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Heat capacities of liquid long-chain alkanes

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Abstract

Liquid heat capacities of *n*-octadecane, *n*-nonadecane, *n*-docosane, *n*-octacosane, *n*-triacontane, *n*-hexatriacontane and *n*-pentacontane in the temperature range 373–473 K and of squalane and 2, 6, 10, 14-tetramethylpentadecane, in the temperature range 303–403 K have been measured by DSC. Experimental results were used to verify the applicability of the Benson group contribution method to heavy *n*- and *iso*-alkanes.

Keywords: Benson group contribution method; DSC; Liquid heat capacities; Long-chain alkanes

List of symbols

C_p^0, C_p^1	parameters for representing liquid heat capacities (Eq. (1)).
C_p	heat capacity ($\text{J mol}^{-1} \text{K}^{-1}$).
$(C_p)_{\text{CH}_2}$	heat capacity of the CH_2 group
$(C_p)_{\text{CH}_3}$	heat capacity of the CH_3 group
N_{CH_2}	number of CH_2 groups
R	gas constant
T	temperature (K)
$T_{\text{min}}, T_{\text{max}}$	start and end of the temperature range (K)
TMPD	tetramethylpentadecane.

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1. Introduction

The heat capacities of liquid alkanes at 298.15 K can be estimated reasonably accurately by using a group contribution method proposed by Benson and Buss [1] and extended by Luria and Benson [2]. However, a data base used by these authors consisted principally of low and medium molecular weight compounds. The heavy petroleum fractions contain high concentrations of long-chain alkanes for which relatively few accurate chemical thermodynamic properties have been determined. Experimental heat capacities are known in the large temperature interval up to *n*-octadecane. A comprehensive compilation of existing experimental data was published by Domalski and Hearing [3] and by Ruzicka et al. [4].

In this paper, we have considered liquid heat capacities of the following *n*-alkanes: *n*-octadecane, *n*-nonadecane, *n*-docosane, *n*-octacosane, *n*-triacontane, *n*-hexatriacontane, and *n*-pentacontane in the temperature range 373–473 K. The heat capacities of squalane and 2, 6, 10, 14-tetramethylpentadecane were determined in the temperature range 303–403 K. New experimental data make it possible to check the applicability of the Benson group contribution method to long chain *n*- and *iso*-alkanes.

2. Experimental

A list of the selected compounds together with the corresponding purities (as declared by the suppliers) is presented in Table 1.

Measurements were performed using a DSC 111 differential scanning calorimeter from Setaram. This apparatus was calibrated with alumina using a temperature interval of 2 K. The sensitivity polynomial was determined for two temperature ranges: between 293 and 573 K and between 543 and 803 K.

To verify the accuracy of our experiment, heat capacities of *n*-octadecane were measured between 310 and 385 K and the results obtained were compared with experimental data reported by Messerly et al. [5]. This comparison is illustrated by Fig. 1. Two remarks may be made. Firstly, there is a systematic deviation of about 4%

Table 1

List of the components studied with their structural formulae, origin and purity

Component	Formula	Source	Purity/%
<i>n</i> -Octadecane	CH ₃ -(CH ₂) ₁₆ -CH ₃	Fluka	99
<i>n</i> -Nonadecane	CH ₃ -(CH ₂) ₁₇ -CH ₃	Aldrich	99
<i>n</i> -Docosane	CH ₃ -(CH ₂) ₂₀ -CH ₃	Fluka	> 98
<i>n</i> -Octacosane	CH ₃ -(CH ₂) ₂₆ -CH ₃	Aldrich	99
<i>n</i> -Triacontane	CH ₃ -(CH ₂) ₂₈ -CH ₃	Fluka	> 99
<i>n</i> -Hexatriacontane	CH ₃ -(CH ₂) ₃₄ -CH ₃	Fluka	> 98
<i>n</i> -Pentacontane	CH ₃ -(CH ₂) ₄₈ -CH ₃	Fluka	> 98
2, 6, 10, 14-TMPD	CH ₃ (CH ₂ CH(CH ₂) ₃) ₃ CH(CH ₃) ₂	Aldrich	98
Squalane	[(CH ₃) ₂ CH(CH ₂) ₃ CH(CH ₃)(CH ₂) ₃ CH(CH ₃)CH ₂ CH ₂] ₂	Aldrich	99

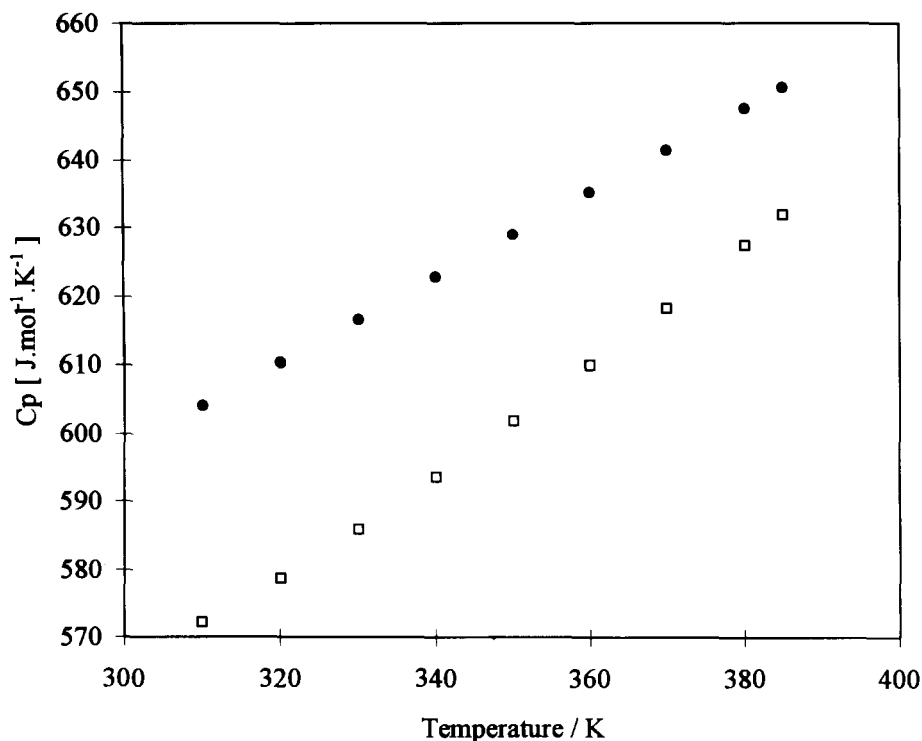


Fig. 1. Heat capacities of *n*-octadecane. Comparison between the present experimental results (●) and Messerly et al. [5] data (□).

between the two sets of data. Secondly, the present results show linear dependence on temperature. Messerly's data do not change linearly with temperature, especially in the low-temperature range. Heat capacity values yielded by our DSC calorimeter are of lower accuracy than Messerly's data obtained using an adiabatic calorimeter.

The objective of this paper is to determine heat capacities of the homologous series of *n*-alkanes in the large temperature interval and to correlate them in terms of the group contribution approach. For this purpose, the announced accuracy may be sufficient, especially in the high temperature range where the temperature-dependence of heat capacities is nearly linear.

3. Results

Heat capacities were measured in a 100 K temperature range, therefore, one set of experimental data contains 50 determinations of C_p . For all compounds studied, a linear dependence of C_p on temperature was observed, the scatter being much smaller than the estimated experimental error. For this reason, experimental results are

presented as the parameters of the following equation:

$$C_p = C_p^0 + C_p^1 T \quad (1)$$

Values of parameters C_p^0 and C_p^1 and the corresponding temperature ranges are reported in Table 2.

3.1. Group contribution approach

3.1.1. Heat capacities at $T = 298.15$ K

3.1.1.1. *n*-Alkanes. Domalski and Hearing [3] compared experimental values of *n*-alkane heat capacities at 298.15 K with estimates calculated according to the Benson method. Small deviations obtained up to *n*-tetradecane increase slightly with heavier hydrocarbons. This comparison was performed up to *n*-heptadecane. For this last compound the observed deviation was of $5 \text{ J mol}^{-1} \text{ K}^{-1}$.

It is interesting to verify Benson's method for higher *n*-alkanes. In this case, heat capacities of supercooled hydrocarbons will be concerned. Our experimental data were obtained at temperatures higher than 373 K. To obtain a direct comparison with Benson's method an extrapolation was performed using Eq. (1) with parameters given in Table 2. Resulting values of heat capacities at 298.15 K are given in Table 3 and plotted in Fig. 2 as a function of the number of CH_2 groups. Linear regression yields the following relationship:

$$(C_p)_{\text{C}_n\text{H}_{2n+2}} = 71.39 + 31.31 N_{\text{CH}_2} (T = 298.15 \text{ K}) \quad (2)$$

The slope of the straight line in Fig. 2 gives directly the contribution of the CH_2 group; this was found to be $31.31 \text{ J mol}^{-1} \text{ K}^{-1}$. This value should be compared with $30.42 \text{ J mol}^{-1} \text{ K}^{-1}$ as given by Domalski and Hearing [3]. The CH_3 contribution found with Eq. (2) is $35.70 \text{ J mol}^{-1} \text{ K}^{-1}$ rather than $36.48 \text{ J mol}^{-1} \text{ K}^{-1}$ as found by Domalski and Hearing [3]. All results are summarized in Table 3. It is interesting to observe that deviations between C_p calculated using Domalski and Hearing parameters and those resulting from Eq. (2) are of about 2% for all the compounds studied.

Table 2
Parameters of Eq. (1) and their validity range

Component	C_p^0	C_p^1	$T_{\min} \leftrightarrow T_{\max}/\text{K}$
2, 6, 10, 14-TMPD	349.49	0.7836	303–403
Squalane	839.24	0.2161	303–403
<i>n</i> -Octadecane	411.79	0.6205	373–473
<i>n</i> -Nonadecane	581.91	0.2815	373–473
<i>n</i> -Docosane	183.90	1.6035	373–473
<i>n</i> -Octacosane	308.31	1.6908	373–473
<i>n</i> -Triacontane	644.31	0.9798	373–473
<i>n</i> -Hexatriacontane	821.53	1.0960	373–473
<i>n</i> -Pentacontane	1038.10	1.8837	373–473

Table 3
Extrapolated heat capacity ($\text{J mol}^{-1} \text{K}^{-1}$) at 298.15 K

Component	Domalski and Hearing [3] (a)	Results obtained by			
		Extrapolation (b)	(a)–(b)	Eq. (2) (c)	(a)–(c)
<i>n</i> -Octadecane	559	597	–38	572	–13
<i>n</i> -Nonadecane	590	658	–67	604	–14
<i>n</i> -Docosane	681	662	19	698	–17
<i>n</i> -Octacosane	864	812	52	855	9
<i>n</i> -Triacontane	925	936	–12	948	–23
<i>n</i> -Hexatriacontane	1107	1148	–41	1136	–29
<i>n</i> -Pentacontane	1533	1600	–67	1574	–41
Squalane	907	904	3	–	–
2, 6, 10, 14-TMPD	578	583	–5	–	–

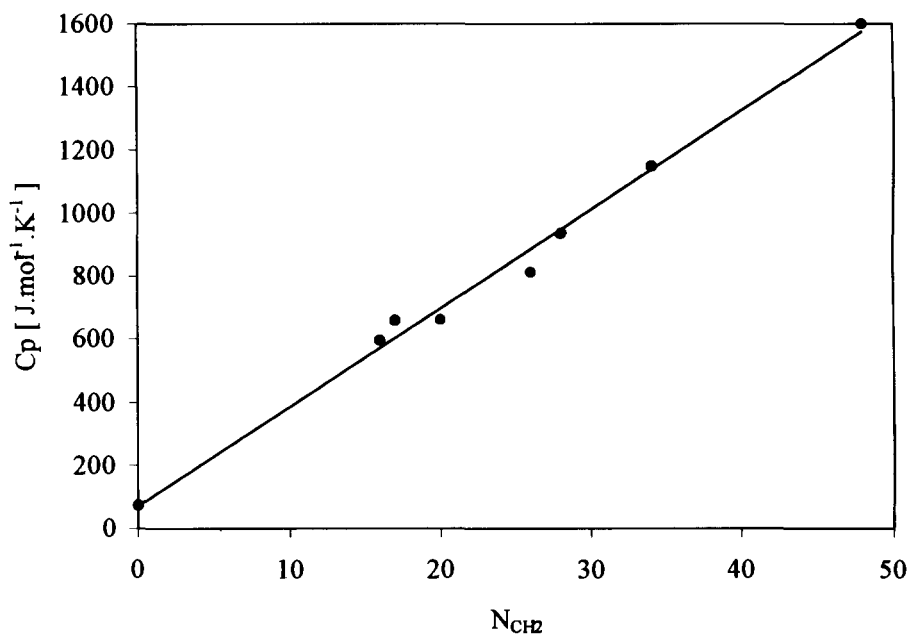


Fig. 2. Heat capacities of *n*-alkanes, at 298.15 K, versus number of CH_2 groups, N_{CH_2} .

Therefore, the observed agreement is satisfactory and confirms the possibility of using Benson's method for higher *n*-alkanes.

3.1.1.2. *iso*-Alkanes. The two *iso*-alkanes studied are liquids at ambient temperature. Therefore, measurements were performed between 303 and 403 K. As previously,

results are presented in Table 1 with parameters of the linear equation, Eq. (1). In this case, the extrapolation towards $T = 298.15$ K was more reliable. In Table 3 the results obtained are compared with Benson's estimates calculated using Domalski's parameters. The agreement observed in this case, is surprisingly good and cannot be significant in view of the estimated accuracy of the data. Nevertheless, it confirms the validity of Benson's method for heavy *iso*-alkanes.

3.1.2. Heat capacities as a function of temperature

Luria and Benson [2] proposed a temperature-dependent version of the Benson method in which the temperature-dependence of group contributions was expressed using cubic polynomials. The contribution of the CH_2 group, calculated according to the expression proposed by Luria and Benson [2]:

$$(C_p)_{\text{CH}_2} = -1.383 + 7.049 \times 10^{-2} T - 2.063 \times 10^{-4} T^2 + 2.269 \times 10^{-7} T^3 \quad (3)$$

is plotted in function of temperature in Fig. 3. It must be mentioned that according to the authors, Eq. (3) is valid for temperatures $90 < T < 380$ K. The dotted line in the same figure, was calculated according to the present results, in exactly the same way, as described for $(C_p)_{\text{CH}_2}$ at 298.15 K. The relationship obtained is linear and

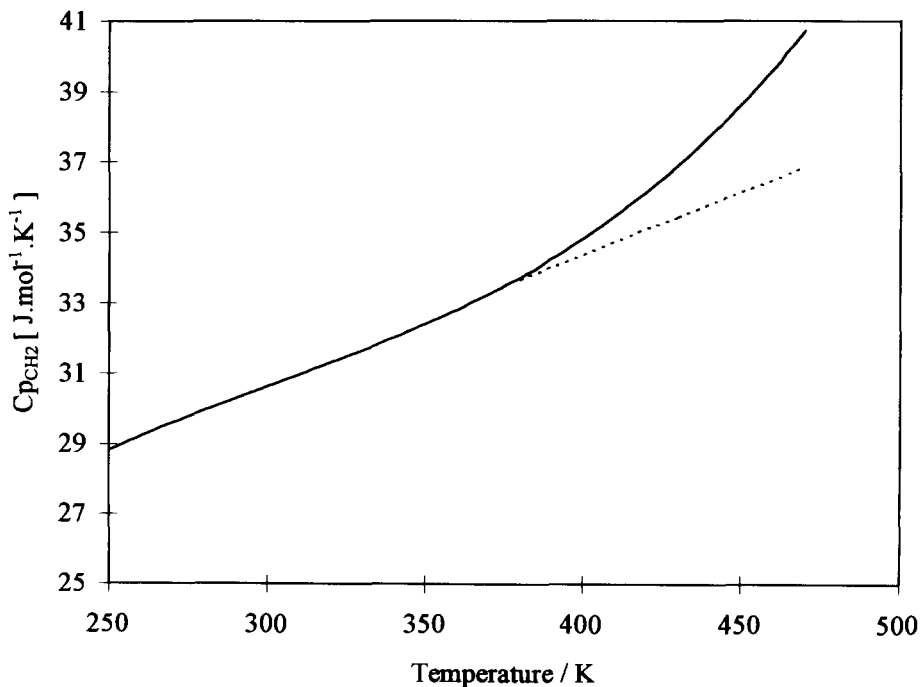


Fig. 3. Heat capacity of the CH_2 group, versus temperature. — Luria and Benson [2], present results.

is given by:

$$(C_p)_{\text{CH}_2} = 0.0354 T + 20.21 \quad (4)$$

As is apparent from Fig. 3, both expressions give very similar results up to 400 K which corresponds to the validity limit of the Luria and Benson method. Deviations increasing sharply with temperature are observed at higher temperatures.

The Luria and Benson method was essentially based on low molecular weight heat capacity data. In the high temperature range, therefore, an equation of state contribution to C_p had to be taken into account. In the case of higher alkanes, this contribution is still negligible. This partly explains the high temperature divergence between Eqs. (3) and (4). Moreover, extrapolating a polynomial is always hazardous. It may be observed that $(C_p)_{\text{CH}_2}$, for $T > 400$ K, can be obtained by a linear extrapolation of the low-temperature part of the Luria–Benson curve.

These experimental results do not enable analysis of the $(C_p)_{\text{CH}_3}$ pattern as a function of temperature. It can, however, be assumed that the same extrapolation procedure used for the low temperature part of the Luria and Benson curve can be used, as in the case of $(C_p)_{\text{CH}_2}$. The resulting expression is as follows:

$$(C_p)_{\text{CH}_3} = 0.1205 T - 1.4721 \quad (5)$$

and represents the Luria and Benson polynomial for $(C_p)_{\text{CH}_3}$ for $340 < T < 380$ K to within 0.15%.

Thus, heat capacities of heavy *n*-alkanes at temperatures lower than 380 K should be calculated using the Luria and Benson method. For higher temperatures, Eqs. (4) and (5) may be used.

4. Conclusion

Global treatment of the present heat capacity data in terms of group contributions made it possible to test the validity of Benson's method for heavy alkanes. Good agreement between experimental and predicted data was obtained both for *n*-alkanes and *iso*-alkanes. Experimental heat capacities at temperatures higher than 298.15 K, were compared with those derived using Luria and Benson's method, i.e. the use of polynomials to represent temperature changes of group contributions. This approach is strictly limited to the temperature validity range announced by the authors. Analysis of our experimental results suggests the possibility of linear extrapolation of the Luria and Benson polynomials to high temperatures. This method was verified for *n*-alkanes only. In fact, extrapolation of the highly non-linear contribution of CH or C groups seems impossible.

References

- [1] S.W. Benson and J.H. Buss, *J. Chem. Phys.*, 29 (1958) 546.
- [2] M. Luria and W. Benson, Heat capacities of liquid hydrocarbons. Estimation of heat capacities at constant pressure as a temperature function, using additivity rules, *J. Chem. Eng. Data*, 22 (1977) 90.

- [3] E.S. Domalski and E.D. Hearing, Estimation of the thermodynamic properties of hydrocarbons, *J. Phys. Chem. Ref. Data*, 17 (1988) 1637.
- [4] V. Ruzicka Jr., M. Zabransky and V. Majer, Heat capacities of organic compounds in the liquid state. II. C₁ to C₁₈ *n*-alkanes, *J. Phys. Chem. Ref. Data*, 20(1991) 405.
- [5] H.L. Finke, J.F. Messerly, S.H. Lee, A.G. Osborn and D.R. Douslin, Comprehensive thermodynamic studies of seven aromatic hydrocarbons, *J. Chem. Thermodyn.*, 9 (1977) 937.