Heat Capacities in the Solid and in the Liquid Phase of Isomeric Pentanols

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Isobaric heat capacities in the liquid and in the solid phases of seven isomeric pentanols were measured by adiabatic calorimetry. Results obtained cover the following temperature ranges: 2-methyl-1-butanol from 85 K to 301 K; 2-methyl-2-butanol from 84 K to 301 K; 3-methyl-1-butanol from 79 K to 158 K; 3-methyl-2-butanol from 85 K to 301 K; 2,2-dimethyl-1-propanol from 6 K to 381 K; 2-pentanol from 80 K to 301 K; and 3-pentanol from 5 K to 309 K. The temperature and enthalpy of phase transition were also determined. Solid to solid and solid to liquid phase transitions were detected for 2-methyl-2-butanol and for 2,2-dimethyl-1-propanol, and a solid to liquid phase transition was detected for 3-pentanol. Only a glass to liquid phase transition was detected for all the remaining compounds. The heat capacity data in the liquid phase obtained in this work were merged with available experimental data from the literature and critically assessed, and sets of recommended data were developed by correlating selected data as a function of temperature.

Introduction

Heat capacities in the 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.

This work was concerned with measurement of heat capacities in the liquid and the solid phases for seven isomeric pentanols using adiabatic calorimeters. The temperature and enthalpy of phase transition were also determined. However, as alkanols are known to be prone to forming a glassy phase (see, e.g., the comprehensive work by Wilhoit and Zwolinski[3]), solid to solid and solid to liquid phase transitions were detected for only three compounds, 2,2-dimethyl-1-propanol, 2-methyl-2-butanol, and 3-pentanol.

Heat capacity data determined in this work extend experimental data available in the literature in particular toward the low-temperature limit.

Experimental Section

All samples were purchased from Aldrich. Their purity was determined by GC Hewlett-Packard 6890 equipped with a column HP 5 (cross-linked 5 % PH ME Siloxan, length = 30 m, film thickness = 0.25 μm, i.d. = 0.32 mm) with an FID detector.

2,2-Dimethyl-1-propanol has a melting point of 328 K. It was purified by zone refining without detectable improvement. The sample was held over molecular sieves (Merck molecular sieve type 4A, 0.4 nm) at 353 K for several days prior to measurements.

Table 1. Sample Purity

compound	CAS registry no.	stated purity 100 *w*	original purity 100 *w* (GC)	final purity 100 *w* (GC)
2,2-dimethyl-1-propanol	75-84-3	99	99.79	99.79
2-methyl-1-butanol	137-32-6	99+	99.41	99.97
2-methyl-2-butanol	75-85-4	99+	99.63	99.99
3-methyl-1-butanol	123-51-3	99+	99.76	99.93
3-methyl-2-butanol	598-75-4	99+	99.50	99.93
2-pentanol	6032-29-7	98	99.21	99.99
3-pentanol	584-02-1	98	98.80	99.96

All others samples with the exception of highly hygroscopic 3-methyl-1-butanol were purified by fractional distillation in a packed column and dried over molecular sieves. The purity of the samples is summarized in Table 1.

Because of the small amounts of the purified samples, the use of the Fischer titration method for determination of water content was impossible. To minimize errors in heat capacity measurements caused by water, we opted for an untraditional method of water removal. The method is typically used for sample degassing prior to vapor pressure measurement.[4] A sample is placed in a stainless-steel cell and evacuated through a semipermeable membrane (made of, e.g., polydimethylsiloxane). The method was first tested with 1-butanol, which was available in an amount sufficient for testing experiments, with an original water mass fraction of 3.8 %. After one week of evacuating, the water mass fraction in the sample of 1-butanol was 0.66 %. After another week of drying, the water mass fraction dropped to 0.55 % which means that after two weeks more than 85 % of water was removed from the 1-butanol sample. After this test experiment, all seven samples of isomeric pentanols were treated in the same way. Next, isomeric pentanols were stored over molecular sieves in glass bottles closed by a septum. Samples were transferred from these bottles to a calorimetric vessel under a dry nitrogen atmosphere. The results of heat capacity measurements indicate that the water

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10.1021/je060411g CCC: $37.00

Table 2. Summary of Heat Capacity Measurements

compound	no. of data points	$T_{\min}$/K	$T_{\max}$/K	phase transition
2,2-dimethyl-1-propanol	314	6	381	solid II to solid I solid I to liquid
2-methyl-1-butanol	263	85	301	glass to liquid
2-methyl-2-butanol	214	84	301	solid III to solid II solid II to solid I solid I to liquid
3-methyl-1-butanol	115	70	158	glass to liquid
3-methyl-2-butanol	232	85	301	glass to liquid
2-pentanol	249	80	301	glass to liquid
3-pentanol	290	5	309	solid to liquid

content was below a limit that would significantly influence the obtained values.

Three adiabatic calorimeters placed in the Utrecht University were used for measurements (laboratory design indication CALV, CALVII, and CALVIII). CALV was used for the measurement of four alkanols (2-pentanol, 3-pentanol, 2-methyl-1-butanol, and 3-methyl-1-butanol). CALVII (3-methyl-2-butanol and 2,2-dimethyl-1-propanol) and CALVIII (2-methyl-2-butanol) were used because a mechanical defect appeared on CALV. The description of CALV and CALVII and the measurements with these devices can be found in refs 5 and 6. The construction and specification of CALVIII was described in ref 7. It was stated in refs 5 and 6 that below 30 K the reproducibility of CALV and CALVII calorimeters is about 1 %; between 30 K and 100 K it is (0.05 to 0.1) %; and above 100 K it is 0.03 %. The CALVII calorimeter is identical to CALV but uses a platinum 100 Ω thermometer instead of a Rh/Fe resistance thermometer. Oxford Instruments calibrated the thermometers to an uncertainty of 0.001 K using the ITS-90 temperature scale. The volume of the sample vessel for CALV and CALVII calorimeters is 11 cm^3. CALVIII is a scaled down version of CALV. It is designed for samples of about 0.6 cm^3. The reproducibility of CALVIII as stated in ref 7 is 0.6 % below 80 K and 0.2 % above 80 K. The measuring procedure that consisted of repeating stabilization and input periods is described in ref 6.

The above-mentioned reproducibility is that stated by researchers from the Utrecht laboratory. Van Miltenburg et al.[6,8] claimed that the uncertainties of the heat capacity measurements were checked with *n*-heptane and synthetic sapphire and found to be within 0.2 %. Zábranský et al.[1,2] critically assessed the data from the Utrecht laboratory and assigned to them the uncertainty of 0.5 %. Taking into account the peculiar dependence of heat capacity of alkanols on temperature[9] and generally an exceptional physical-chemical behavior of alkanols, the uncertainty of the measured heat capacities in this work was raised to 1.0 %.

A summary of heat capacity measurements is given in Table 2. The direct experimental heat capacity data are given in the Supporting Information and are shown in Figures 1 to 7. Phase transition experiments are summarized in Table 3. A more detailed account of phase transition experiments is given in the Results and Discussion.

Results and Discussion

The correction for sample vaporization was applied only for 2,2-dimethyl-1-propanol as the vapor pressure of all other studied substances was below 5 kPa at all experimental temperatures. This correction was discussed in Zábranský et al.[1,2] The final relationship between saturation heat capacity C_{sat} and a two-phase vapor−liquid equilibrium system (containing N moles of a sample) capacity C_{t} can be written as

$$C_{\text{sat}} = \frac{C_{\text{t}}}{N} + T\cdot\left(\frac{\partial p}{\partial T}\right)_{\text{sat}}\cdot\left(\frac{\partial V_m^{1}}{\partial T}\right) - T\cdot\left(\frac{V}{N} - V_m^{1}\right)\cdot\left(\frac{\partial^2 p}{\partial T^2}\right)_{\text{sat}} \qquad (1)$$

Terms on the right-hand side can be calculated from the vapor pressure equation and *pVT* properties of the liquid (except when in or near the critical region).

The liquid heat capacity data determined in this work were combined with all other calorimetrically determined heat capacities available in the literature and correlated as a function of temperature. 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 uncertainty of the 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 temperature correlation of the measured heat capacities in the solid phase was not performed. The industrial use of heat capacities in the solid phase is very limited compared to those in the liquid phase, and thus there is little demand for critically assessed data expressed in terms of parameters of a correlating equation. On the other hand, the absolute entropy and enthalpy difference, the desired quantities derived from solid heat capacities, are tabulated at rounded temperatures in Table 4 for two compounds, 2,2-dimethyl-1-propanol and 3-pentanol.

The selected data, that is, our own experimental data and the literature data selected in the process described above, were fitted with the polynomial equation using the weighted least-squares method:

$$\frac{C_p}{R} = \sum_{i=0}^{n} A_{i+1}\left(\frac{T/\text{K}}{100}\right)^{i} \qquad (R = 8.314472\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) \qquad (2)$$

Considering the width of the temperature range of experimental values for 3-methyl-2-butanol, the data were correlated by cubic splines in two subintervals. In this case, the correlation is constrained to yield the identical C, $\text{d}C/\text{d}T$, and $\text{d}^2C/\text{d}T^2$ 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.[1,2]

For 2-methyl-1-butanol, 3-methyl-1-butanol, 3-methyl-2-butanol, 2-pentanol, and 3-pentanol, where the selected experimental data cover a wide temperature range and where a reliable experimental value or a reliable estimate of the 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

$$\frac{C_p}{R} = A_1 \ln(1 - T_{\text{r}}) + \frac{A_2}{1 - T_{\text{r}}} + A_3 + A_4 T_{\text{r}} \qquad (3)$$

where $T_{\text{r}} = T/T_{\text{c}}$ and T_{c} is the critical temperature. The derivation of eq 2 (see Zábranský et al.[1,2]) is based on the assumption that

Table 3. Summary of Phase Transition Measurements

compound	type of phase transition	T_{trans}/K (this work)	T_{trans}/K (lit.)	T_{trans} (lit. citation)	H_{trans}/kJ·mol^{-1} (this work)	H_{trans}/kJ·mol^{-1} (lit.)	H_{trans} (lit. citation)
2,2-dimethyl-1-propanol	solid II to solid I	233.3	242	11	4.1	4.5	11
2,2-dimethyl-1-propanol	solid I to liquid	328.2	327.15	11	2.9	4.1	11
2-methyl-1-butanol	glass to liquid	around 118					
2-methyl-2-butanol	solid III to solid II	145.8	146	12	0.9	1.96	12
2-methyl-2-butanol	solid II to solid I	212.5	213	12			
2-methyl-2-butanol	solid I to liquid	264.7	264	12	2.0	4.46	12
3-methyl-1-butanol	glass to liquid	around 118					
3-methyl-2-butanol	glass to liquid	around 130					
2-pentanol	glass to liquid	around 129					
2-pentanol	glass to liquid	around 129					
3-pentanol	solid to liquid	203.2	204.15	3			

Table 4. Thermodynamic Properties at Selected Temperatures[a]

T/K	C_p^0/J·K^{-1}·mol^{-1}	S_m^0/J·K^{-1}·mol^{-1}	ΔH_m^0/J·mol^{-1}	T/K	C_p^0/J·K^{-1}·mol^{-1}	S_m^0/J·K^{-1}·mol^{-1}	ΔH_m^0/J·mol^{-1}
			2,2-Dimethyl-1-propanol				
10	4.09	1.50	11.25	150	97.11	102.7	7915
15	9.00	3.86	41.15	160	102.4	109.1	8913
20	14.89	7.24	100.7	170	107.8	115.5	9963
25	20.35	11.14	188.7	180	113.1	121.8	11070
30	25.41	15.31	303.4	190	119.2	128.1	12230
35	29.80	19.57	441.8	200	125.7	134.4	13450
40	33.67	23.82	601.2	210	132.5	140.7	14740
45	37.23	28.00	778.6	220	145.0	147.0	16110
50	40.59	32.09	973.2	230	287.8	155.2	17950
55	43.96	36.12	1185	240	160.1	177.5	23180
60	47.18	40.08	1412	250	167.3	184.2	24810
65	49.10	43.95	1654	260	175.3	190.9	26520
70	49.50	47.54	1896	270	184.0	197.7	28320
75	54.63	51.19	2161	280	194.5	204.6	30210
80	58.60	54.82	2443	290	206.0	211.6	32210
85	61.31	58.46	2743	298.15	214.3	217.6	33970
90	64.25	62.04	3056	300	216.4	218.9	34370
95	66.91	65.60	3385	310	227.8	226.1	36570
100	69.96	69.10	3727	320	411.1	236.5	39840
105	72.80	72.59	4084	330	256.6	253.4	45350
110	75.58	76.04	4455	340	277.1	260.9	47850
120	81.21	82.86	5239	350	283.8	269.0	50660
130	86.60	89.57	6077	360	290.2	277.1	53540
140	91.85	96.18	6970	370	295.4	285.1	56440
			3-Pentanol				
10	3.50	1.23	9.00	120	82.36	84.88	5499
15	8.21	3.49	38.0	130	110.5	93.79	6616
20	13.21	6.49	91.0	140	71.89	97.2	7067
25	18.82	10.05	171	150	150.8	114.1	9528
30	23.56	13.90	277	160	118.8	115.3	9741
35	28.96	17.93	408	170	110.3	118.3	10200
40	33.19	22.07	563	180	123.2	127.2	11730
45	37.81	26.25	741	190	129.8	134.0	12990
50	42.29	30.47	941	200	155.5	139.5	14070
55	46.14	34.68	1162	210	164.2	155.9	17420
60	49.88	38.86	1403	220	169.1	164.5	19280
65	53.44	42.99	1661	230	175.1	172.3	21030
70	56.86	47.08	1937	240	183.5	177.1	22150
75	60.13	51.11	2229	250	191.4	187.4	24680
80	63.27	55.09	2538	260	201.0	195.5	26750
85	66.36	59.02	2862	270	213.6	202.3	28550
90	69.21	62.90	3201	280	227.0	209.8	30610
95	72.17	66.72	3554	290	238.7	218.8	33170
100	76.23	70.51	3924	298.15	248.7	225.5	35160
105	79.46	74.34	4316	300	250.7	227.1	35620
110	83.89	78.18	4730				

[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.

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 in the form

$$S = \sum_{i=1}^{n} \left(\frac{\Delta C_i}{R}\right)^2 (\sigma_{C/R,i})^{-2} \tag{4}$$

where the variance $\sigma_{C/R,i}$ was estimated for each value on the basis of the assumed uncertainty of the set of data used in the correlation. The input information was the uncertainty of the experimental data $\sigma_r C$ given by the author or estimated by the evaluator for the whole data set. The variance of the ith data point was expressed as

$$\sigma_{C/R,i} = 10^{-2} \frac{C_i \cdot \sigma_r C}{R} \tag{5}$$

Table 5. Survey of All Available Calorimetrically Measured Heat Capacities for Isomeric Pentanols

compound	selected data, ref	temp range/K	uncertainty/%	purity 100w	rejected data, ref	temp range/K
2,2-dimethyl-1-propanol	10	310−360	1.0	99.79		
	this work	6−381		99.79		
2-methyl-1-butanol	33	303−326	0.5	99.8	18	347
	10	307−337	1.0	99.92	24	313−343
	35	298	1	99		
	this work	85−301		99.92		
2-methyl-2-butanol	12	275−294	1.0	n.s.[a]	18	332
	27	288−298	0.3	n.s.[a]	24	313−343
	28	298	0.3	n.s.[a]		
	29	298	0.5[b]	99.5		
	33	303−326	0.5	98.8		
	34	298	0.5[b]	99.99		
	10	308−347	1.0	99.91		
	35	298	1	98+		
	this work	84−301		99.91		
3-methyl-1-butanol	18	349	3.0[b]	n.s.[a]	17	310−337
	19	224−264	3.0[b]	n.s.[a]	20	321
	25	348	1.0[b]	n.s.[a]	21	303−353
	33	303−326	0.5	100.0	23	281−320
	10	308−357	1.0	99.72	24	313−343
	35	298	1	99		
	this work	70−158		99.72	30	318−333
				32	302−368	
3-methyl-2-butanol	31	218−317	1.0[b]	99.9	33	303−326
	10	304−347	1.0	99.99		
	35	298	1	98+		
	this work	85−301		99.99		
2-pentanol	33	303−326	0.5	99.6	22	308−367
	34	298	0.5[b]	99.8		
	10	308−367	1.0	99.93		
	35	298	1	98+		
	this work	80−301		99.93		
3-pentanol	33	303−326	0.8[b]	99.6	24	313−343
	34	298	0.5[b]	99.5	26	298
	10	308−367	1.0	99.90		
	35	298	1	98+		
	this work	5−309		99.90		

[a] n.s. = not specified. [b] Assigned by the authors of this paper.

A survey of all selected data used to determine the parameters of eqs 1 and 2 as well as a list of rejected data is given in Table 5.

Correlation of liquid heat capacity data was performed from either a temperature slightly above the melting temperature (for 2,2-dimethyl-1-propanol, 2-methyl-2-butanol, and 3-pentanol where the crystalline state was reached) or a temperature above the glass transition temperature to the upper limit of available experimental data by Čenský et al.[10]

Data for six alkanols, 2-methyl-1-butanol, 3-methyl-1-butanol, 3-methyl-2-butanol, 2-pentanol, and 3-pentanol cover a wide temperature range, and thus correlation was performed by cubic splines. Four knot points were used, except for 2-methyl-2-butanol, where only three knot points were used. One knot point was always fixed at the boundary line between data from adiabatic calorimeters from Utrecht and other data as the assumed accuracy of the data is changing at this point. Data for 2,2-dimethyl-1-propanol were correlated by a simple third-degree polynomial because the temperature range of liquid-phase data is too short.

Parameters of eq 1 and eq 2 derived from the fit are given in Table 6 and in Table 7, respectively, along with the relative standard deviation of the fit. 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 6 and 7.

Experimental heat capacities for all studied compounds are given in Tables 1, 3, 5, 7, 9, 11, and 13 in the Supporting Information and are shown in Figures 1, 3, 5, 7, 9, 11, and 13. Experimental enthalpy increments are given in Tables 2, 4, 6, 8, 10, 12, and 14 in the Supporting Information. A deviation plot in Figures 2, 4, 6, 8, 10, 12, and 14 shows how experimental heat capacities measured by different authors deviate from the recommended data.

2,2-Dimethyl-1-propanol. A sample of 2,2-dimethyl-1-propanol (about 3.76 g was used) was measured on a CALVII calorimeter from 5 K to 380 K. A solid II to solid I phase transition appeared at 233.34 K, and a solid I to liquid phase transition appeared at 328.15 K (see Table 3). A large difference between temperature and enthalpy of phase transition determined in this work and reported by Murrill et al.[11] (see Table 3) may be attributed to impurities in the Murrill sample.

2-Methyl-1-butanol. A sample of 2-methyl-1-butanol (about 2.73 g was used) was measured on a CALV calorimeter in the temperature range from 84 K to 301 K. A glass transition

Table 6. Parameters of Equation 2 for Liquid Isobaric Heat Capacity

	parameters				temperature range		
compound	A_1	A_2	A_3	A_4	T_{min}/K	T_{max}/K	s_r[a]
2,2-dimethyl-1-propanol	−2029.17	1725.65	−482.861	45.2159	331.6	362.6	0.38
2-methyl-1-butanol	15.4467	4.14293	−3.21006	0.98015	124.0	215.0	0.32
	10.6610	10.8205	−6.31593	1.46168	215.0	301.0	
	162.091	−140.106	43.8259	−4.09112	301.0	337.6	
2-methyl-2-butanol	297.052	−269.155	85.1028	−8.37070	267.6	302.0	1.42
	1177.55	−1143.82	374.727	−40.3380	302.0	347.6	
3-methyl-1-butanol	19.5765	−4.72768	2.65152	−0.205458	138.7	250.0	0.26
	−3.97838	28.1396	−12.6356	2.16464	250.0	300.0	
	303.026	−278.864	89.6990	-9.20588	300.0	357.4	
3-methyl-2-butanol	5.16802	19.9942	−12.5049	2.93540	138.7	250.0	0.32
	225.477	−244.376	93.2433	−11.1644	250.0	302.0	
	−14.3367	−6.15090	14.3607	−2.45768	302.0	370.7	
2-pentanol	17.0581	2.91226	−3.67176	1.33119	137.2	240.0	0.46
	44.1565	−30.9308	10.4420	−0.62052	240.0	301.0	
	506.374	−491.642	163.492	−17.5781	301.0	367.4	
3-pentanol	142.405	−149.008	57.1133	−6.63897	210.2	310.0	0.61
	219.115	−223.243	81.0602	−9.21390	310.0	367.7	

[a] $$s_r = 10^2 \cdot \left(\sum_{i=1}^{n} \left[\frac{\{C_p - C_p^{calcd}\}/C_p}{n - m} \right]_i^2 \right)^{1/2}$$

where n is the number of fitted data points and m is the number of independent adjustable parameters.

Table 7. Parameters of Equation 3 for Liquid Isobaric Heat Capacity

	parameters						temperature range		
compound	A_1	A_2	A_3	A_4	A_5	A_6	T_{min}/K	T_c/K	s_r[a]
2-methyl-1-butanol	−48.5721	3.42665	13.6746	−42.9527	−8.7353	107.742	124.1	575.4	0.38
3-methyl-1-butanol	124.625	5.60302	11.3139	140.888	−6.6116	273.298	138.7	579.4	1.29
3-methyl-2-butanol	7332.90	840.824	−861.076	6947.81	9.0865	4703.97	138.7	556.1	1.70
2-pentanol	2367.87	239.287	−235.095	2304.54	1.6384	1841.76	137.2	560.3	0.78
3-pentanol	7653.57	861.367	−893.416	7369.73	6.6503	5214.29	210.2	559.6	0.59

[a] $$s_r = 10^2 \cdot \left(\sum_{i=1}^{n} \left[\frac{\{C_p - C_p^{calcd}\}/C_p}{n - m} \right]_i^2 \right)^{1/2}$$

where n is the number of fitted data points and m is the number of independent adjustable parameters.

appeared at around 118 K (see Table 3). It was not possible to reach the crystalline solid phase even though the compound was kept at adiabatic conditions at a temperature slightly above the glass transition temperature for more than 2 days. A similar approach, i.e., keeping at adiabatic conditions a compound under study which showed signs of glass transition during the first experimental run, was repeated for all other compounds studied in this work. However, only for 3-pentanol was a crystalline state reached.

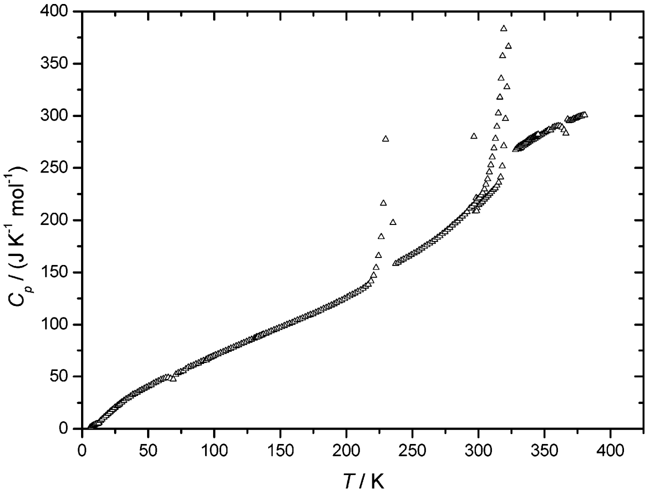

Figure 1. Experimental heat capacities for 2,2-dimethyl-1-propanol.

2-Methyl-2-butanol. A sample of 2-methyl-2-butanol (about 0.57 g was used) was measured on a CALVIII (small sample) calorimeter from 7 K to 300 K (data between 30 K and 50 K were lost due to a hard disk failure). Considerable disagreement of almost 3 % between experimental heat capacity data from this work and the data by Parks et al.[12] may be accounted for as in the case of 1-pentanol in the paper by Van Miltenburg and van den Berg[13] who stated that "the data of Parks are

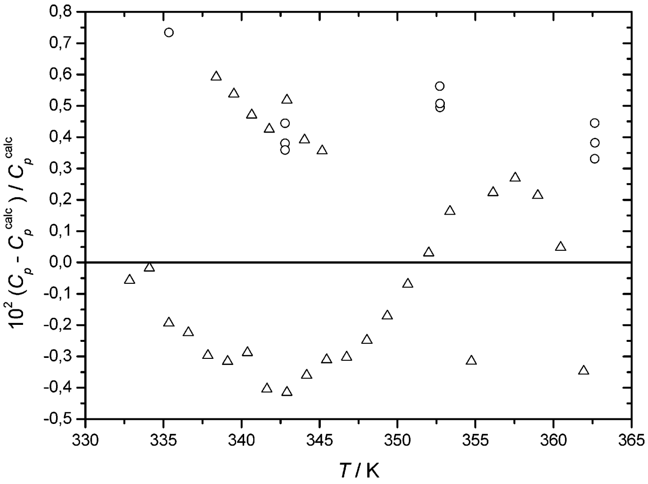

Figure 2. Deviation plot of liquid heat capacity data for 2,2-dimethyl-1-propanol. C_p^{calcd} is calculated from eq 2 with parameters from Table 6: ○, this work; △, Čenský et al.[10]

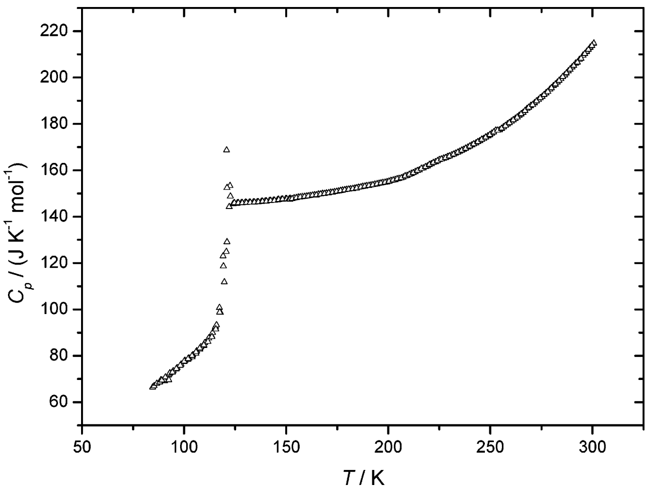

Figure 3. Experimental heat capacities for 2-methyl-1-butanol.

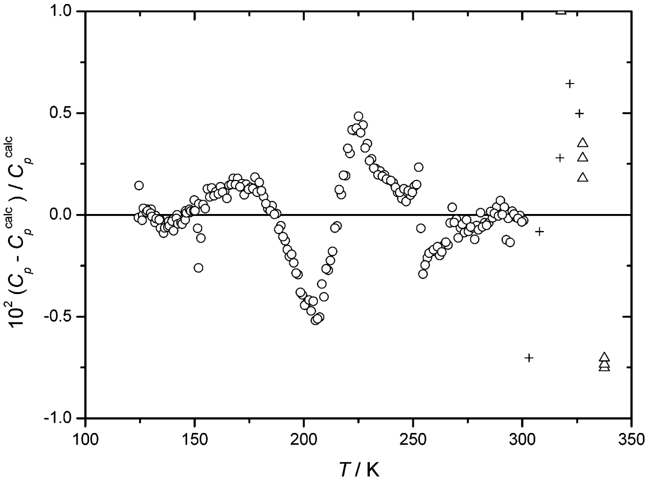

Figure 4. Deviation plot of liquid heat capacity data for 2-methyl-1-butanol. C_p^{calcd} is calculated from eq 2 with parameters from Table 6: ○, this work; △, Čenský et al.[10] Partially displayed: +, Svoboda et al.[33] Not displayed: refs 18, 24, and 35.

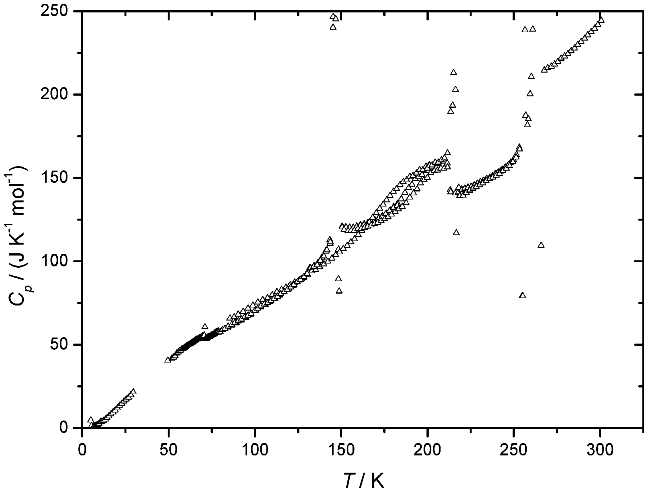

Figure 5. Experimental heat capacities for 2-methyl-2-butanol.

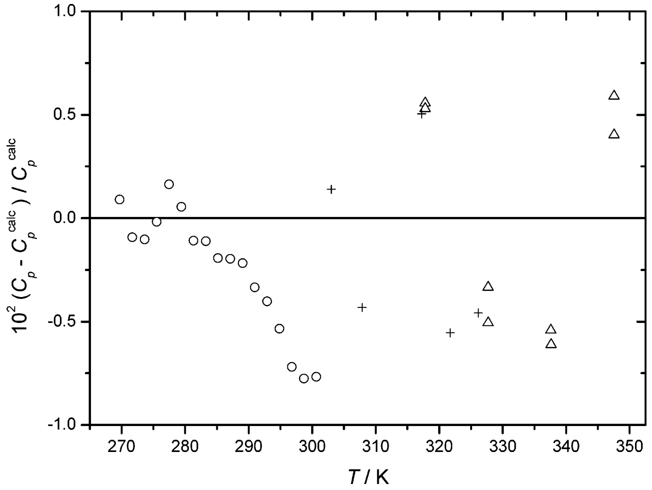

Figure 6. Deviation plot of liquid heat capacity data for 2-methyl-2-butanol. C_p^{calcd} is calculated from eq 2 with parameters from Table 6: ○, this work. Partially displayed: +, Svoboda et al.;[33] △, Čenský et al.[10] Not displayed: refs 12, 18, 24, 27−29, 34, and 35.

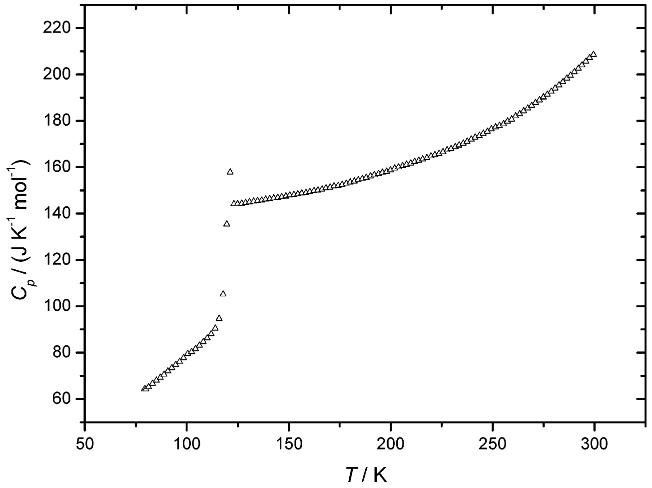

Figure 7. Experimental heat capacities for 3-methyl-1-butanol.

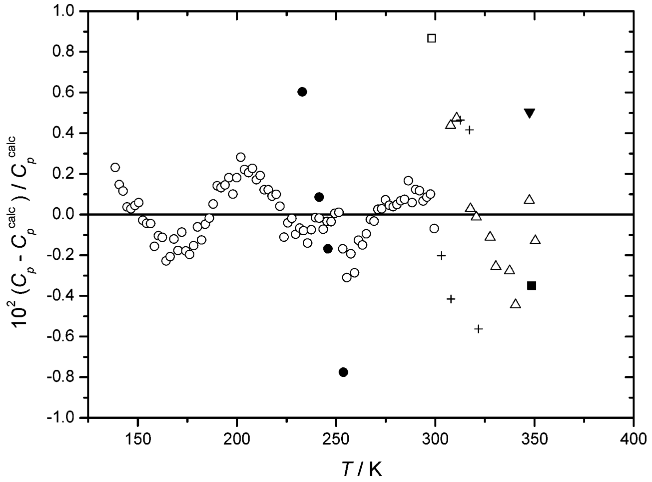

Figure 8. Deviation plot of liquid heat capacity data for 3-methyl-1-butanol. C_p^{calcd} is calculated from eq 2 with parameters from Table 6: ○, this work; △, Čenský et al.;[10] □, Fenclová et al.;[35] ■, Louguinine;[18] ▼, Swietoslawski and Zielenkiewicz.[25] Partially displayed: ●, Batelli;[19] +, Svoboda et al.[33] Not displayed: refs 17, 18, 20, 21, 23, 24, 30, and 32.

probably measured on a less pure sample. This assumption is based on the premelting visible in their data". Three transitions were found in this temperature range. A solid III to solid II phase transition was found at 145.78 K. At 212.5 K, another solid II to solid I transition was found. Heat capacity values are higher below the solid II to solid I phase transition temperature than values above that temperature. Parks et al.[12] observed a similar effect, calling it a "hump", and suggested that possibly a small portion of a supposedly crystalline sample

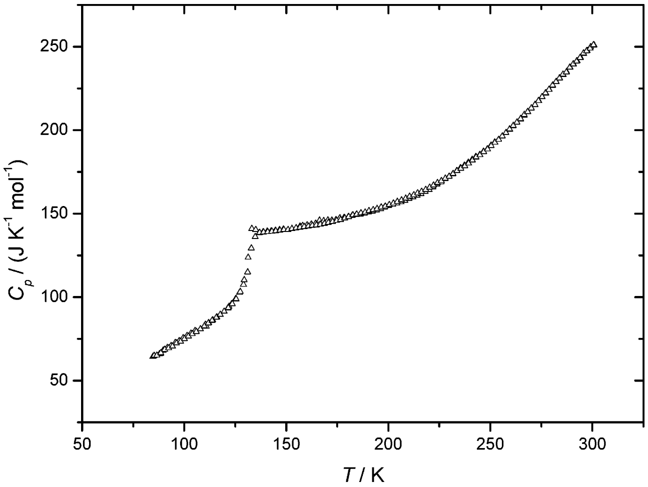

Figure 9. Experimental heat capacities for 3-methyl-2-butanol.

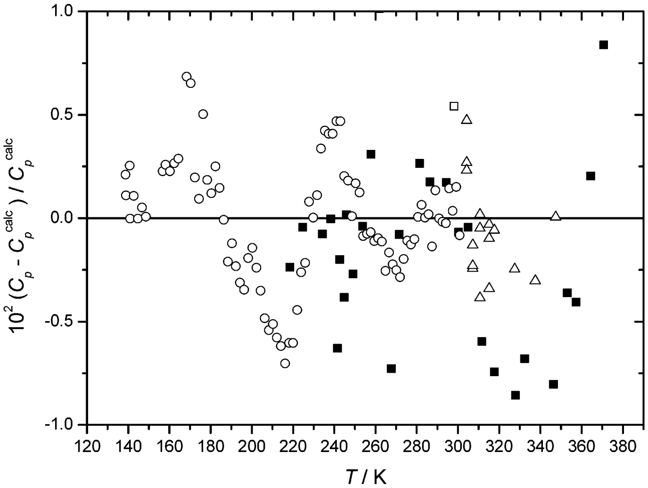

Figure 10. Deviation plot of liquid heat capacity data for 3-methyl-2-butanol. $C_p^{\text{calcd}}$is calculated from eq 2 with parameters from Table 6: ○, this work; △, Čenský et al.;[10] □, Fenclová et al.[35] Partially displayed: ■, Atrashenok et al.[31] Not displayed: ref 33.

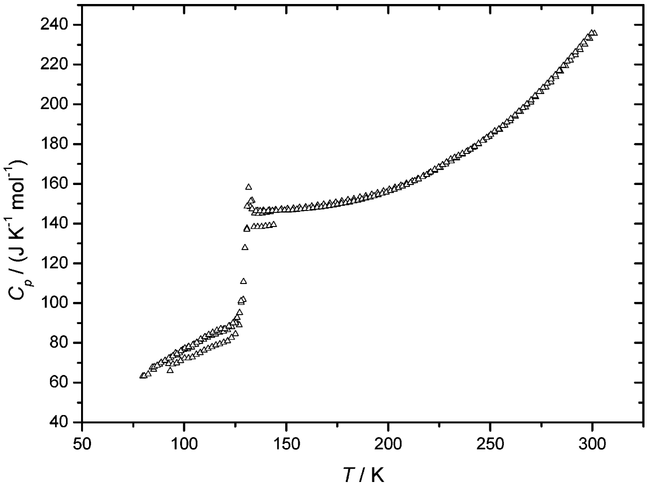

Figure 11. Experimental heat capacities for 2-pentanol.

was in the form of a glass at the lowest temperatures. Although Domalski and Hearing[14] attributed the hump to a normal phase transition, Domalski later in a personal communication, after re-examining the data, agreed it was more an anomaly. A third transition, a melting, was found at 264.67 K.

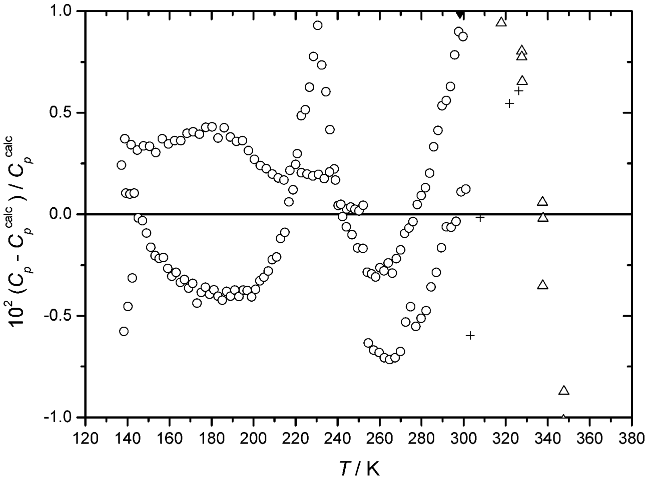

Figure 12. Deviation plot of liquid heat capacity data for 2-pentanol. C_p^{calcd} is calculated from eq 2 with parameters from Table 6: ○, this work; ▼, Tanaka and Toyama.[34] Partially displayed: △, Čenský et al.;[10] +, Svoboda et al.[33] Not displayed: refs 22 and 35.

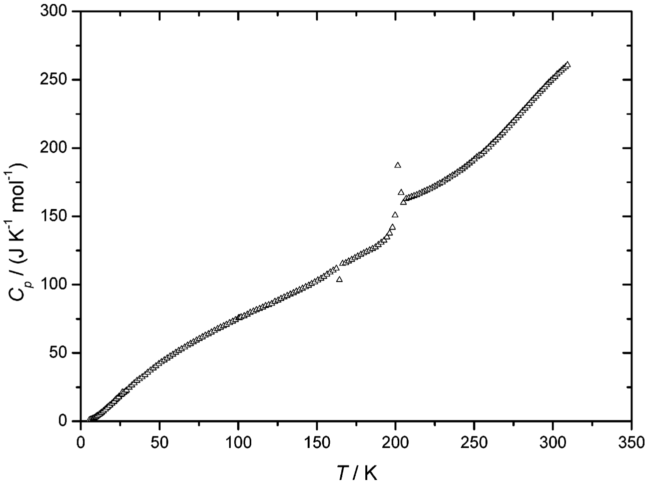

Figure 13. Experimental heat capacities for 3-pentanol.

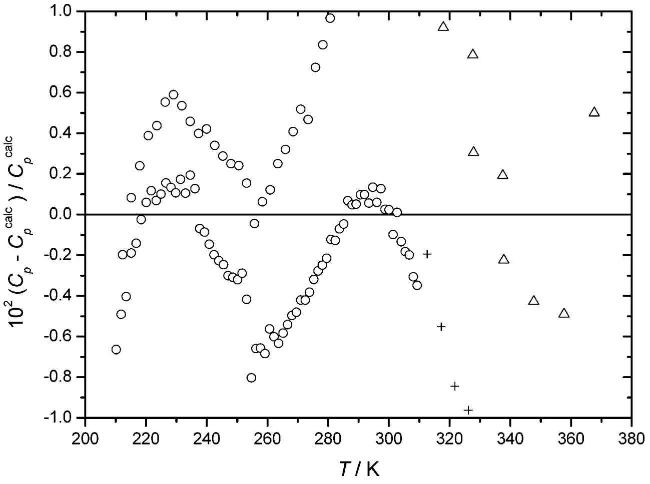

Figure 14. Deviation plot of liquid heat capacity data for 3-pentanol. C_p^{calcd} is calculated from eq 2 with parameters from Table 6: ○, this work. Partially displayed: △, Čenský et al.;[10] +, Svoboda et al.[33] Not displayed: refs 24, 26, 34, and 35.

3-Methyl-1-butanol. The sample of 3-methyl-1-butanol (about 2.51 g was used) was measured in the CALV calorimeter in the temperature range from 80 K to 300 K. Only one series of measurements is available as a hard disc failure caused the loss of some data. The glass transition was found at about 118 K (see Table 3).

3-Methyl-2-butanol. The sample of 3-methyl-2-butanol (about 2.10 g was used) was measured on the CALVII calorimeter in the temperature range from 84 K to 301 K. During the first measurement, the glass transition was found. A glass transition appeared at around 130 K (see Table 3).

2-Pentanol. The sample of 2-pentanol (about 2.33 g was used) was measured in the CALV calorimeter in the temperature range from 79 K to 301 K. During the first experiment, the glass transition was found. The sample was cooled down, and the experiment was repeated. During the second experiment, the glass transition appeared again, but the heat capacity of the glass phase before the transition and the heat capacity of the liquid phase after the transition, as well as ΔC_p, were slightly different than during the first experiment. It is possible that some crystalline solid phase was formed before this second experiment. This is shown in Figure 11. The procedure was repeated again, but no sign of the crystal phase was found. A glass transition appeared at around 129 K (see Table 3).

3-Pentanol. The sample of 3-pentanol (about 2.62 g was used) was measured on the CALV calorimeter in the temperature range from 5 K to 300 K. During one experiment, a glass transition and following recrystallization appeared at around 130 K (see Table 3). The melting point was found at 203.17 K. The fusion temperature and also the enthalpy of fusion determined in this work differ from values reported by Wilhoit el al.[3] and by Lohmann et al.[15] Lohmann took the value from the Dortmund Data Bank with no specification of the source of the original data, whereas Wilhoit used unpublished values obtained by Cook in 1952.

It should be emphasized that the dependence of liquid heat capacities on temperature for studied isomeric pentanols differs from a typical dependence of the majority of simple organic liquids showing a monotonically increasing curve. Zábranský et al.[9] classified heat capacity curves of pure liquid compounds into four categories using the shape of the curve that depicts the dependence of the heat capacity on temperature as a criterion. They reported that a group of compounds including pyrrolidine and alkanols with more than two carbon atoms in the molecule show an inflection point on $C = f(T)$. At the time of publication of the work,[9] this type of curve was known for 1-alkanols C_3 to C_{10} and for 2-propanol, 2-methyl-1-propanol, and 2-methyl-2-propanol. Zábranský et al.[9] proposed that there is a relationship between the inflection point and the breakdown of hydrogen bonds in the liquid phase.

Conclusions

Liquid heat capacity data for seven isomeric pentanols obtained in this work supplement the literature data so that recommended data could be developed that cover the temperature range from the melting temperature to about 300 K. Data in this temperature range are important for a simultaneous treatment of vapor pressures and of the related thermal data (see, e.g., ref 16) aimed at extrapolation of vapor pressures down to the triple point. Agreement of experimental data from this work with the literature data is only moderate, most probably due to compound purity and the water content of samples measured in the past. It should be noted that in the previous works water content was reported only rarely. Reproducibility of the data obtained in this work is worse than was the case in previous works from the Utrecht laboratory, despite all experimental care during measurements, the high purity of samples, and the low water content achieved by sample evacuation through a membrane.

Solid heat capacity measurements are complete for two compounds only, 2,2-dimethyl-1-propanol and 3-pentanol. For the five remaining isomeric pentanols studied in this work, technical problems during measurements and formation of a glassy phase prohibited filling in the so far missing data.

Supporting Information Available:

Experimental heat capacities for all studied compounds are given in Tables 1, 3, 5, 7, 9, 11, and 13 and experimental enthalpy increments are given in Tables 2, 4, 6, 8, 10, 12, and 14 in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review September 20, 2006. Accepted January 22, 2007. This work was supported by the Ministry of Education of the Czech Republic under Grant MSM 604 613 7307.

JE060411G