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Heat capacities of alkanols
Part I. Selected 1-alkanols C_2 to C_{10} at elevated temperatures and pressures

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Abstract

Measurements of isobaric heat capacities in the liquid phase were carried on the following 1-alkanols: 1-hexanol, 1-heptanol, 1-octanol, and 1-decanol in the temperature range from 325 to 570 K and at pressures of 2, 10 and 30 MPa using a commercial heat conduction SETARAM C-80 calorimeter. Additional measurements, which provided saturation heat capacities, were carried out in a slightly different experimental arrangement for ethanol, 1-propanol, 1-butanol, 1-hexanol, 1-heptanol, 1-octanol, and 1-decanol at a pressure considered within the expected pressure variation of heat capacity close to the saturation vapour pressure. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Liquid heat capacity; 1-Alkanols; Temperature dependence; Pressure dependence; Correlation

1. Introduction

Two types of heat capacities in the liquid phase, the isobaric C_p and the saturation C_{sat}, are measured most often and are defined by the following equations:

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p = -T\left(\frac{\partial^2 G}{\partial^2 T}\right)_p, \tag{1}$$

$$C_{\text{sat}} = T\left(\frac{\partial S}{\partial T}\right)_{\text{sat}}. \tag{2}$$

Both of these liquid heat capacities are equal within the error of measurement below the normal boiling temperature. Their mutual relationship is given by the following equation:

$$C_{\text{sat}}(T, p_{\text{sat}}) = C_p(T, p_{\text{sat}}) - T\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\text{d}p}{\text{d}T}\right)_{\text{sat}} \tag{3}$$

The temperature dependence of heat capacity is usually described by an empirical polynomial equation (see e.g. [1,2]):

$$\frac{C}{R} = \sum_{j=0}^{m} A_j \left(\frac{T}{100}\right)^j, \tag{4}$$

where R is the universal gas constant and A_j are adjustable parameters, usually $3 \geq m \geq 1$.

For extrapolation, in particular towards the critical point, the so-called quasi-polynomial equation was proposed [2]:

$$\frac{C}{R} = \sum_{i=-1}^{m} E_i \tau^i, \tag{5}$$

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where $\tau = 1 - T/T_C$, T_C is the critical temperature, E_i are adjustable parameters, $m \leq 5$. This equation guarantees an infinite heat capacity at the critical temperature, in accordance with theory.

The pressure dependence of isobaric heat capacity C_p is expressed by the equation:

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 V}{\partial^2 T}\right)_p \qquad (6)$$

A conversion of the heat capacity from a pressure p to the saturation pressure p_{sat} may be subject to a large error as the second derivative of volume with respect to temperature is needed.

Only for methanol are reliable liquid heat capacities available over a wide temperature range far above the normal boiling temperature. For other 1-alkanols, new data are needed, in particular at higher temperatures. In addition to providing reliable data at temperatures above normal boiling point, new measurements should either confirm or refute any peculiar dependence of the saturated heat capacity on temperature, which may not be observed for other compounds.

A survey of literature sources on saturation liquid heat capacities of 1-alkanols is given in the monograph by Zábranský et al. [2]. In general, reliable data from different sources are available for 1-alkanols C_2 to C_{10} at temperatures below and slightly above normal boiling temperature. Data extending far above the normal boiling temperature were reported only by Grigor'ev et al. [3] and/or by Vasil'ev et al. [4] and for 1-butanol by San Jose [5]. Zábranský et al. critically assessed all available literature data and correlated the selected data as a function of temperature to develop the so-called recommended data. The recommended data were presented in terms of parameters of Eq. (4) and, if the selected data covered a temperature range wider than about 50 K, then Eq. (5) was used. For 1-hexanol, 1-heptanol and 1-octanol at temperatures above 318 K Zábranský et al. selected only the data by Grigor'ev et al. [3] for correlation and noticed that it is not apparent from the original paper what type of heat capacity was measured. For the correlation of 1-decanol at elevated temperatures, Zábranský et al. selected the data by Grigor'ev et al. [3] and by Vasil'ev et al. [4]. Zábranský et al. rated the data from [3] as of medium quality and the data from [4] as of low reliability. For 1-alkanols higher than 1-decanol, if literature data from authors other than Vasil'ev and coworkers were available and covered approximately the same temperature range, Zábranský et al. rejected the data from this laboratory for the development of the recommended data due to their lower reliability compared to other authors' data.

The plot of saturation heat capacity versus temperature for the family of 1-alkanols indicates a presence of inflexion point starting with 1-propanol [6]. A similar temperature dependence of saturation heat capacity was not observed for compounds other than 1-alkanols [7].

Measurements of heat capacities of 1-alkanols at elevated pressures come mainly from laboratories of the former Soviet Union. Arutyunyan [8] determined the heat capacity of 1-hexanol in the pressure range from 0.1 to 60 MPa and at temperatures from 293 to 533 K. Arutyunyan and Movsesyan [9] published heat capacity data for 1-heptanol in the same pressure and temperature range. Naziev and Bashirov [10] published heat capacity data for 1-heptanol and 1-decanol in the pressure range from 0.1 to 50 MPa and at temperatures from 303 to 523 K.

Randzio et al. [11] measured the isobaric expansivity of 1-hexanol from the saturated vapour pressure up to 400 MPa at temperatures from 302 to 503 K. From the isobaric expansivity, they calculated the difference between heat capacity at the experimental pressure and that at the saturated pressure. Adding this difference to the heat capacity at the saturated pressure, taken from Zábranský et al. [6], the heat capacity at an elevated pressure was then calculated.

New heat capacity data were obtained in this work for 1-hexanol, 1-heptanol, 1-octanol and 1-decanol at pressures of 2, 10 and 30 MPa and in the temperature range from 323 to 573 K using commercial heat conduction SETARAM C-80 calorimeter. In addition, saturation heat capacities were also determined for ethanol, 1-propanol and 1-butanol in the temperature range from 325 to 470, 505, 550 K, respectively, and for 1-hexanol, 1-heptanol, 1-octanol and 1-decanol in the temperature range from 323 to 573 K.

2. Experimental

2.1. Materials

Ethanol was used as-received from the supplier. No further purification was needed. 1-Propanol was dried

Table 1
Chemicals

Compound	Supplier	Stated purity (mol%)	Final purity (mol%)	Water content (wt.%)
Ethanol	Riedel-de Haën	>99	99.99	0.010
1-Propanol	Lachema	>99	99.99	0.015
1-Butanol	Lachema	>99	99.99	0.010
1-Hexanol	Merck	98	99.95	0.0044
1-Heptanol	Aldrich	98	99.92	0.0026
1-Octanol	Merck	>99	99.94	0.0074
1-Decanol	Merck	>99	99.87	0.0120

over CaO prior to its fractional distillation in a 150 cm long packed column. 1-Butanol was fractionally distilled in a 100 cm long packed column. All higher 1-alkanols were purified by fractional distillation at a reduced pressure of approximately 70 Pa in a 110 cm long packed column with a heated outer housing. After distillation compounds were stored over molecular sieves (Merck) with a pore diameter of 0.4 nm for a minimum of 4 days.

Purity of compounds was determined using a Hewlett Packard 6890 series gas chromatograph using a Hewlett Packard Innovax 30 m long column and a flame ionisation detector. Water content was determined by a Fischer titration. The final purity is given in Table 1.

2.2. Heat capacity measurement

Heat capacity was measured using a C-80 heat conduction calorimeter by SETARAM (France). Special flow cells shown in Fig. 1 made by Top Industrie (France) were employed. The cells of inner volume of 8 cm^3 are made of Hastelloy and have a working range from ambient temperature and pressure up to 573 K and 40 MPa.

The cells were connected by stainless steel capillaries having an inner diameter of 1 mm to a pressure control assembly (see Fig. 2). The assembly consisted of an HPLC 4000 pump (Ecom, Czech Republic), a back pressure regulator (Circle Seals Controlers, USA), and a buffer volume (Whitey, USA) of 500 cm^3 filled with nitrogen which served to reduce pressure pulses generated by the HPLC pump. Pressure in the system was measured by a Druck DPI 280 manometer (Druck, UK) with a precision of 0.02 MPa. We concluded that pressure recording during the experiment was unnecessary as the maximum pressure change in one experimental run was below 0.1 MPa. This pressure change is negligible compared to the pressure dependence of the heat capacity of measured compounds. Contamination of a measured compound by pressurising liquid water is prevented by using a 12 m long capillary between the measuring cell and the HPLC pump. In addition, experiments were usually conducted in a temperature rising mode, i.e. the measured compound was expanding from the cell. To reduce heat losses through metal capillaries leading

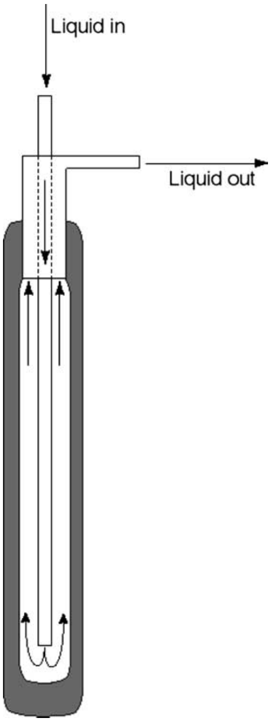

Fig. 1. Flow cell.

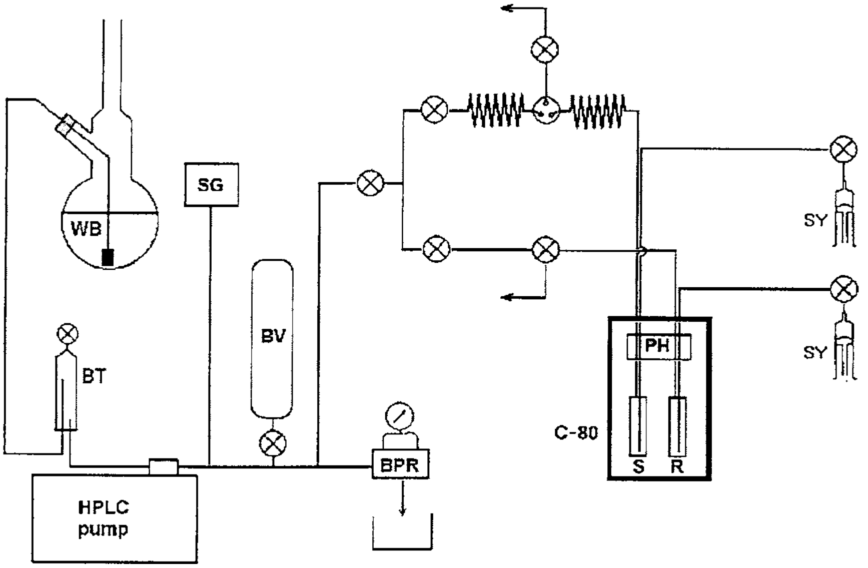

Fig. 2. Heat capacity measurement assembly (WB: boiler with distilled and demineralised water; BT: bubble trap; SG: strain pressure gauge; BV: buffer volume; BPR: back-pressure regulator; C-80: SETARAM C-80 calorimeter; S: measuring cell; R: reference cell; PH: preheater; SY: syringes).

to and from the cells, a preheater was installed just above the upper lid of each cell.

An experimental assembly with similar features like that used in this work was recently described by Bessieres et al. [12]. It is based on a C-80 SETARAM calorimeter and can be used over the temperature range from 303 to 473 K and at pressures up to 100 MPa. Bessieres et al. [13] also reported isobaric and isochoric heat capacities of liquid *n*-tridecane from 313 to 373 K and at pressures up to 100 MPa. A measurement of the isobaric heat capacities of *n*-alkanes C_8 to C_{10} and C_{16} at temperatures from 318 to 373 K and at pressures up to 10 MPa was reported by Banipal et al. [14] using a C-80 SETARAM calorimeter.

A method of temperature increments [15] was adopted in this work with a temperature rise or drop of 5–10 K (using water in the reference cell) or of 3–6 K (using air in the reference cell) and a temperature change of 0.2 K min^{-1}. Smaller steps in temperature were used at lower and upper temperature limits of measurement where a smaller reproducibility was anticipated. Two negative steps in temperature were used after reaching 573 K to detect a possible decomposition of a measured compound.

Heat capacity measurement followed the method proposed by Coxam et al. [16] and entailed three steps, (1) measurement with a compound under investigation, (2) measurement with a calorimetric standard, and (3) measurement where both the reference and the measuring cell contained the same compound (a blank experiment). In all experiments carried out at a pressure of 2, 10 and 30 MPa, the reference cell was filled with demineralised water from Milli-Q_{RG} unit (Millipore, France). After several test experiments with *n*-heptane, aqueous solution of NaCl and nitrogen, we concluded that nitrogen (which can be replaced by air within the measurement error) was the most suitable calorimetric standard for our experiments. Heat capacity of a sample $c_{p,\mathrm{s}}$ at temperature T_{avg} was then calculated from the equation:

$$c_{p,\mathrm{s}} = \left[\frac{q_{\mathrm{sw}} - q_{\mathrm{ww}}}{q_{\mathrm{Aw}} - q_{\mathrm{ww}}}(\rho_{\mathrm{A}} c_{p,\mathrm{A}} - \rho_{\mathrm{w}} c_{p,\mathrm{w}}) + \rho_{\mathrm{w}} c_{p,\mathrm{w}}\right]\frac{1}{\rho_{\mathrm{s}}}, \qquad (7)$$

where $T_{\mathrm{avg}} = (T_1 + T_1)/2$, T_1 and T_2 are the lower and upper limit of temperature increment in a given experimental run, ρ_{w}, ρ_{A} and ρ_{s} are densities of water, of air and of a sample, respectively, $c_{p,\mathrm{w}}$ and $c_{p,\mathrm{A}}$ are heat capacities of water and of air, q is the heat flow detected by the C-80 calorimeter related to a 1 K temperature change. Subscripts denote compounds in the reference and measuring cell (w, water, s, sample, A, air).

To improve the sensitivity of the calorimeter and consequently to improve the reliability of the saturated liquid heat capacity data, additional measurements were carried out in a slightly modified experimental arrangement. The reference cell was filled with air and demineralised water was used as a calorimetric standard. In this case, the heat capacity of a sample $c_{p,\mathrm{s}}$ at temperature T_{avg} was calculated from the equation:

$$c_{p,\mathrm{s}} = \left[\frac{q_{\mathrm{sA}} - q_{\mathrm{AA}}}{q_{\mathrm{wA}} - q_{\mathrm{AA}}}(\rho_{\mathrm{w}} c_{p,\mathrm{w}} - \rho_{\mathrm{A}} c_{p,\mathrm{A}}) + \rho_{\mathrm{A}} c_{p,\mathrm{A}}\right]\frac{1}{\rho_{\mathrm{s}}} \tag{8}$$

Due to a large difference in heat capacity of the measured compound and that of air the temperature rise or drop had to be reduced to 3–6 K, otherwise a heat overflow of the thermopile signal in the C-80 calorimeter was detected and heat capacity could not be calculated for such experimental run.

2.3. Density measurement

The liquid density as a function of temperature and of pressure is needed for calculating heat capacity from results of measurement when employing the method by Coxam et al. [16]. A critical evaluation of liquid densities of 1-alkanols published in literature up to 1994 is given in the paper by Cibulka and Ziková [17]. After 1994, only one new measurement was published by Randzio et al. [11].

We measured densities for 1-hexanol, 1-heptanol, 1-octanol, and 1-decanol at pressures from 2 to 30 MPa and at temperatures from 373 K (from 298 K for 1-hexanol) to 573 K using a vibration tube densimeter described by Hynek et al. [18].

To calculate the density of a compressed liquid, the Tait equation was used:

$$\tilde{n}(T,p,\vec{c},\vec{b}) = \frac{\tilde{n}(T,p_{\mathrm{ref}}(T))}{1 - C(T,\vec{c})\ln\{[B(T,\vec{b}) + p]/[B(T,\vec{b}) + p_{\mathrm{ref}}(T)]\}} \tag{9}$$

where

$$C(T,\vec{c}) = \sum_{i=0}^{N_{\mathrm{c}}} c_i \left(\frac{T - T_0}{100}\right)^i \tag{10}$$

$$B(T,\vec{b}) = \sum_{i=0}^{N_{\mathrm{b}}} b_i \left(\frac{T - T_0}{100}\right)^i \tag{11}$$

where $\vec{c} = \{c_0, \ldots, c_{N_{\mathrm{c}}}\}$, $\vec{b} = \{b_0, \ldots, b_{N_{\mathrm{b}}}\}$ are adjustable parameters, T_0 is a parameter, for which it holds that: $C(T_0) = c_0$ and $B(T_0) = b_0$, $p_{\mathrm{ref}}(T)$ is a reference pressure which is equal to 101.325 kPa below and at the normal boiling point of the compound. Above the normal boiling point, $p_{\mathrm{ref}}(T)$ equals the vapour pressure of the compound. The density of the saturated liquid $\rho(T, p_{\mathrm{ref}}(T))$ is expressed from a suitable correlating equation. In this work, we used the Martin equation:

$$\rho(T, p_{\mathrm{ref}}(T)) = \rho_{\mathrm{C}}\left[1 + \sum_{i=1}^{m} A_i (1 - T_{\mathrm{r}})^{1/3}\right], \tag{12}$$

where ρ_{C} is the critical density, T_{r} is the reduced temperature ($T_{\mathrm{r}} = T/T_{\mathrm{C}}$), and A_i are adjustable parameters, usually $3 \le m \le 11$.

Densities of ethanol, 1-propanol and 1-butanol required for the conversion of heat capacities obtained in this work were taken from the paper by Cibulka and Ziková [17].

3. Results

3.1. Density

Raw experimental data (density as a function of temperature and pressure) are given in a table in a MSc thesis [19] and will be published elsewhere. To test the reliability of our data, we also measured the density of *n*-heptane at 373 K and at pressures of 2, 10, and 30 MPa and compared it with critically evaluated data [20]. Our results deviate from the recommended data by approximately 0.05, −0.4, and −1.0% at pressures of 2, 10, and 30 MPa, respectively. The results of experiments are summarised as parameters of the Eq. (9) in Table 2.

3.2. Heat capacity

Heat capacities were calculated from experimental data using Eq. (7) or (8) and the following literature

Table 2
Parameters of the Tait Eq. (9)

	1-Hexanol	1-Heptanol	1-Octanol	1-Decanol
c_0	0.093145	0.094682	0.090335	0.282077
c_1 (K^{-1})	0	0	0	0
b_0 (MPa)	97.3209	129.8789	103.2910	421.6762
b_1 (MPa K^{-1})	−63.1718	−57.6622	−62.7866	−234.3998
b_2 (MPa K^{-2})	25.4454	3.8699	9.8784	56.5955
b_3 (MPa K^{-3})	−11.8356	0.5219	0	−6.3614
b_4 (MPa K^{-4})	2.2618	0	0	0
T_0 (K)	323.150	273.150	323.150	298.150
T_{min} (K)	298.150	323.150	298.150	298.150
T_{max} (K)	573.106	573.108	573.107	573.108
p_{min} (MPa)	0.150	1.000	0.150	1.000
p_{max} (MPa)	40.020	30.280	200.000	40.200
Absolute deviation (kg m^{-3})	0.87774	0.26028	0.25415	0.39757
Relative deviation (%)	0.131	0.034	0.037	0.054
Data used for correlation	This work and [11,27,28]	This work and [27]	This work and [27–29]	This work and [28]

Table 3
Experimental isobaric heat capacities C_p of 1-alkanols[a]

T (K)	1-Hexanol (C_p)			1-Heptanol (C_p)			1-Octanol (C_p)			1-Decanol (C_p)		
	2[b]	10[b]	30[b]	2[b]	10[b]	30[b]	2[b]	10[b]	30[b]	2[b]	10[b]	30[b]
325.7	266	266	263	301	300	297	341	338	331	405	405	400
330.7	272	271	268	306	306	302	346	342	337	411	411	406
340.7	282	281	277	318	317	312	357	353	349	424	424	418
350.7	292	291	287	329	328	322	368	364	360	437	435	431
360.7	302	299	295	339	338	332	378	374	370	448	446	442
370.7	310	308	303	348	346	340	388	384	379	459	457	452
380.7	318	315	310	356	354	348	396	392	387	468	465	460
390.7	325	321	316	363	360	354	403	399	393	475	472	467
400.7	330	326	321	368	365	359	408	404	399	480	478	472
410.7	334	329	325	372	369	363	412	409	403	484	482	476
420.7	338	332	328	375	372	366	416	411	406	487	485	479
430.7	340	334	330	376	374	368	418	414	407	488	487	480
440.7	342	336	331	378	376	369	419	415	409	489	488	481
450.7	343	336	332	378	376	370	420	416	409	489	488	481
460.7	343	337	332	379	376	370	421	416	409	488	488	481
470.7	344	337	332	379	376	370	421	416	409	488	488	481
480.7		337	331		376	369		417	408		488	480
490.7		337	331		376	369		417	408		487	480
500.7		337	331		376	369		417	408		488	480
510.7		338	330		377	369		417	408		488	481
520.7		338	330		378	369		418	408		489	481
530.7		340	330		379	369		418	409		491	482
540.7		341	329		381	369		419	410		492	483
550.7		342	329		383	370		421	411		494	485
560.7		344			385	371			411		497	486
570.7		348			388	371			412		501	488

[a] C_p is given in J K^{-1} mol^{-1}.

[b] Pressure in MPa.

sources were used to calculate the auxiliary parameters in Eq. (7) or (8). They consist of: density and heat capacity of water by equation of state from Archer [21], density of 1-alkanol from the Tait equation (see Table 2), density of saturated liquid 1-alkanol from Cibulka [22], heat capacity of nitrogen from Frenkel et al. [23], and density of nitrogen from Jacobsen et al. [24]. The smoothed values of heat capacities (obtained for 1-hexanol, 1-heptanol, 1-octanol, and 1-decanol from 134, 81, 86, and 78 raw experimental data points, respectively) are given in Table 3 and in Fig. 3. The estimated experimental uncertainty in heat capacity was 1%. The C-80 calorimeter equipped with standard batch cells was calibrated with synthetic sapphire (α-Al_2O_3), NIST standard reference material 720, as described by Roháč et al. [25]. The C-80 calorimeter equipped with special flow cells and the whole experimental

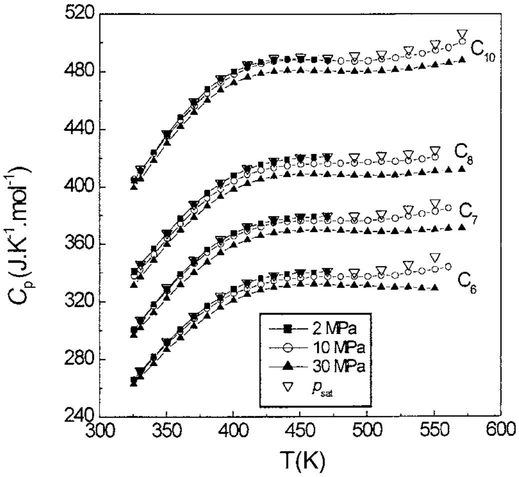

Fig. 3. Temperature dependence of isobaric heat capacity of 1-hexanol, 1-heptanol, 1-octanol, and 1-decanol at 2, 10, 30 MPa and at the saturation pressure.

Table 4
Heat capacities of 1-alkanols at a moderate pressure[a]

T (K)	C_{sat} (J K^{-1} mol^{-1})							
	Ethanol, $p = 4.9$ MPa	1-Propanol, $p = 6.4$ MPa	1-Butanol, $p = 6.4$ MPa	1-Hexanol, $p = 1.5$ MPa	1-Hexanol, $p = 3.4$ MPa	1-Heptanol, $p = 2$ MPa	1-Octanol, $p = 2$ MPa	1-Decanol, $p = 2$ MPa
325.7	124	162	198	266	267	302	337	407
330.7	127	166	203	271	272	307	342	412
340.7	132	173	212	282	282	317	353	424
350.7	138	180	220	292	292	328	364	436
360.7	143	187	228	302	301	338	374	447
370.7	150	193	236	311	309	347	383	457
380.7	156	199	242	319	317	355	392	466
390.7	162	204	248	325	323	362	399	473
400.7	168	208	253	330	329	367	404	479
410.7	173	212	257	334	333	371	409	483
420.7	178	216	261	337	336	374	412	486
430.7	184	218	264	339	338	376	415	488
440.7	190	221	266	340	340	377	416	489
450.7	198	223	268	341	340	378	417	489
460.7	207	226	269	342	341	379	418	489
470.7	219	228	271	342	341	379	418	489
480.7		231	272	343	341	380	419	489
490.7		234	274	344	342	380	420	489
500.7		239	277		344	381	421	490
510.7			280		347	383	423	491
520.7			285		349	383	423	491
530.7					353	385	426	493
540.7					359	389	429	495
550.7					365	396	433	497
560.7					372	407	437	498
570.7					379	424	441	500

[a] Heat capacities presented are equal to saturation heat capacities within the experimental error of the measurement.

assembly was tested by measuring the heat capacity of aqueous solutions of NaCl (5 and 6 kg mol^{-1}). The results obtained agreed with the data from Archer [21] within 0.5%.

Saturation heat capacities determined by extrapolation from measured heat capacities at several elevated pressures are given in Fig. 3. For extrapolation, a linear dependence of heat capacity on pressure was assumed. The extrapolation resulted in reliable saturation heat capacities at temperatures below 473 K, where values at three pressures were available. When extrapolating over a wide pressure range using only values determined at 10 and 30 MPa, temperature dependence of the saturation heat capacity exhibited a minimum at a temperature immediately following that obtained by extrapolation of values determined at three different pressures.

To obtain more reliable saturation heat capacities, in particular at temperatures above 473 K, additional experiments were carried out at one or two pressures above the saturation pressure of the compound. It was assumed the pressure dependence of heat capacity is negligible compared to the error of measurement in the range between the saturation pressure and pressure of measurement. In these experiments, the reference cell was filled with air and water was used as a calorimetric standard. Smoothed heat capacity values from these measurements (obtained for 1-hexanol, 1-heptanol, 1-octanol, and 1-decanol from 134, 81, 86, and 78 raw experimental data points, respectively) are given in Table 4.

4. Discussion

Saturation heat capacities of 1-alkanols from ethanol to 1-decanol, with the exception of 1-pentanol and 1-nonanol, determined in this work considerably extend the temperature range of available data towards the critical point. A family plot of saturation heat capacities as a function of temperature for the homologous series of 1-alkanols (Fig. 4) clearly shows the presence of an inflexion point for all 1-alkanols starting with 1-propanol. The plot also demonstrates that the data in the family are consistent within the error of measurement as each subsequent member of the series differs from the previous one by an almost constant increment attributed to the contribution of a CH_2 group.

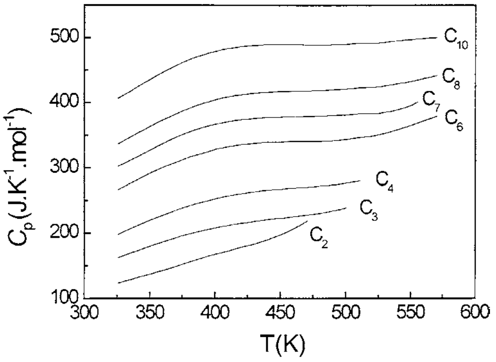

Fig. 4. Temperature dependence of saturation heat capacities of 1-alkanols.

A comparison of saturation heat capacities obtained in this work with critically assessed literature data from the compilation by Zábranský et al. [2] is given in Fig. 5. Also shown in the figures are so far unpublished data from our laboratory [26] obtained with a C-80 SETARAM calorimeter using batch cells and the stepwise measurement method [25]. The recommended data from the compilation by Zábranský et al. [2] systematically deviate from the present data at temperatures above about 400–450 K, depending on the compound. This may be attributed to the fact that above about 400 K, the recommended data were developed by using the data by Grigor'ev et al. [3]

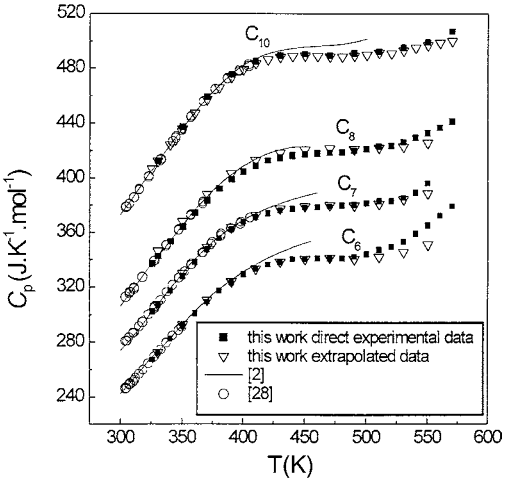

Fig. 5. Comparison of saturation heat capacities for 1-hexanol, 1-heptanol, 1-octanol, and 1-decanol.

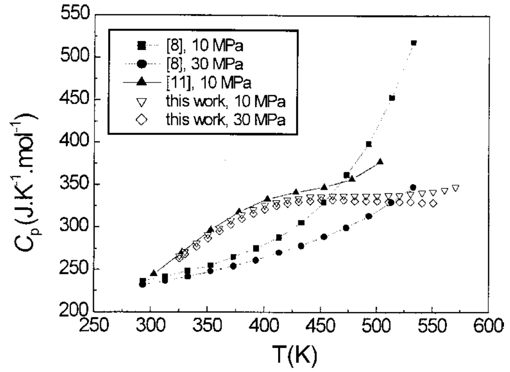

Fig. 6. Comparison of heat capacities of 1-hexanol at pressures of 10 and 30 MPa with literature data.

and/or by Vasil'ev et al. [4] which were shown by Zábranský et al. [2,6] to be generally less reliable than data from other laboratories.

A comparison of heat capacities at elevated pressures determined in this work with the data from literature shows unsatisfactory agreement.

For 1-hexanol there are direct experimental data by Arutyunyan [8] and indirect data by Randzio et al. [11]. The agreement is satisfactory with the latter data, but only for temperatures up to 460 K (see Fig. 6). This may be attributed to the fact that Randzio et al. [11] added the difference $c_p(p = 10\ \text{MPa}) - c_p(p_{\text{sat}})$ obtained by measuring isobaric expansivity to $c_p(p_{\text{sat}})$ taken from Zábranský et al. [6]. However, $c_p(p_{\text{sat}})$ is an extrapolated value calculated from a quasi-polynomial equation which may be subject to a large uncertainty.

A comparison for 1-heptanol and 1-decanol is shown in Figs. 7 and 8. The data by Naziev and Bashirov [10] deviate from the data obtained in this work substantially at temperatures above about 450 K, whereas the data by Arutyunyan and Movsesyan [9] (available for 1-heptanol only) deviate from this work data over the whole range. We found no heat capacity data for 1-octanol at elevated pressures in the literature.

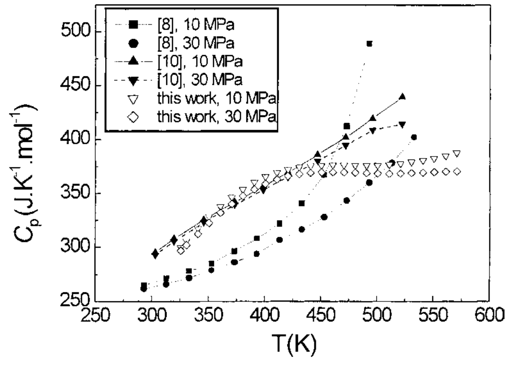

Fig. 7. Comparison of heat capacities of 1-heptanol at pressures of 10 and 30 MPa with literature data.

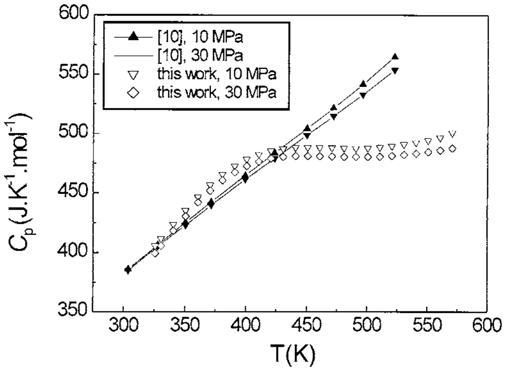

Fig. 8. Comparison of heat capacities of 1-decanol at pressures of 10 and 30 MPa with literature data.

5. Conclusions

A method of heat capacity measurement of pure liquids using a C-80 heat conduction calorimeter equipped with special flow cells was described for measurements at temperatures up to 570 K and at pressures up to 30 MPa. Heat capacities for 1-hexanol, 1-heptanol, 1-octanol, and 1-decanol determined in the range from 325 to 570 K and at pressures of 2, 10, and 30 MPa exhibited a dependence with temperature similar to that for saturation heat capacities. Other direct experimental data at elevated pressures published in the literature are obviously suspect. The data by Arutyunyan [8] increased with temperature exponentially and tended to approach an infinite value of heat capacity at temperatures far below the critical temperature. The data by Naziev and Bashirov [10] increased almost linearly with temperature over an extended temperature range. Such dependence of the heat capacity on temperature was not observed for other compounds [7].

Saturation heat capacities determined in this work for all 1-alkanols from C_2 to C_{10} with the exception of C_5 and C_9 extended the range of data so far available in the literature. An untypical dependence of the saturation heat capacity of 1-alkanols was found which was not observed for other compounds.

Densities of 1-alkanols obtained in this work and covering the range 373–573 K and 2–30 MPa extended the range of data available in the literature. New data also lead to improvement of the reliability of the available density data as corroborated by their critical evaluation.

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