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Heat capacities of alkanols
II. Some isomeric C_5 alkanols

Miroslav Čenský*, Květoslav Růžička, Vlastimil Růžička, Milan Zábranský

Department of Physical Chemistry, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic

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Abstract

Isobaric heat capacities C_p in the liquid phase of seven isomeric C_5 alkanols and in the solid phase for 2,2-dimethyl-1-propanol were measured by a commercial SETARAM heat conduction calorimeter. Results obtained cover the following temperature range: 2-methyl-1-butanol (CAS-RN 137-32-6) 308–338 K, 2-methyl-2-butanol (75-85-4) 308–348 K, 3-methyl-1-butanol (123-51-3) 308–357 K, 3-methyl-2-butanol (598-75-4) 304–347 K, 2-pentanol (6032-29-7) 308–367 K, 3-pentanol (584-02-1) 308–368 K, 2,2-dimethyl-1-propanol (75-84-3) 310–363 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: Isomeric C_5 alkanols; Heat capacity; In liquid phase; Temperature dependence

1. 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.

This work, which is the second paper in a series devoted to heat capacities of alkanols (for the first paper in the series see Fulem et al. [3]), was concerned with measurement of heat capacities in the liquid phase for seven isomeric C_5 alkanols. Heat capacity in the solid phase and enthalpy of fusion was determined for 2,2-dimethyl-1-propanol only, as the temperature of fusion of all other compounds falls below the measuring range of the SETARAM C80 calorimeter.

2. Experimental

2.1. Materials

All samples were purchased from Aldrich. Its purity was determined by GC (Hewlett-Packard 6890

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* Corresponding author. Present address: Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 182 21 Prague 8, Czech Republic. Tel.: +420-266052603; fax: +420-286890265.
E-mail addresses: censky@fzu.cz (M. Čenský), vlastimil.ruzicka@vscht.cz (V. Růžička).

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equipped with column HP 5 (cross-linked 5% PH ME Siloxan, length 30 m, film thickness 0.25 μm, i.d. 0.32 mm) with FID detector.

3-Methyl-1-butanol, which is highly hygroscopic, was used as received. Water content as determined by Fischer method was 0.04 wt.% and sample was transferred directly from SureSeal flask into vessel under inert atmosphere.

2,2-Dimethyl-1-propanol has melting point of 327 K. It was purified by zone refining without detectable improvement. Sample was held over molecular sieves at 353 K for several days prior to measurements. Stability of boiling temperature during ebulliometric measurements [4] indicates that its water content was lower than in the case of 3-methyl-1-butanol.

All others samples were purified by fractional distillation in a packed column and dried over molecular sieves type 4A. Water content was lower than 0.004 wt.% (detection limit of the Schot Geräte apparatus for Fisher analysis).

2.2. Apparatus and procedure

A commercial C80 calorimeter made by SETARAM (Caluire, France) was used for measurement of saturation heat capacities. In this work the calorimeter was equipped with standard cells having the inner volume of 9.5 cm^3 reduced by a raised bottom. In a typical heat capacity experiment with samples of several grams, the temperature was increased in steps of 5–10 K with a heating rate of 0.2 K min^{-1}. The average heat capacity for a given temperature step ΔT is obtained from the time integrals of the differential thermopile signal for the filled and empty sample cells and is related to the temperature $T = T_{\text{in}} + \Delta T/2$ (T_{in} is the initial temperature). A correction for sample vaporization was applied where it was significant (all compounds with exception of 2-methyl-1-butanol and 3-methyl-2-butanol) using a formula given in Čenský et al. [5]. The C80 calorimeter was also used for measurement of enthalpy of fusion of 2,2-dimethyl-1-propanol.

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 50 K below the known normal boiling temperature. The reported saturation heat capacities are identical to isobaric heat capacities C_p.

The calorimeter was calibrated with synthetic sapphire (α-Al_2O_3), the NIST Standard Reference Material 720 [6]. In our previous experiments we estimated the uncertainty of data measured by C80 calorimeter to be ±1% by making test experiments with several compounds of well-known heat capacity values.

3. Results

The direct experimental T–C_p values are presented in Table 1.

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:

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

where $\boldsymbol{R} = 8.31451\ \text{J K}^{-1}\,\text{mol}^{-1}$.

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

Table 1
Experimental heat capacities

Substance	T (K)	$C_p/\boldsymbol{R}$	$\Delta C_p/\boldsymbol{R}$	phase
2-Methyl-1-butanol	307.8	27.1	0.2	ℓ
	307.8	27.1	0.2	ℓ
	307.8	27.1	0.3	ℓ
	317.7	28.4	0.0	ℓ
	317.7	28.4	0.1	ℓ
	317.7	28.4	0.0	ℓ
	327.6	29.7	−0.1	ℓ
	327.6	29.7	0.0	ℓ
	327.6	29.7	0.0	ℓ
	337.6	30.9	0.1	ℓ
	337.6	30.9	0.1	ℓ
	337.6	31.0	0.1	ℓ
2-Methyl-2-butanol	307.9	31.3	0.2	ℓ
	307.9	31.3	0.2	ℓ
	317.8	32.5	0.2	ℓ
	317.8	32.5	0.2	ℓ
	327.7	33.6	0.2	ℓ
	327.7	33.6	0.1	ℓ
	337.6	34.5	0.0	ℓ
	337.6	34.5	−0.1	ℓ
	347.5	35.2	−0.4	ℓ
	347.6	35.1	−0.5	l
3-Methyl-1-butanol	307.7	26.1	0.1	ℓ
	310.7	26.5	0.1	ℓ
	317.7	27.2	0.0	ℓ
	320.6	27.6	0.1	ℓ
	327.6	28.4	0.1	ℓ
	330.6	28.8	0.0	ℓ
	337.5	29.6	0.0	ℓ
	340.5	29.9	−0.1	ℓ
	347.4	30.8	0.0	ℓ
	350.4	31.0	−0.1	ℓ
	357.4	31.8	0.0	ℓ
3-Methyl-2-butanol	304.2	30.7	0.1	ℓ
	304.2	30.8	0.2	ℓ
	304.2	30.7	0.1	ℓ
	307.2	31.0	0.0	ℓ
	307.2	31.0	−0.1	ℓ
	307.2	31.0	−0.1	ℓ
	310.7	31.3	−0.1	ℓ
	310.7	31.5	0.0	ℓ
	310.7	31.5	0.0	ℓ
	315.1	32.0	−0.1	ℓ
	315.1	32.0	0.0	ℓ
	315.1	31.9	−0.1	ℓ
	317.6	32.2	−0.1	ℓ
	327.6	33.1	−0.1	ℓ
	337.5	33.9	−0.1	ℓ
	347.4	34.6	0.1	ℓ
2-Pentanol	307.8	29.6	0.2	ℓ
	308.0	29.5	0.1	ℓ
	308.9	29.8	0.2	ℓ
	317.7	31.0	0.1	ℓ
	317.8	31.0	0.1	ℓ
	317.9	30.8	0.0	ℓ
	327.7	32.1	0.1	ℓ
	327.7	32.1	0.0	ℓ
	327.8	32.1	0.0	ℓ
	337.6	33.2	0.0	ℓ
	337.6	33.1	−0.1	ℓ
	337.8	33.2	0.0	ℓ
	347.5	34.1	0.0	ℓ
	347.5	34.0	−0.1	ℓ
	347.7	34.2	0.1	ℓ
	357.4	34.8	0.0	ℓ
	357.5	34.8	−0.1	ℓ
	357.6	35.0	0.1	ℓ
	367.4	35.5	0.0	ℓ
	367.4	35.5	0.0	ℓ
3-Pentanol	307.8	31.9	0.4	ℓ
	308.0	31.7	0.2	ℓ
	317.7	33.0	0.4	ℓ
	318.0	32.9	0.3	ℓ
	327.7	34.0	0.4	ℓ
	327.9	33.9	0.2	ℓ
	337.6	34.8	0.3	ℓ
	337.9	34.7	0.2	ℓ
	347.8	35.3	0.1	ℓ
	357.7	35.8	−0.1	ℓ
	367.7	36.2	−0.1	ℓ
2,2-Dimethyl-1-propanol	310.4	27.6	0.1	s
	310.4	27.4	0.0	s
	310.4	27.4	0.0	s
	315.4	28.3	0.1	s
	315.4	28.2	0.0	s
	315.4	28.1	−0.1	s
	320.3	29.1	0.1	s
	320.4	29.0	0.0	s
	320.4	28.9	−0.1	s
	335.2	33.0	0.1	ℓ
	335.2	32.8	−0.1	ℓ
	340.2	33.2	0.0	ℓ
	345.2	33.6	0.1	ℓ
	350.1	34.0	0.1	ℓ
	355.1	34.2	0.0	ℓ
	360.1	34.6	0.0	ℓ
	360.1	34.6	0.0	ℓ

$\boldsymbol{R} = 8.31451\,\mathrm{J\,K^{-1}\,mol^{-1}}$, $\Delta C_p/\boldsymbol{R} = (C_p - C_p^{\mathrm{calc}})/\boldsymbol{R}$, where C_p^{calc} was calculated from Eq. (1) using parameters from Table 3.

(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 2-methyl-2-butanol, 3-methyl-1-butanol and 3-methyl-2-butanol, 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

$$\frac{C_p}{\boldsymbol{R}} = A_1 \ln(1 - T_r) + \frac{A_2}{1 - T_r} + A_3 + A_4 T_r \qquad (2)$$

where $T_r = T/T_c$ and T_c is the critical temperature. The derivation of Eq. (2) (see 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:

$$S = \sum_{i=1}^{n} \left(\frac{\Delta C_i}{\boldsymbol{R}} \right)^2 (\sigma_{c/\boldsymbol{R},i})^{-2} \qquad (3)$$

where the variance $\sigma_{c/\boldsymbol{R},i}$ 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 $\sigma_r C$ given by the author or estimated by the evaluator for the whole data set. The variance of the ith data

Table 2
Survey of all available calorimetrically measured heat capacities for isomeric pentanols

Compound	Selected data	Temperature range (K)	Error (%)	Purity (%)	Rejected data	Temperature range (K)
2-Methyl-1-butanol	[26]	303–326	0.5	99.8	[15]	347
	This work	307–337	1.0	99.92	[20]	313–343
2-Methyl-2-butanol	[7]	275–294	1.0	n.s.[a]	[15]	332
	[22]	288–298	0.3	n.s.[a]	[20]	313–343
	[23]	298	0.3	n.s.[a]		
	[24]	298	0.5[b]	99.5		
	[26]	303–326	0.5	98.8		
	[27]	298	0.5[b]	99.99		
	This work	308–347	1.0	99.91		
3-Methyl-1-butanol	[15]	349	3.0[b]	n.s.[a]	[14]	310–337
	[8]	224–264	3.0[b]	n.s.[a]	[16]	321
	[21]	348	1.0[b]	n.s.[a]	[17]	303–353
	[26]	303–326	0.5	100.0	[19]	281–320
	This work	308–357	1.0	99.72	[20]	313–343
					[9]	318–333
					[10]	302–368
3-Methyl-2-butanol	[25]	218–317	1.0[b]	99.9	[26]	303–326
	This work	304–347	1.0	99.99		
2-Pentanol	[26]	303–326	0.5	99.6	[18]	308–367
	[27]	298	0.5[b]	99.8		
	This work	308–367	1.0	99.93		
3-Pentanol	[26]	303–326	0.8[b]	99.6	[20]	313–343
	[27]	298	0.5[b]	99.5	[11]	298
	This work	308–367	1.0	99.90		
2,2-Dimethyl-1-propanol	This work	310–360	1.0	99.79		

[a] n.s.: not specified.

[b] Assigned by evaluator.

Table 3
Parameters of Eq. (1) for isobaric heat capacity

Compound	Parameters					Temperature range		Uncertainty	
	Phase	A_1	A_2	A_3	A_4	$T_{\min}$ (K)	$T_{\max}$ (K)	s_r (%)[a]	%
2-Methyl-1-butanol	ℓ	−120.252	79.0093	−10.1423	0	303.0	337.6	0.5	1
2-Methyl-2-butanol	ℓ	−29.6289	27.0956	−2.39623	0	275.0	347.5	0.9	1
3-Methyl-1-butanol	ℓ	114.553	−101.007	33.9279	−3.39607	224.0	357.4	0.5	1
3-Methyl-2-butanol	ℓ	195.360	−214.072	83.2014	−10.0688	218.4	310.0		1
	ℓ	−213.907	181.992	−44.5613	3.66917	310.0	370.7	0.3	1
2-Pentanol	ℓ	−89.4170	62.4616	−7.74717	0	298.1	367.4	0.4	1
3-Pentanol	ℓ	−71.5459	54.6449	−6.88223	0	298.1	367.7	1.1	3
2,2-Dimethyl-1-propanol	ℓ	10.4887	6.69024	0	0	335.2	360.1	0.2	2
2,2-Dimethyl-1-propanol	s	−19.8525	15.2412	0	0	310.4	320.4	0.3	2

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

Table 4
Parameters of Eq. (2) for liquid isobaric heat capacity

Compound	Parameters						Temperature range		Uncertainty	
	A_1	A_2	A_3	A_4	A_5	A_6	$T_{\min}$ (K)	T_c (K)	s_r (%)	%
2-Methyl-2-butanol	46.1350	3.43145	−26.0909	155.069	0	0	275.0	543.7	0.8	1
3-Methyl-1-butanol	0.137205	12.6047	−0.588750	$3.73376\cdot10^{-4}$	0	0	224.0	579.4	1.0	3
3-Methyl-2-butanol	8295.30	955.136	−983.528	7881.95	965.637	5340.52	218.4	556.1	0.5	1

point was expressed as

$$\sigma_{c/\boldsymbol{R},i} = 10^{-2}\frac{C_i\cdot\sigma_r C}{\boldsymbol{R}} \qquad (4)$$

A survey of all selected data used to determine parameters of Eqs. (1) and (2) as well as a list of rejected data is given in Table 2.

Parameters of Eq. (1) derived from the fit are given in Table 3 along with the relative standard deviation of the fit. Parameters of Eq. (2) are given in Table 4. 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 3 and 4.

4. Discussion

Table 2 presents a survey of literature sources of calorimetrically measured heat capacity data of isomeric pentanols, for the selected sets of data together with temperature range, measurement error and purity of the sample. The rejected sets of data that is those not used in the calculation of parameters of Eqs. (1) and (2) are represented by mostly old and inaccurate measurements carried out with compounds of low purity. The rejected data show large deviations from the recommended data as demonstrated in deviation plots (Figs. 1–6). Only for 2-methyl-2-butanol ([7]) and 3-methyl-1-butanol ([8]) the old data were included among the selected data in order to extend the temperature range towards low temperatures.

There were also some more recent sets of data rejected for the following reasons. For 3-methyl-1-butanol the data by Rao et al. [9] were determined by a simple “deferential heating and cooling technique” assuming the measured and the reference compounds have the same heat conductivity; the stated

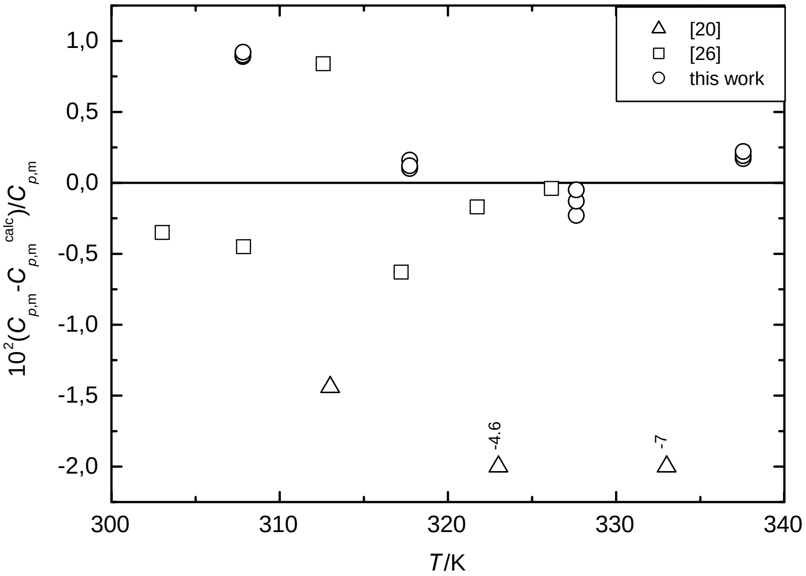

Fig. 1. Deviation plot for heat capacity of liquid 2-methyl-1-butanol.

measurement error was 4% and purity of the compound was not given in the paper. For the same compound we also rejected the data by Naziev et al. [10] with the stated measurement error of 2.2%. The main objective of Naziev et al. was to carry out measurements up to 50 MPa. Their data at a normal pressure deviate from other data by almost 7% (see Fig. 3). For 3-pentanol we rejected a single value determined in an excess heat capacity experiment by Conti et al. [11]; in these experiments the purity of compounds used is often low resulting in a 5% deviation from the recommended data.

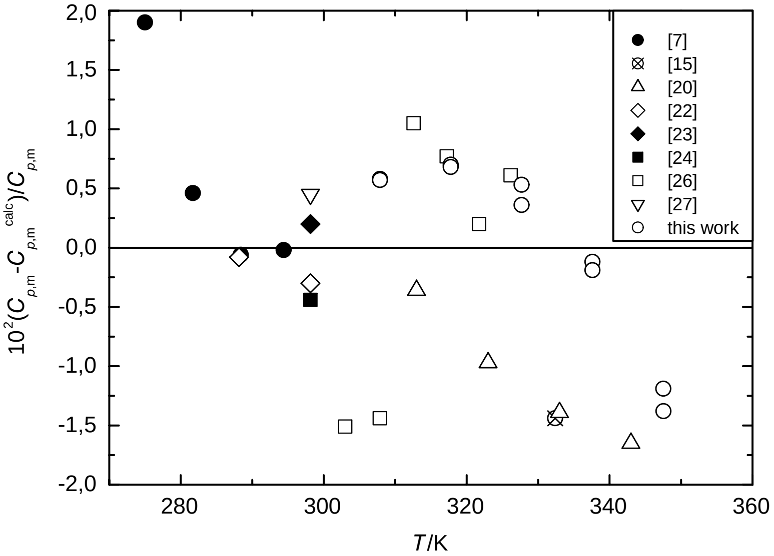

Fig. 2. Deviation plot for heat capacity of liquid 2-methyl-2-butanol.

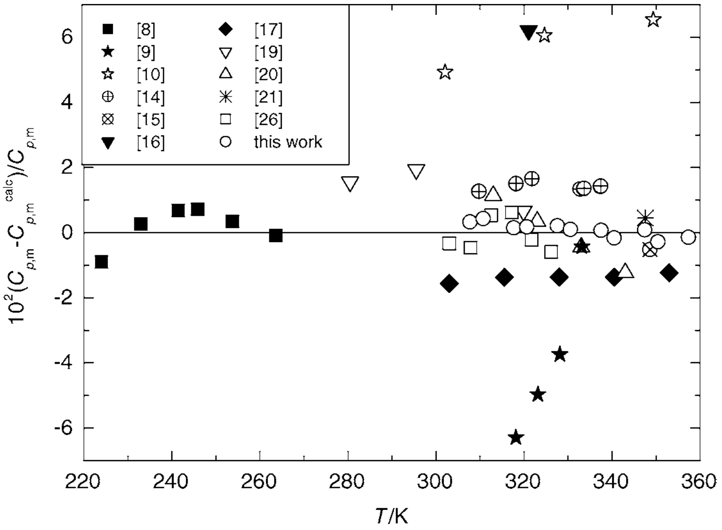

Fig. 3. Deviation plot for heat capacity of liquid 3-methyl-1-butanol.

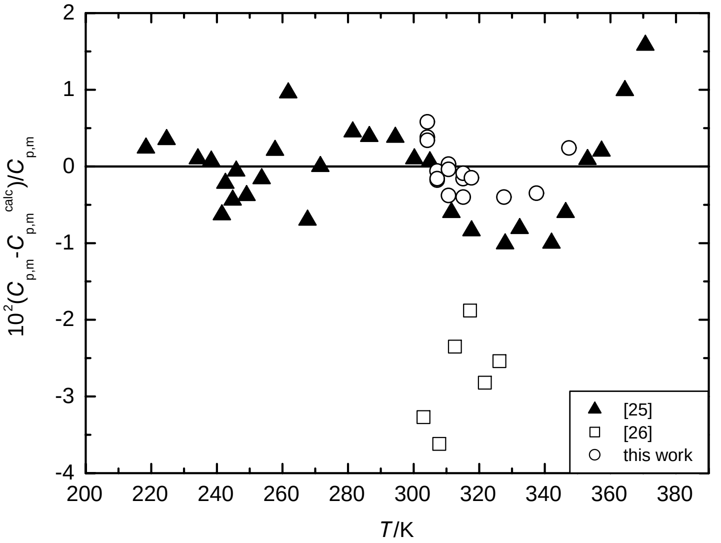

Fig. 4. Deviation plot for heat capacity of liquid 3-methyl-2-butanol.

Temperature and enthalpy of fusion of 2,2-dimethylpropanol are given in Table 5 along with literature data. Temperature of fusion reported by [12] (unpurified sample) and by [13] (sample purified by sublimation) is lower than in this work, which might be caused by the presence of impurities or water in the sample.

Table 5
Temperature and enthalpy of fusion of 2,2-dimethyl-1-propanol

Temperature of fusion (K)	Enthalpy of fusion (J mol^{-1})	Literature source
329.8 ± 0.1	3870 ± 50	This work
324.2	4037.6	[12]
328.2	3500	[13]

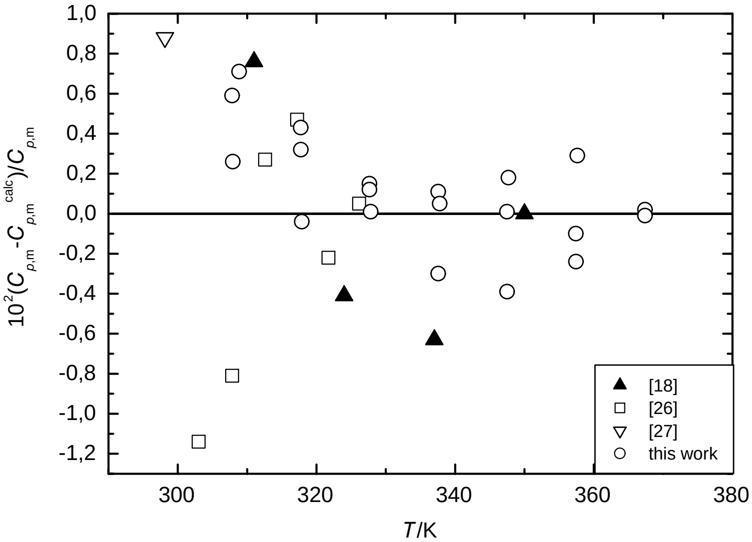

Fig. 5. Deviation plot for heat capacity of liquid 2-pentanol.

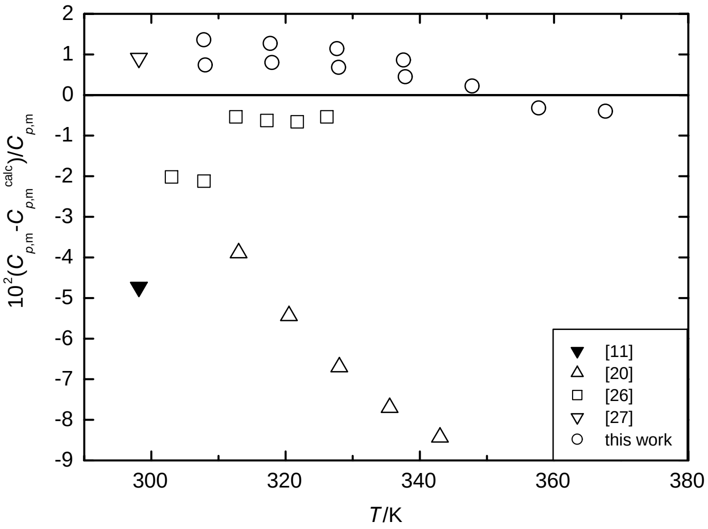

Fig. 6. Deviation plot for heat capacity of liquid 3-pentanol.

5. Conclusions

Recommended data on heat capacity of seven liquid aliphatic pentanols were developed by critical assessment of newly determined and available literature data. Some sets of data published in the literature were rejected due to their large systematic deviations. The recommended data are presented in terms of parameters of empirical correlating equations expressing their dependence on temperature.

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