyl acetate ($C_5H_{10}O_2$, 102.13 g/mol, CAS Registry No. 109-60-4), octyl acetate ($C_{10}H_{20}O_2$, 172.27 g/mol, CAS Registry No. 112-14-1), dimethyl sulfoxide (C_2H_6OS, 78.13 g/mol, CAS Registry No. 67-68-5), diethyl phthalate ($C_{12}H_{14}O_4$, 222.24 g/mol, CAS Registry No. 84-66-2), and diethyl carbonate ($C_5H_{10}O_3$, 118.13 g/mol, CAS Registry No. 105-58-8) were measured. (CAS Registry No. were provided by the author.) All chemicals were obtained from Aldrich and stored over molecular sieve 3 Å. All compounds were distilled under vacuum using a Vigreux column with a height of 1.5 m. The purities (determined using gas chromatography) of all compounds were >99.95% by mass.

Results

The results are listed in Table 1 and presented in Figure 2 together with the published data. For a clear presentation not all 1500 data points but the data in 5 K steps are given.

Discussion

One of the aims of the pure component properties project is the test of estimation methods. For this study substances are suitable that were not used for fitting the parameters, for example, compounds for which no experimental data are available so far. For 1,2-dimethoxybenzene, *N*-ethyl-2-pyrrolidone, isopentyl acetate, 2-ethylhexanal, and 1-phenylethanol no experimental heat capacity data are available. For 2,5,8,11-triethylene glycol dimethyl ether, propyl acetate, octyl acetate, dimethyl sulfoxide, diethyl phthalate, and diethyl carbonate only a small temperature range was covered. The measured heat capacities were compared with heat capacities predicted by the group contribution methods of Missenard,[3] Luria and Benson,[4] and Ruzicka and

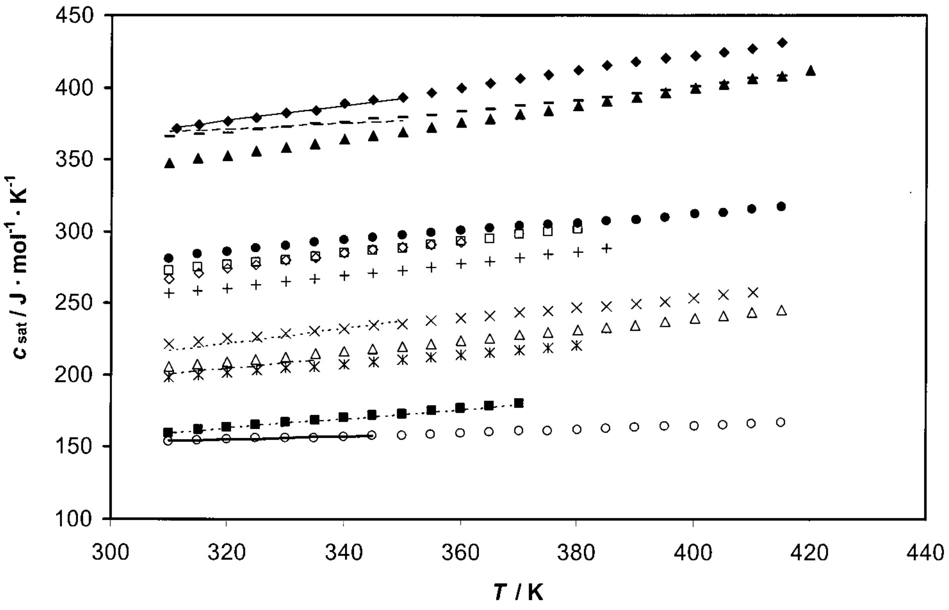

Figure 2. Experimental saturated heat capacity data c_{sat} measured with the three-step method compared with published data: ●, 1,2-dimethoxybenzene, this work; -, 2,5,8,11-tetraoxadodecane, this work; - - -, 2,5,8,11-tetraoxadodecane, Domalski et al.;[8] △, *N*-ethyl-2-pyrrolidone, this work; +, isopentyl acetate, this work; □, 2-ethylhexanal, this work; ■, toluene, this work; — · · — ·, toluene, Domalski et al.;[8] ◇, 1-phenylethanol, this work; ∗, propyl acetate, this work; — · — · ·, propyl acetate, Domalski et al.;[8] ▲, octyl acetate, this work; ○, dimethyl sulfoxide, this work; —, dimethyl sulfoxide, Domalski et al.;[8] ◆, diethyl phthalate, this work; —, diethylphthalate, Domalski et al.;[8] ×, diethyl carbonate, this work; · · ·, diethyl carbonate, Domalski et al.[8]

Table 1. Experimental Molar Saturated Heat Capacity Data c_{sat} for 1,2-Dimethoxybenzene, 2,5,8,11-Triethylene Glycol Dimethyl Ether, *N*-Ethyl-2-pyrrolidone, Isopentyl Acetate, 2-Ethylhexanal, Toluene, 1-Phenylethanol, Propyl Acetate, Octyl Acetate, Dimethyl Sulfoxide, Diethyl Phthalate, and Diethyl Carbonate Measured Using the Three-Step Method

T/K	c_{sat}/J·mol^{-1}·K^{-1}	T/K	c_{sat}/J·mol^{-1}·K^{-1}	T/K	c_{sat}/J·mol^{-1}·K^{-1}	T/K	c_{sat}/J·mol^{-1}·K^{-1}
1,2-dimethoxybenzene		triethylene glycol dimethyl ether		*N*-ethyl-2-pyrrolidone		isopentyl acetate	
310.02	280.98	310.07	365.50	310.04	205.42	310.03	256.57
315.00	283.87	315.06	367.10	315.02	207.41	315.01	258.80
320.05	286.03	320.04	368.60	320.07	208.99	320.06	260.43
325.00	288.04	325.07	371.00	325.01	210.60	325.01	262.27
330.06	290.18	330.05	372.70	330.07	212.16	330.06	265.07
335.04	292.60	335.03	375.19	335.05	214.47	335.05	266.73
340.02	294.20	340.02	376.00	340.04	216.26	340.03	269.00
345.02	295.90	345.01	378.29	345.03	218.09	345.02	271.23
350.01	297.22	350.00	378.77	350.02	219.53	350.01	272.62
355.08	298.98	355.07	380.90	355.01	221.59	355.00	275.04
360.07	300.63	360.07	382.73	360.00	223.52	360.07	277.22
365.06	302.04	365.05	384.48	365.08	225.51	365.07	279.31
370.05	303.81	370.04	387.00	370.07	227.63	370.05	281.86
375.04	304.68	375.03	388.87	375.05	229.44	375.04	283.79
380.03	305.82	380.02	390.49	380.04	231.21	380.03	285.49
385.01	307.16	385.01	393.02	385.03	233.02	385.01	287.83
390.08	308.39	390.08	395.75	390.01	234.84		
395.06	310.01	395.06	398.32	395.08	236.84		
400.04	311.74	400.05	400.78	400.06	239.29		
405.02	312.89	405.03	402.70	405.04	241.03		
410.00	315.25	410.00	405.88	410.02	243.62		
415.06	317.06	415.06	407.90	415.08	245.37		
2-ethylhexanal		toluene		1-phenylethanol		propyl acetate	
310.05	272.67	310.02	159.66	310.06	266.85	310.08	198.18
315.02	274.69	315.04	161.59	315.04	270.78	315.06	199.86
320.08	276.32	320.03	163.25	320.01	273.91	320.03	201.31
325.02	277.93	325.00	164.90	325.03	276.94	325.06	202.80
330.07	279.59	330.07	166.76	330.00	280.19	330.03	204.60
335.06	282.51	335.07	168.19	335.07	281.86	335.01	205.92
340.04	284.52	340.06	170.03	340.06	285.19	340.08	207.71
345.03	286.67	345.06	171.80	345.05	287.39	345.07	208.79
350.03	288.23	350.05	172.96	350.04	288.84	350.06	211.01
355.01	290.51	355.21	175.02	355.03	290.67	355.06	212.55
360.01	292.95	360.04	176.60	360.02	292.43	360.05	214.09
365.08	295.19	365.03	178.22			365.04	215.74
370.07	298.01	370.02	180.08			370.03	217.51
375.07	299.72					375.02	219.01
380.05	301.25					380.00	220.48
octyl acetate		dimethyl sulfoxide		diethyl phthalate		diethyl carbonate	
310.03	347.47	310.04	153.81	311.29	371.48	310.00	221.18
315.01	350.69	315.02	154.67	315.02	373.92	315.06	223.35
320.06	352.97	320.06	155.24	320.07	376.56	320.03	225.09
325.01	355.62	325.01	155.75	325.02	379.14	325.06	226.49
330.06	358.78	330.07	156.20	330.08	382.31	330.03	229.02
335.05	360.94	335.05	156.48	335.06	383.71	335.02	230.39
340.03	364.13	340.04	157.10	340.05	388.58	340.00	232.42
345.02	367.02	345.03	157.64	345.04	391.15	345.08	234.30
350.01	369.11	350.02	158.02	350.03	393.40	350.07	235.66
355.00	372.32	355.01	158.78	355.02	396.69	355.06	237.81
360.08	375.39	360.00	159.40	360.02	399.91	360.05	239.73
365.06	378.29	365.08	160.06	365.00	402.70	365.04	241.46
370.05	381.55	370.06	160.89	370.08	406.38	370.03	243.52
375.0	384.19	375.05	161.45	375.07	409.05	375.02	244.12
380.03	387.01	380.04	161.95	380.05	411.70	380.01	246.70
385.01	390.16	385.03	162.64	385.04	415.26	385.07	247.90
390.08	393.29	390.01	163.34	390.02	417.92	390.06	249.30
395.07	396.18	395.08	164.01	395.01	420.15	395.05	250.97
400.05	399.44	400.06	164.75	400.07	421.58	400.03	253.90
405.03	402.44	405.04	165.25	405.06	424.20	405.01	256.13
410.00	406.02	410.02	165.96	410.04	427.02	410.07	257.90
415.06	408.29	415.07	166.63	415.01	431.22		
420.02	412.30						

Domalski in the valid temperature range.[1,2] The results are shown in Table 2.

Column 1 of Table 2 displays the temperature range covered by the experimental data. In columns 2−4 the average absolute relative deviations, given by $100/n_p\Sigma|(c_{sat,exptl} - c_{sat,calcd})/c_{sat,exptl}|$ (whereby n_p is the number of points), between the calculated and the experimental values are listed. Column 5 displays the average deviation from the recommended values of Domalski et al.[8] together with the temperature range covered by the parameters of the recommended values listed in column 6. The comparison with the recommended values of Domalski et al.[8] shows that the deviations are small (<0.2%) for toluene, dimethyl sulfoxide, and diethyl phthalate. Domalski et al.[8] state that

Table 2. Comparison of the Experimental Data with Results of the Group Contribution Method of Missenard,[3] Ruzicka and Domalski,[1,2] and Luria and Benson[4] and Recommended Values

temp range of exptl data/K	av deviation of Missenard/%	av deviation of Ruzicka and Domalski/%	av deviation of Luria and Benson/%	av deviation of Domalski (recommended values)/%	temp range covered by recommended values/K
1,2-Dimethoxybenzene					
310−415	n.a.	3.28	n.a.	n.a.	n.a.
Triethylene Glycol Dimethyl Ether					
310−415	4.02	1.23	n.a.	0.52	230−350
N-Ethylpyrrolidone					
310−415	n.a.	n.a.	n.a.	n.a.	n.a.
Isopentyl Acetate					
310−385	n.a.	0.2	n.a.	n.a.	n.a.
2-Ethylhexanal					
310−380	n.a.	3.03	n.a.	n.a.	n.a.
Toluene					
310−370	1.70	0.28	1.02	0.20	310−370
1-Phenylethanol					
310−360	9.71	n.a.	n.a.	n.a.	n.a.
Propyl Acetate					
310−380	n.a.	1.43	n.a.	1.78	298−338
Octyl Acetate					
310−420	n.a.	0.32	n.a.	n.a.	n.a.
Dimethyl Sulfoxide					
310−415	n.a.	n.a.	n.a.	0.08	296−348
Diethyl Phthalate					
311−415	n.a.	0.34	n.a.	0.20	273−353
Diethyl Carbonate					
310−410	n.a.	n.a.	n.a.	0.82	295−359

the parameters for these compounds agree with the experimental data within ±0.5%, but for triethylene glycol dimethyl ether, diethylene carbonate, and especially propyl acetate the deviations are larger. However, for all of these compounds Domalski et al.[8] give an error of ±3%. This means that the deviation of the experimental values in comparison to the recommended values of Domalski et al.[8] is within the uncertainty of the parameters. The deviations for the three group contribution methods are quite different. Only three components can be calculated by using the Missenard[3] method, and also four components cannot be calculated with the Ruzicka and Domalski[1,2] method, although this is a quite new group contribution method with a large assortment of groups. The group contribution method of Luria and Benson[4] can be used only for hydrocarbons, for example, toluene. The deviations for the Missenard[3] method are quite large. In particular, the deviations for toluene are remarkably high, although a great number of data for this component are available. The average deviations of the Ruzicka and Domalski[1,2] method are all within reasonable limits. The deviations for propyl acetate and isopentyl acetate are especially small considering that these components were not included during the development of the group contribution method.

Also, the reproducibility of the results is an important indicator for the quality of the measured data. For this reason (and to check the calibration) toluene was measured in this work a second time. Table 3 shows the experimental data of toluene measured in this work together with data published by Becker et al.,[9] both measured with the Tian−Calvet calorimeter. In column 4 the relative deviations, given by $100(c_{\mathrm{sat,lit.}} - c_{\mathrm{sat}})/c_{\mathrm{sat,lit.}}$, from the recommended values of Domalski et al. and the experimental data are shown. In both cases the deviations are within ±0.3%. This demonstrates the high reproducibility of the heat capacity measurements obtained by the Tian−Calvet calorimeter. This result also confirms the precision of ±0.5% in heat capacity measurement above 100 K with a SETARAM Tian−Calvet calorimeter (BT type) found by Handa et al.[10]

Table 3. Comparison of the Experimental Data of Toluene in This Work and by Becker et al.[9] with Recommended Values of Domalski et al.[8]

	c_{sat}/J·mol^{-1}·K^{-1}			
T/K	this work	Becker, 2000	recommended values	deviation/%
310.02	159.66		160.51	0.529
312.05		161.01	161.11	0.061
315.04	161.59		161.99	0.248
317.00		162.44	162.58	0.085
320.03	163.25		163.49	0.148
321.95		164.05	164.07	0.011
325.00	164.90		165.00	0.059
326.95		165.81	165.59	−0.130
330.07	166.76		166.56	−0.124
331.95		167.12	167.14	0.013
335.07	168.19		168.12	−0.041
336.95		169.00	168.71	−0.172
340.06	170.03		169.70	−0.194
345.06	171.80		171.30	−0.293
350.05	172.96		172.92	−0.027
355.21	175.02		174.61	−0.230
360.04	176.60		176.22	−0.215
365.03	178.22		177.90	−0.177
370.02	180.08		179.60	−0.265

Conclusion

Liquid molar heat capacities of 12 organic substances were measured from 310 K to 420 K. The experimental data were compared with recommended values of Domalski et al.[8] and with data calculated using the group contribution methods of Ruzicka and Domalski,[1,2] Missenard,[3] and Luria and Benson.[4] Additionally, the reproducibility of the Tian−Calvet calorimeter was verified. Comparison with the recommended values of Domalski et al.[8] (as far as data are available) shows the high accuracy of the heat capacity measurements. Comparison of the group contribution methods with the experimental data shows that the method of Missenard is not suitable to predict the heat capacities of the measured components. The main problem with the Missenard method is that the number of structural groups is very limited. Only three of the measured components could be calculated. The deviations of the method of Ruzicka and Domalski, on the other hand, are within reasonable limits. For propyl acetate and isopentyl acetate the deviations are remarkably small. However, also for this method the necessary parameters for 4 of the 12 components are not available. Comparison of the heat capacities measured in this work and by Becker et al.[9] show that the reproducibility of the Tian−Calvet calorimeter is very high. This means that Tian−Calvet calorimetry is a very effective technique to measure heat capacities. Heat capacity measurements are necessary not only for the design of chemical processes but also for the further development of group contribution methods. Comparison of the experimental data with the three group contribution methods shows that for all prediction methods the number of available structural groups is very limited. This demonstrates that an extension of these methods is desirable.

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Received for review June 18, 2001. Accepted September 19, 2001.

JE010177O