



Thermochemical parameters of formation and vaporisation of alkanethiols: From experiment to prediction

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ABSTRACT

Alkanethiols are an important class of organic compounds and are used in materials science. In some cases, the production of materials based on alkanethiols requires knowledge of reliable values for vapour pressures and thermochemical parameters of phase transitions. Reliable enthalpies of vaporisation and enthalpies of formation in the condensed state are also required in order to obtain the enthalpy of formation in the gas phase. The experimental determination of enthalpies of formation in condensed state for sulfur-containing compounds is a challenging experimental task. The development of accurate predictive approaches is therefore a relevant task. In the present study, the available saturation vapour pressures at different temperatures and enthalpies of vaporisation of the alkanethiols were critically reviewed. In addition, the solution calorimetry method was developed and used to determine the enthalpy of vaporisation of alkanethiols. These data were also used to determine reliable experimental enthalpies of formation in the gas phase. Reliable experimental enthalpies of formation were then used to find the most accurate functional and basis set for estimation of the unknown enthalpy of formation in the gas phase using quantum chemical methods. In summary, the most consistent functional and basis set for calculating the enthalpies of formation of alkanethiols and the enthalpies of vaporisation obtained by solution calorimetry approach were used to estimate the enthalpies of formation of alkanethiols in the condensed state.

1. Introduction

Alkanethiols, also known as mercaptans, are sulfur-containing hydrocarbons characterized by their pungent odour. Many alkanethiols emit such a strong scent that the human nose can detect even trace amounts [1]. Skunk spray, for example, contains low molecular weight alkanethiols that serve as a defense mechanism against predators [2,3]. Due to their strong unpleasant odor, thiols are used to add to natural gas to detect leaks by odor. Also, alkanethiols can be used as a container of a malodorous warning liquid for malfunctioning mine ventilation [4]. The concept of odor value can be applied to develop effective the malodorous composition of matter [5,6]. This approach allows for the calculation of odor intensity and the necessary alkanethiol concentration in composition based on the thermochemical parameters of phase transitions, such as vapor pressure and activity coefficients in solution.

Another significant application of alkanethiols is in the production of self-assembled monolayers (SAMs). Thin-film SAMs are extensively used in fields such as biology, medicine, electrochemistry, and biosensor technology. These SAMs can be created through various methods, including physical vapor deposition techniques, electrodeposition, or electroless deposition [7]. Therefore, understanding the vapor pressures, thermochemical parameters of phase transitions of alkanethiols, and their behavior in solvents can be instrumental in developing new materials and effective aerosols.

Experimental values for the enthalpies of vaporization/sublimation and the enthalpies of formation in the condensed state are essential for determining the enthalpy of formation in the gas phase. Reliable data on gas-phase enthalpies of formation are crucial for enhancing estimation methods based on quantum chemical calculations. However, applying quantum chemical approaches to sulfur-containing compounds presents

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Table 1
Origin and purity of used compounds.

Sample	CAS No.	Source	Mass fraction purity ^a
1-pentanethiol (I)	110-66-7	TCI	0.988
1-hexanethiol (I)	111-31-9	Alfa Aesar	0.97
1-heptanethiol (I)	1639-09-4	Alfa Aesar	0.97
1-octanethiol (I)	111-88-6	Alfa Aesar	0.98
<i>n</i> -heptane (I)	142-82-5	Ekos-1	0.99

^a According to manufacturer certificate. No additional purification was applied.

several challenges, as detailed by Paulechka and Kazakov [8]. Generally, calculating the enthalpy of formation using quantum chemical methods involves several steps, each influencing the final value. The first critical task is to conduct a conformational analysis to identify the most stable conformers. The next step is to determine the total electronic energy (E_{total}) and the enthalpy of formation from the elementary substances at 298 K. Various functionals (such as BMK, CAM-B3LYP, LC-wPBE, M06, wB97, wB97x, etc.) with various basis sets can be employed for this purpose [9,10]. If adequate computational resources are available, one can screen for the functional and basis set that the best align with experimental results. Alternatively, composite methods like *G-n* (G3MP2, G4MP2, G4) are frequently used to find enthalpies of formation in the gas phase. Depending on the functional used, discrepancies in the calculated enthalpy of formation can reach up to 20 – 30 kJ·mol⁻¹.

In the present work, a comparative analysis of different approaches for the determination of the enthalpy of formation of alkanethiols was carried out in order to determine the approach that agrees with the reliable experimental enthalpies of formation the best of all. This was preceded by the challenge of obtaining a reliable experimental enthalpy of formation in the gas phase. To solve this issue, it was necessary to review the experimental values of the vapour pressure. Experimental vapour pressures at different temperatures from all available literature sources [11–49] were compared in order to determine the parameters of the relationship and the enthalpy of vaporisation. In addition, the solution calorimetry method [50–52] was developed for determination of the enthalpy of vaporisation of the alkanethiols. Then, the various functional and basis set that best matched the experimental enthalpies of formation were tested to calculate the enthalpies of formation of alkanethiols. Finally, the most accurate approach to calculate the enthalpies of formation and enthalpies of vaporisation calculated using solution calorimetry approach were used to estimate the enthalpies of formation of 1-alkanethiols in the condensed state.

2. Experimental part

2.1. Materials

The alkanethiol samples used in this work are commercially available substances with a mass fraction of the main substance of over 97 %. *n*-Heptane was selected as a solvent to study the thermal effects of the dissolution of alkanethiols by solution calorimetry method. All alkanethiols and *n*-heptane were used without further purification. Details of the chemicals used in this work are listed in Table 1.

2.2. Experimental and theoretical thermochemical methods

A method to obtain the $\Delta_f^{\circ}H_m^{\circ}$ -values is based on the high-precision solution calorimetry [53]. We used the TAM III solution calorimeter (TA Instruments, USA) to measure the solution enthalpies of 1-alkanethiols in *n*-heptane. A detailed description of the calorimetric experiment has been published in previous works [54,55]. The detailed methodology for calculating of $\Delta_f^{\circ}H_m^{\circ}$ from calorimetric results can be found elsewhere [53,56,57]. All experimental enthalpies of solution of 1-alkanethiols in *n*-heptane are listed in Table S1. The theoretical solution enthalpies at

infinite dilution, $\Delta_{soln}H^{A_i/S}$, were calculated using the following equation:

$$\frac{\ln(\gamma_{\infty}^{A_i/S})}{\ln\left(\frac{1}{7}\right)} = \frac{\Delta_{soln}H^{A_i/S}}{R} \quad (1)$$

where $\gamma_{\infty}^{A_i/S}$ is the activity coefficient of solute A_i in solvent S at infinite dilution, R is a gas constant.

The activity coefficients at infinite dilution were calculated by using Python Thermo [58]. UNIFAC (Dortmund) model [59] was implemented in the Thermo library.

The enthalpies of formation in the gas phase for 1-alkanethiols were computed using various DFT functionals: BMK, CAM-B3LYP, LC-wPBE, M06, wB97, wB97x with the triple-zeta basis set 6-311++G(3df,3pd) of spherical harmonics (5d 7f), and also by means of functionals M06 and wB97x with the quadruple-zeta basis set aug-cc-pvQZ 5d 7f in GAUSSIAN 09 software [60]. The enthalpy of formation of the most stable conformer was calculated from the atomization reaction described in detail in [61]. The experimental enthalpies of formation of atoms were taken from NIST Standard Reference Database [62].

The conformational analysis of the alkanethiols was carried out using the ADF software [63]. Linear *trans* conformers (with linear *trans* carbon chain and with *trans* position of the hydrogen atoms of the SH group) were taken as initial structures. The conformational space of each alkanethiol was generated using the RDKit [64]. The resulting structures of the individual compounds were optimized by the molecular mechanics with the UFF valence force field. After optimization for ethanethiol, 1-propanethiol, 1-butanethiol, 1-pentanethiol, 1-hexanethiol, 1-octanethiol, 1-decanethiol, the main conformers proved to be the initial linear *trans* structures. For 1-heptanethiol, 1-nonanethiol, 1-undecanethiol, 1-dodecanethiol, the UFF-optimized structure of the alkyl chain of the main conformers proved to be non-linear with the *gauche* position of the hydrogen atom of the SH group.

The selection of the most stable conformer for the compounds of the investigated homological series was carried out within the framework of the DFT. Several structures were taken for each alkanethiol. Since a "gauche effect" [65] is observed for alkanethiols, linear conformers with *gauche* hydrogen position of the SH group were added to all basic alkanethiols (optimized with UFF), as well as linear *trans* conformers to non-linear compounds (1-heptanethiol, 1-nonanethiol, 1-undecanethiol, 1-dodecanethiol). In the case of DFT computation no contribution accounting for the equilibrium mixture of the conformers was introduced. The results of the calculations are listed in Table S2.

Additionally, the $\Delta_f H_m^{\circ}$ (g) values were calculated using composite methods *G-n* (G3MP2, G4MP2, G4), *ab initio* protocol aLL5 developed by Paulechka and Kazakov [8,66], and by interpolating the available experimental $\Delta_f H_m^{\circ}$ (g, exp) values.

The results of composite methods and aLL5 protocol were corrected accounting for the equilibrium mixture of conformers in the gas phase. For this purpose, the most stable conformer settled using RDKit software was used to form the initial ensemble of conformers for each studied compounds using metadynamic approach implicated by Prof. Grimme in Conformer Rotamer Ensemble Sampling Tool (CREST) software [67] and limited to the maximal energy difference to 25 kJ·mol⁻¹. It should be noted, that the most stable geometries in both toolkits are equal except the mirroring C–C–SH dihedral angle. Further, each conformer was optimized at B3LYP/cc-PVTZ level of the theory with D3 dispersion correction and Becky-Jonson damping [68–70]. The normal vibration modes were computed at the same level of theory. The whole batch of conformers for each compound (up to 6500 conformers in the case of 1-dodecanethiol) was checked for duplicates. Due to the recommendations of the reviewer much attention was payed to the enantiomeric pair of conformers for the molecules for which one conformer has the Cs symmetry. The applied CREST technique can remove some enantiomeric conformers at the step of ensemble analysis. Therefore, any

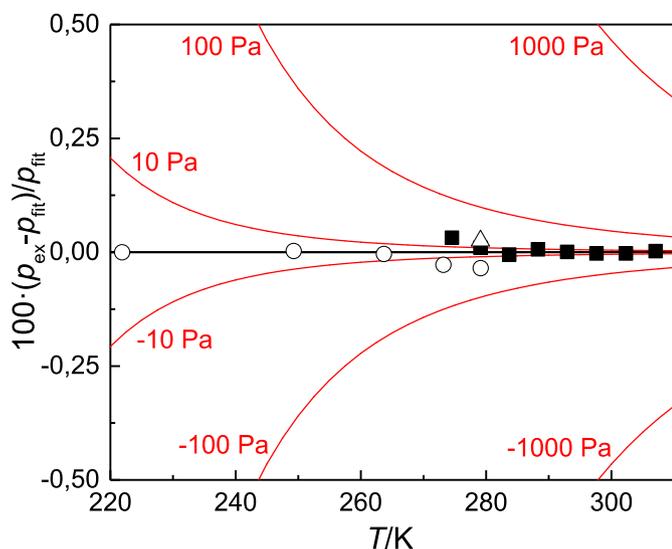


Fig. 1. Deviation plot of temperature dependencies of vapor pressure of methanethiol: o - mercury manometer by Russell et al. [15], ■ - ebullimetry by Osborn and Scott [40], Δ - boiling point at 1 atm by Morris et al. [29].

enantiomeric conformers were removed from the evaluated ensemble. At the next stage the amount of all conformers, except one with Cs symmetry, were doubled to simulate the presence of the enantiomeric pairs of conformers. The uncertainty of the applied procedure was assumed to be equal of 10 % of the applied correction. The Gibbs energy differences were applied for evaluation of the mole composition of the gas phase and the corresponding enthalpy correction for conformer mixing.

In additional the parameters of conformers used in the $\Delta_f H_m^0$ (g) values calculations were provided in Table S3-S30 as supporting information.

3. Results and discussion

3.1. Review of consistency of vapor pressure data of 1-alkanethiols

In the present work, the experimental vapor pressures of 1-alkanethiols available in the literature were collected and analyzed. The systematic studies of the temperature dependencies of the vapor pressure of 1-alkanethiols [12–15,19,20,26,28,31,32,40,46,49] are accompanied by literature values of the boiling points at various pressures, which are summarized in Table S31. Since the vapour pressures of 1-alkanethiols from different literature sources are of varying reliability, all vapour pressures were analysed using the weighting factors given in Table S32. The temperature dependence of the vapor pressure of 1-alkanethiols (from methanethiol to 1-heptanethiol) was approximated using the equation of Wagner 25 [71,72]

$$\ln\left(\frac{p_{\text{ex}}}{p_c}\right) = T_c / T (A_1 \tau + A_2 \tau^{1.5} + A_3 \tau^{2.5} + A_4 \tau^5) \quad (2)$$

where $\tau = 1 - T/T_c$ and $p^0 = 10^5$ Pa, p_{ex} and p_c - absolute and critical vapor pressures, respectively, T and T_c - critical and absolute temperature, respectively, A_n - fitting parameters were obtained with the help of the least square method. A_n , p_c and T_c parameters of Eq. (2) are listed in Tables S33 and S34, respectively. Eq. (2) can be used if precision vapour pressure measurements are available. In the case of 1-octanethiol, 1-nonanethiol and 1-decanethiol, no high-precision data were available and the temperature dependencies of the vapour pressure were fitted using the Clark and Glew equation [73]. The fitting parameters of Clarke and Glew equation are listed in Table S35.

The relative deviations of the experimental and fitted (p_{fit}) vapor

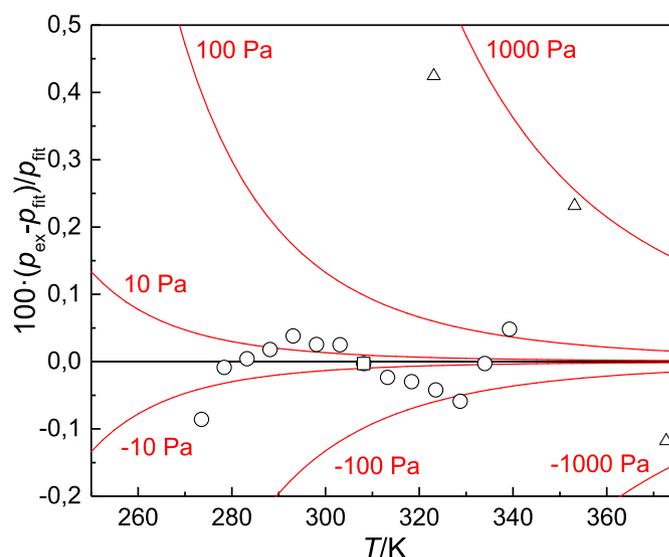


Fig. 2. Deviation plot of temperature dependencies of vapor pressure of ethanethiol: o - ebullimetry by McCullough et al. [20], □ - boiling points at 1 atm by Haines et al. [22], Marvel et al. [24] and Abel [30], Δ - baratron pressure gauge by Kilner et al. [46].

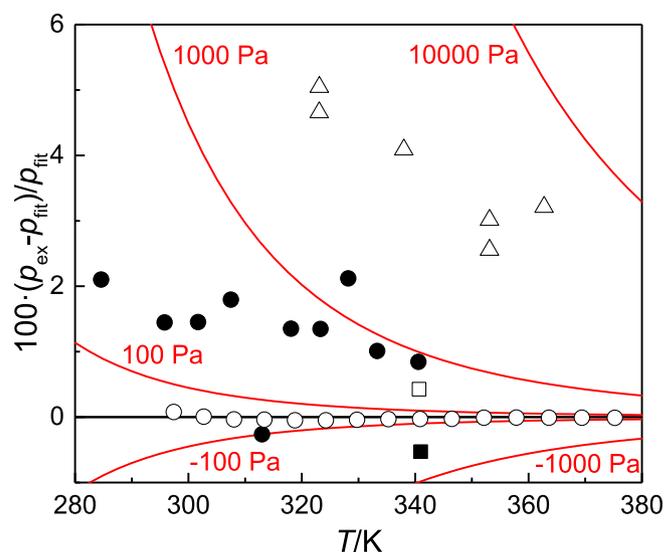


Fig. 3. Deviation plot of temperature dependencies of vapor pressure of 1-propanethiol: ● - static technique by Taylor et al. [13], o - ebullimetry by Pennington et al. [26], ■ - boiling point at 1 atm by Morris et al. [29], □ - boiling point at 1 atm by Vaughan et al. [16], Δ - baratron pressure gauge by Kilner et al. [46].

pressures for 1-alkanethiols are shown in Figs. 1–10.

3.1.1. Methanethiol

As can be seen from Fig. 1, the boiling point of methanethiol (5.9 °C) determined by Morris et al. [29] at atmospheric pressure agrees well with the systematic measurements of vapor pressures by Russell et al. [15] and Osborn and Scott [40].

3.1.2. Ethanethiol

A comparison of the relative deviations of the vapor pressures for ethanethiol is shown in Fig. 2.

The mutually consistent boiling point of 308.15 K obtained in works [22,24,30] agrees well with the consistent data measured by McCullough

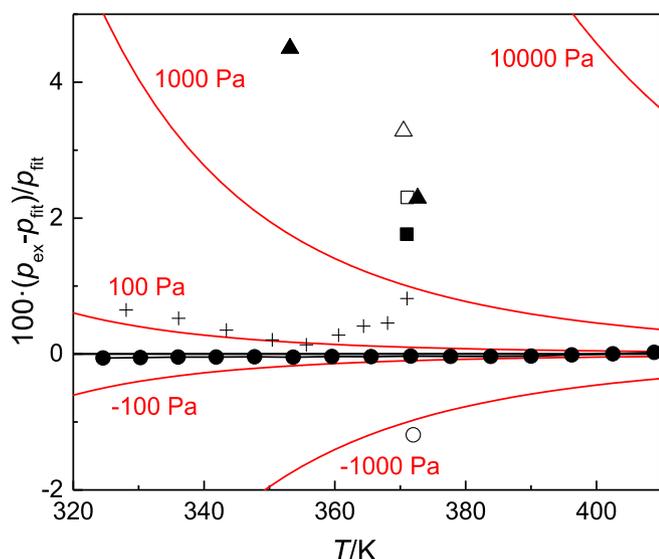


Fig. 4. Deviation plot of temperature dependencies of vapor pressure of 1-butanethiol: ● - ebulliometry by Scott et al. [28], ○ - boiling point at 1 atm by Borgogno et al. [34], ■ - boiling point at 1 atm by Blotny [41], □ - boiling point at 1 atm by Stepanov et al. [36] and Brown et al. [42], ▲ - baratron pressure gauge by Kilner et al. [46], + - Druck pressure transducer by Sapei et al. [49].

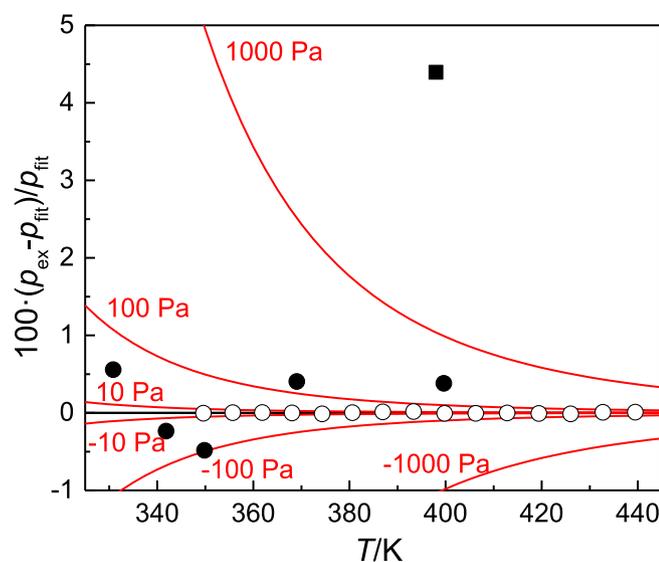


Fig. 5. Deviation plot of temperature dependencies of vapor pressure of 1-pentanethiol: ● - ebulliometry by Ellis et al. [12], ○ - ebulliometry by Finke et al. [19], ■ - boiling point at 1 atm by Nametkin et al. [18].

et al. [20] and Kilner et al. [46]. The boiling point measured at atmospheric pressure (310.15 K) in Blotny's work [41] differs by approximately 7 % from most consistent data and is outside the range of Fig. 2. The vapour pressures measured by Thompson et al. [14] are over-estimated by an average of 19 % compared to all other data and is also outside the range of Fig. 2.

3.1.3. 1-Propanethiol

As can be seen in Fig. 3, the boiling points of 1-propanethiol at atmospheric pressure [22,29] and those obtained from the temperature dependence of the vapor pressure [13,26] are in good agreement and lie

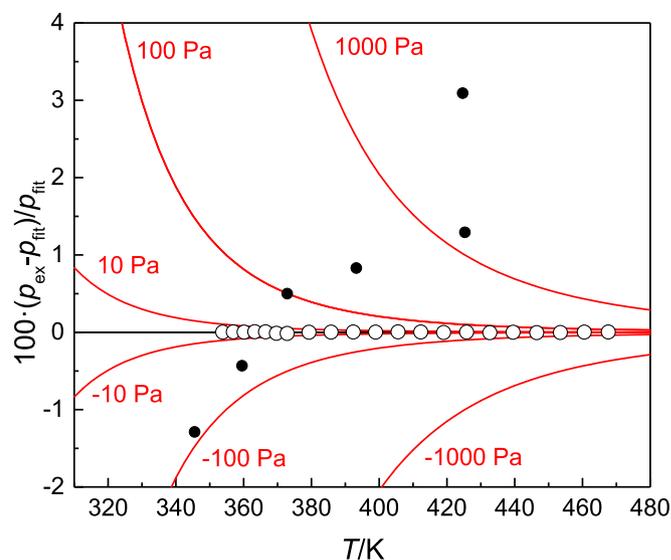


Fig. 6. Deviation plot of temperature dependencies of vapor pressure of 1-hexanethiol: ● - ebulliometry by Ellis et al. [12], ○ - ebulliometry by Osborn et al. [32].

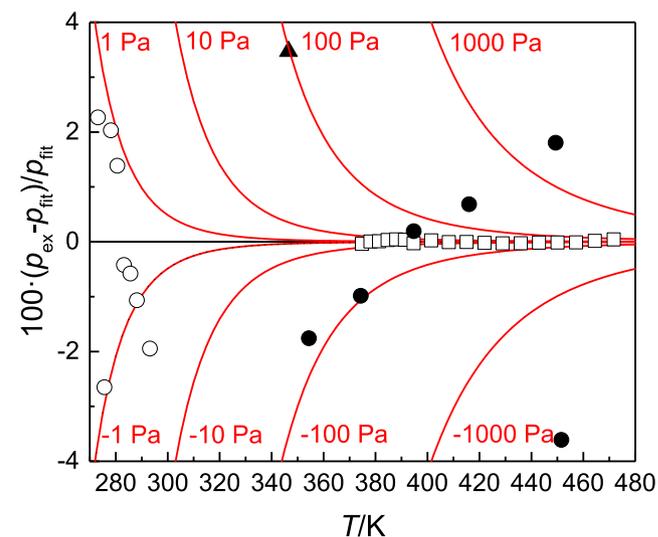


Fig. 7. Deviation plot of temperature dependencies of vapor pressure of 1-heptanethiol: ● - ebulliometry by Ellis et al. [12], ○ - static technique by Douslin et al. [31], □ - ebulliometry by Douslin et al. [31], ▲ - boiling point at 2933.1 Pa by Gryazev et al. [33].

in the temperature range from 340.6 to 341 K.

Most of the available values of 1-propanethiol vapor pressures agree within 2 %, with the exception of one value determined by Taylor et al. [13] in the low temperature range. Also, the vapour pressures from Kilner et al. [46] are on average 3.9 % higher than the data from Pennington et al. [26].

3.1.4. 1-Butanethiol

The comparison of the relative deviations of the vapor pressures for 1-butanethiol is shown in Fig. 4.

Systemic measurements of the temperature dependence of the vapor pressures of 1-butanethiol were carried out by Scott et al. [28] and Sapei et al. [49]. The vapour pressures measured by Scott et al. [28] and Sapei et al. [49] agree within 1 %. According to Fig. 4, the vapour pressures determined by Kilner et al. [46] deviate from the data of Scott et al. [28]

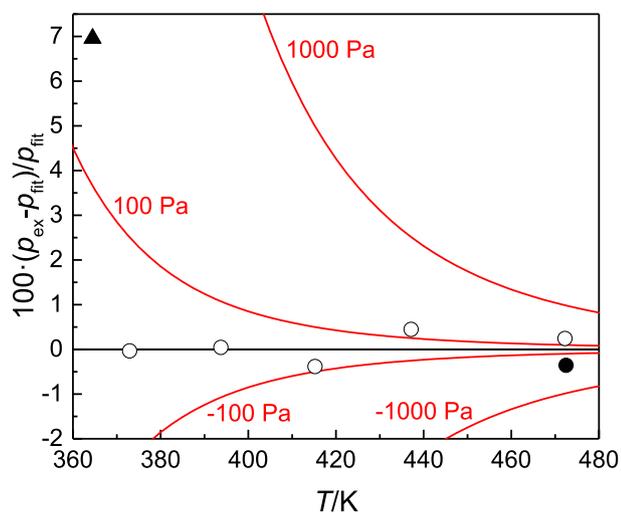


Fig. 8. Deviation plot of temperature dependencies of vapor pressure of 1-octanethiol: o - ebulliometry by Ellis et al. [12], ● - boiling point at 1 atm by Mazitova et al. [39], ▲ - boiling point at 2933.1 Pa by Degani et al. [35].

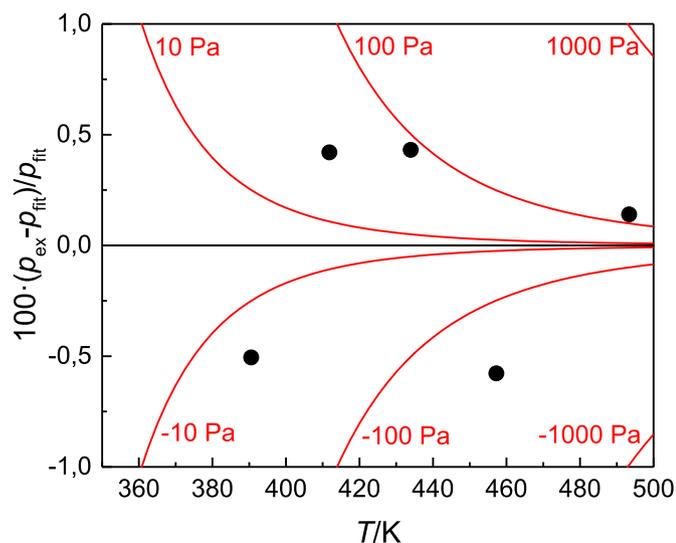


Fig. 9. Deviation plot of temperature dependencies of vapor pressure of 1-nonanethiol: ● - ebulliometry by Ellis et al. [12].

and Sapei et al. [49] by 2 and up to 10 %. The measured boiling temperatures at atmospheric pressure in [11,36,41,42] agree within 2 % with the results in Ref [28]. Only the value (367.5 K) determined by Noda et al. [21] deviates by >12 % and is outside the range of Fig. 4.

3.1.5. 1-Pentanethiol

Fig. 5 shows the deviation plot of temperature dependencies of vapor pressure of 1-pentanethiol.

The boiling point of 1-pentanethiol determined by Nametkin et al. [18] deviates by about 1.7 K from the corresponding data determined by Ellis et al. [12] and Finke et al. [19] using ebulliometry method.

3.1.6. 1-Hexanethiol

Deviation plot of vapor pressure for 1-hexanethiol is illustrated in Fig. 6.

Vapor pressures measured by Ellis et al. [12] and Osborn et al. [32] using ebulliometry agree within 1–2 % with each other. The relative deviations for literature boiling points at atmospheric and reduced pressures [17,23,25,37] are 10 % or more. These values are outside the

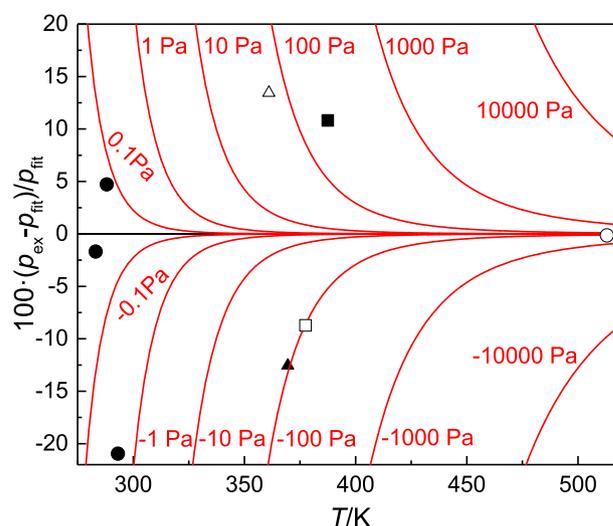


Fig. 10. Deviation plot of temperature dependencies of vapor pressure of 1-decanethiol: ● - static technique by Douslin et al. [31], o - boiling point at 1 atm by Sohmiya et al. [47], ■ - boiling point at 2133.2 Pa by Degani et al. [35], □ - boiling point at 1066.6 Pa by Mazitova et al. [39], ▲ - boiling point at 666.6 Pa by Tanchuk et al. [37], Δ - boiling point at 533.3 Pa by Lutz et al. [45].

range of Fig. 6.

3.1.7. 1-Heptanethiol

The deviation plot of temperature dependencies of vapor pressure of 1-heptanethiol is shown on Fig. 7.

The vapor pressures measured by Ellis et al. [12] and Douslin et al. [31] agree within 2 % with each other. The boiling point at atmospheric pressure (445 K) determined by Katritzky et al. [44] is about 5 K below that the boiling point determined by Ellis et al. [12] и Douslin et al. [31] and is outside of the range of Fig. 7. The boiling points at reduced pressure determined by Gryazev et al. [33] and Mazitova et al. [39] agree within 4 % or more. The vapour pressure determined by Obolentseva et al. [27] differs significantly from the most reliable data.

3.1.8. 1-Octanethiol

The temperature dependence of vapor pressure for 1-octanethiol was only systematically investigated by Ellis et al. [12]. As can be seen from Fig. 8, the boiling point at atmospheric pressure determined by Mazitova et al. [39] and the boiling point value obtained at 2933.1 Pa by Degani et al. [35] agree well with the data from Ellis et al. [12].

At the same time, the values determined in another study by Degani et al. [38] and Ookawa et al. [43] deviate by around 40 and 70 %, respectively.

3.1.9. 1-Nonanethiol

As in the case of 1-octanethiol, limited vapor pressure data are also observed for 1-nonanethiol, which are shown in Fig. 9.

The boiling points at reduced pressures given in the literature [39, 48] deviate considerably from the temperature dependence of the vapor pressure, which was determined by Ellis et al. [12]. The boiling point (371.0 K) determined by Mazitova et al. [39] at 5199.6 Pa deviates by >220 %, and the value from the work by Cao [48] deviates by >180 % from calculated on the temperature dependence equation.

3.1.10. 1-Decanethiol

Fig. 10 shows a comparison of vapor pressures for 1-decanethiol at various temperatures.

The temperature dependence of the vapor pressure for 1-decanethiol has not been systematically studied. Only Douslin et al. [31] measured three vapor pressures in the range of ten degrees using the static method.

Table 2Compilation of data on molar heat capacities $C_{p,m}^o$ and differences $\Delta_1^s C_{p,m}^o$ for alkanethiols, in $J.K^{-1}.mol^{-1}$, at 298.15 K.

Compound	$C_{p,m}^o$ (liq) ^a	$C_{p,m}^o$ (liq) ^c	$C_{p,m}^o$ (gas) ^d	$C_{p,m}^o$ (gas) ^e	$-\Delta_1^s C_{p,m}^o$ ^f	$-\Delta_1^s C_{p,m}^o$ ^g	$-\Delta_1^s C_{p,m}^o$ ⁱ	$-\Delta_1^s C_{p,m}^o$
1	2	3	4	5	6	7	8	9
methanethiol		82.1		51.4		31.9 ^h	37.2	34.5 ^j
ethanethiol	118.0 ^b [20]	114.0	72.6 [20]	71.9	46.1	41.3	42.4	45.4 ^k
1-propanethiol	144.6 ^b [26]	145.9	94.3 [26]	93.2	51.4	48.2	49.2	50.3 ^k
1-butanethiol	172.2 ^b [28]	177.8	117.1 [28]	114.3	58.0	55.4	56.2	55.1 ^k
1-pentanethiol	201.2 ^b [19]	209.7	140.4 [77]	135.0	66.2	62.9	63.5	60.8 ^k
1-hexanethiol	230.7 [78]	241.6		156.8	73.9	70.6	71.7	72.1 ^j
1-heptanethiol	259.3 [78]	273.5		176.5	82.8	78.0	80.1	80.3 ^j
1-octanethiol	300.1 [79]	305.4		197.5	102.6	88.6	88.9	93.4 ^j
1-nonanethiol		337.3		219.1		98.3 ^h	96.4	96.4 ^j
1-decanethiol	350.41 [78]	369.2		239.6	110.8	101.7	100.8	104.4 ^j

^a experimental molar heat capacities of liquid 1-alkanethiols.^b heat capacities at the saturation pressure.^c heat capacity of liquid thiols calculated by additive scheme of *Chickos* et al. [80].^d experimental molar heat capacities of gaseous 1-alkanethiols.^e calculated by CAM-B3LYP/6-311++G(3df,3pd) 5d 7f, model "rigid rotator - anharmonic oscillator".^f the difference between columns (5) and (2).^g estimated using empirical procedure of *Chickos* et al. [81] and the $C_{p,m}^o$ (liq) values were taken from column (2).^h estimated using empirical procedure of *Chickos* et al. [81] and the $C_{p,m}^o$ (liq) value was taken from column (3).ⁱ estimated using empirical procedure of *Sokolov* et al. [82].^j average $-\Delta_1^s C_{p,m}^o$ values between columns (6–8).^k the difference between columns (4) and (2).

The available in the literature boiling points [35,37,39,45,47] were used to determine the parameters of Clarke and Glew equation, which are compiled in Table S35. The resulting equation for the temperature dependence does not possess high reliability but cannot be neglected in the absence of systematic studies.

3.2. Standard molar enthalpies of vaporization of 1-alkanethiols at 298.15 K

The enthalpy of vaporization ($\Delta_1^s H_m$) was determined using the following equation:

$$RT^2 \left(\frac{d \ln p}{dT} \right) \cdot \Delta_1^s Z = \Delta_1^s H_m \quad (3)$$

The deviation of the gas phase from ideal state ($\Delta_1^s Z$) was calculated using the second virial coefficient ($B_{2,m}$) and molar volume of liquid ($V_m(l)$):

$$\Delta_1^s Z = 1 + \frac{P}{RT} (B_{2,m} - V_m(l)) \quad (4)$$

The second virial coefficient $B_{2,m}$ was calculated using the Pitzer-Curl correlation modified by Tsonopoulos [74]. The parameters required for calculating the $B_{2,m}$ - coefficient: critical temperatures (T_c) and pressures (P_c), dipole moments (μ) and values of the acentricity factor (ω) for 1-alkanethiols are listed in Table S34. The $V_m(l)$ values were calculated using literature density values in Table S34. The $\Delta_1^s Z$ - values obtained for alkanethiols are in the range of 0.94 - 0.999.

The standard vaporisation enthalpy ($\Delta_1^s H_m^o$) were calculated by using contribution of gas nonideality [75,76]:

$$\Delta_1^s H_m^o = \Delta_1^s H_m - P \left(B_{2,m} - T \frac{dB_{2,m}}{dT} \right) \quad (5)$$

The experimental vaporization enthalpies from the temperature of measurement need to be adjusted to 298.15 K. According to the Kirchhoff's law, this requires knowledge of the heat capacity difference ($\Delta_1^s C_{p,m}^o$) between the gas ($C_{p,m}^o$ (gas)) and liquid ($C_{p,m}^o$ (liq)) phases:

$$\Delta_1^s H_m^o (298.15 \text{ K}) = \Delta_1^s H_m^o (T) + \Delta_1^s C_{p,m}^o (298.15 \text{ K} - T) \quad (6)$$

All the $C_{p,m}^o$ (gas), $C_{p,m}^o$ (liq) and $\Delta_1^s C_{p,m}^o$ values are summarized in Table 2.

Since experimental results for $C_{p,m}^o$ (gas) and $C_{p,m}^o$ (liq) are not available for all alkanethiols, empirical methods [81,82] and our own quantum chemical calculations were used to determine $\Delta_1^s C_{p,m}^o$ values. In the case of the ethanethiol, 1-propanethiol, 1-butanethiol and 1-pentanethiol the heat capacities at the saturation pressure ($C_{s,m}^o$) of liquid phase and $C_{p,m}^o$ (gas) values were found in the literature [19,20,26,28,77]. For methanethiol, 1-hexanethiol, 1-heptanethiol, 1-octanethiol and 1-decanethiol, only experimental $C_{p,m}^o$ (liq) values were found in the literature [78,79]. The comparison of the experimental $C_{s,m}^o$ and $C_{p,m}^o$ values of liquid alkanethiols (column 2) [19,20,26,28] with the values calculated according to the additive scheme of *Chickos* et al. [80] (column 3) showed a good agreement of the results within 3–4 %. Only the $C_{p,m}^o$ values of methanethiol showed deviations of around 9 %. The experimental $C_{p,m}^o$ (gas) values of ethanethiol, 1-propanethiol, 1-butanethiol and 1-pentanethiol [20,26,28,77] and the values calculated with CAM-B3LYP/6-311++G(3df,3pd) 5d 7f, model 'rigid rotator - anharmonic oscillator', also agree well within 1–3 %. Despite the generally good agreement between experimental and calculated $C_{p,m}^o$ values, to increase the reliability of the $\Delta_1^s C_{p,m}^o$ values for long-chain alkanethiols, additional empirical determination methods were used, which were proposed by *Chickos* et al. [81] and *Sokolov* et al. [82]. As shown in Table 2, there is generally reasonable agreement within 15 % between the different methods for determining the $\Delta_1^s C_{p,m}^o$ values. Therefore, experimental $\Delta_1^s C_{p,m}^o$ values [19,20,26,28,77] and averaged $\Delta_1^s C_{p,m}^o$ values of various calculation methods were used for adjustment the enthalpies of vaporisation from the experimental temperature to 298.15 K, which are given in column 9 of Table 2.

The enthalpies of vaporization of 1-alkanethiols at 298.15 K taken from the literature and obtained in this work using Eq. (6) are listed in Table 3. In addition, Table 3 summarizes the measurement methods, temperature ranges and enthalpies of vaporization at the experimental temperature.

The enthalpies of vaporization determined by calorimetric and vapor pressure data are in good agreement for 1-alkanethiols from methanethiol to 1-pentanethiol. To increase the reliability of the enthalpy of vaporization data for 1-alkanethiols, the solution calorimetry method was improved (see Section 3.3). A comparison of the most reliable enthalpies of vaporization of methanethiol, ethanethiol, 1-propanethiol, 1-butanethiol and 1-pentanethiol in Table 3 showed good agreement with

Table 3
Compilation of vaporization enthalpies ($\Delta_1^g H_m^0$) of 1-alkanethiols.

Compounds [CAS No.]	Method ^a	T-range/ K	$\Delta_1^g H_m^0(T)/$ kJ·mol ⁻¹	$\Delta_1^g H_m^0(298.15\text{ K})^b/$ kJ·mol ⁻¹	Ref.
methanethiol (I) [74-93-1]	C	279.0	24.6 ± 0.1	24.0 ± 0.1	[15]
	p_{fit}	222–307		23.9 ± 0.1 24.0 ± 0.1	This work Average ^c Table 5
ethanethiol (I) [75-08-1]	SC	298.15		24.4 ± 0.8	Table 5
	C	281.0	28.2 ± 0.1	27.5 ± 0.1	[20]
	C	298.15	27.3 ± 0.1	27.3 ± 0.1	[20]
	C	308.0	26.8 ± 0.1	27.2 ± 0.1	[20]
1-propanethiol (I) [107-03-9]	p_{fit}	273–339		27.5 ± 0.1 27.4 ± 0.1	This work Average ^c Table 5
	SC	298.15		26.8 ± 0.8	Table 5
	C	303.0	31.6 ± 0.1	31.8 ± 0.1	[26]
	C	320.6	30.7 ± 0.1	31.8 ± 0.2	[26]
	C	340.9	29.5 ± 0.1	31.6 ± 0.3	[26]
1-butanethiol (I) [109-79-5]	p_{fit}	284–375		32.1 ± 0.1 31.9 ± 0.1	This work Average ^c Table 5
	SC	298.15		31.2 ± 0.8	Table 5
	C	330.6	34.7 ± 0.1	36.5 ± 0.3	[28]
	C	349.7	33.6 ± 0.1	36.5 ± 0.4	[28]
	C	371.6	32.2 ± 0.1	36.3 ± 0.6	[28]
1-pentanethiol (I) [110-66-7]	p_{fit}	323–409		36.5 ± 0.4 36.5 ± 0.2	This work Average ^c Table 5
	SC	298.15		35.7 ± 0.8	Table 5
	C	356.1	37.7 ± 0.1	41.2 ± 0.5	[77]
	C	376.4	36.4 ± 0.1	41.2 ± 0.7	[77]
	C	399.8	34.9 ± 0.1	41.1 ± 0.9	[77]
1-hexanethiol (I) [111-31-9]	p_{fit}	330–439		41.2 ± 0.5 41.2 ± 0.3	This work Average ^c Table 5
	SC	345–468		45.8 ± 0.8	This work
	p_{fit}	354–471		50.2 ± 0.9	This work
1-octanethiol (I) [111-88-6]	p_{fit}	364–472	47.8 ± 0.3	58.4 ± 1.3	This work
	SC	298.15		55.2 ± 0.7 55.9 ± 0.6	This work Average ^c Table 5
1-nonanethiol (I) [1455-21-6]	p_{fit}	356–493	52.4 ± 0.3	63.0 ± 1.5	This work
	SC	298.15		59.4 ± 0.9 60.4 ± 0.7	This work Average ^c Table 5
1-decanethiol (I) [143-10-2]	C	298.15	65.5 ± 0.5	65.5 ± 0.5	[83]
	p_{fit}	283–513	62.9 ± 0.9	68.0 ± 2.4	This work
	SC	298.15		64.2 ± 0.9 65.3 ± 0.4	Table 5 Average ^c Table 5
1-undecanethiol (I) [5332-52-5]	SC	298.15		69.0 ± 0.9	Table 5
1-dodecanethiol (I) [112-55-0]	SC	298.15		73.2 ± 0.9	Table 5

^a Experimental methods for determining enthalpies of vaporization: C – calorimetry, SC – solution calorimetry (Table 5), p_{fit} – obtained by fitting of experimental data of vapor pressure (see the text).

^b Uncertainties of the vaporization enthalpies $U(\Delta_1^g H_m^0)$ are the expanded uncertainties (0.95 level of confidence). They include uncertainties from the fitting equation and uncertainties from temperature adjustment to $T = 298.15$ K. Uncertainties in the temperature adjustment of vaporization enthalpies to the reference temperature $T = 298.15$ K are estimated to account with 20 % to the total adjustment.

^c Weighted mean value (uncertainties were taken as the weighting factor).

the values obtained by the solution calorimetry method. In this regard, the method was applied to determine the enthalpies of vaporization of other 1-alkanethiols ($C_8 - C_{12}$). The enthalpies of vaporization obtained by solution calorimetry method for 1-octanethiol and 1-nonanethiol were approximately 3 kJ·mol⁻¹ lower than the values obtained from the temperature dependence of the vapor pressure. At once, the enthalpy of vaporization of 1-decanethiol (65.5 ± 0.5 kJ·mol⁻¹) obtained by *Månsson* et al. [83] using the calorimetric method is in good agreement with the solution calorimetry data (64.2 ± 0.8 kJ·mol⁻¹). For all subsequent thermochemical calculations, weighted average enthalpies of vaporization of 1-octanethiol, 1-nonanethiol and 1-decanethiol were calculated using values obtained by solution calorimetry method.

The average weighted values of the enthalpies of vaporisation of 1-alkanethiols at 298.15 K were used to obtain a linear dependence on the number of carbon atoms, N_C (Fig. S1):

$$\Delta_1^g H_m^0 = (4.70 \pm 0.03) \cdot N_C + (17.8 \pm 0.1) \quad (7)$$

Eq. (7) is typical for homological series and is often used for the prediction and validation of thermochemical parameters of evaporation of homologous series. Slope coefficient in Eq. (7) is the methylene group contribution into vaporization enthalpy of 1-alkanethiols. Uncertainties of fitting parameters of Eq. (7) correspond to standard error.

Earlier in [84], the relationship between the enthalpy of solution of alkanes in the homologous series of solvents and the contribution of the methylene group into the enthalpy of vaporization in the homologous series of solvents was found:

$$\Delta_{\text{soln}} H^{n\text{-alkane}/S} / \text{kJ} \cdot \text{mol}^{-1} = (\Delta_1^g H^{-(CH_2)_i-} - 4.87) \cdot V_x^{n\text{-alkane}} / (-0.109 \cdot V_x^S) \quad (8)$$

where $V_x^{n\text{-alkane}}$ and V_x^S are McGowan volumes of corresponding n -alkane and solvent. $\Delta_1^g H^{-(CH_2)_i-}$ is a methylene contribution into vaporisation enthalpy for homologous series of solvents. The $\Delta_1^g H^{-(CH_2)_i-}$ value for 1-alkanethiols is equal to 4.70 kJ per mole. In the present work, this

Table 4

Prediction of the enthalpy of solution of *n*-heptane ($\Delta_{\text{soln}}H_m^{\text{n-heptane/S}}$) in some 1-alkanethiol solvents at 298.15 K based on the McGowan volumes (V_x^S) and the contribution of methylene to the enthalpy of vaporization ($\Delta_1^S H_m^{\text{-(CH}_2)_-}$).

Solvent (S)	$V_x^S \cdot 10^{-2} / \text{cm}^3 \cdot \text{mol}^{-1}$	$\Delta_1^S H_m^{\text{-(CH}_2)_-} / \text{kJ} \cdot \text{mol}^{-1}$	$V_x^{\text{n-heptane}} \cdot 10^{-2} / \text{cm}^3 \cdot \text{mol}^{-1}$	$\Delta_{\text{soln}}H_m^{\text{n-heptane/S}} / \text{kJ} \cdot \text{mol}^{-1}$	$\Delta_{\text{soln}}H_m^{\text{n-heptane/S}} / \text{kJ} \cdot \text{mol}^{-1}$
1	2	3	4	5	6
1-pentanethiol	0.9766	4.70	1.0949	1.7	1.9
1-hexanethiol	1.1175			1.5	1.6
1-heptanethiol	1.2584			1.4	1.3
1-octanethiol	1.3993			1.2	1.1

^a Standard uncertainty of solution enthalpy estimated by Eq. (8) is $\pm 0.5 \text{ kJ} \cdot \text{mol}^{-1}$.

^b Solution enthalpies of *n*-heptane in 1-alkanethiols were evaluated using Python Thermo [58] and UNIFAC (Dortmund) model [59].

Table 5

Experimental and estimated enthalpies of solvation ($\Delta_{\text{soln}}H_m^{A_i/S}$) of 1-alkanethiols in *n*-heptane and their difference (Δ) in $\text{kJ} \cdot \text{mol}^{-1}$ at 298.15 K.

Compound	$-\Delta_{\text{soln}}H_m^{A_i/S}(\text{exp})$	$-\Delta_{\text{soln}}H_m^{A_i/S}(\text{est})$	Δ
1	2	3	4
1-pentanethiol	38.5 ± 0.3	38.4	-0.1
1-hexanethiol	43.3 ± 0.6	43.3	-0.0
1-heptanethiol	48.0 ± 0.7	48.2	0.2

^a Uncertainties correspond to expanded uncertainties of the mean (0.95 level of confidence and $k \approx 2$).

Table 6

Solution ($\Delta_{\text{soln}}H_m^{A_i/S}$), solvation ($\Delta_{\text{soln}}H_m^{A_i/S}$) and vaporization ($\Delta_1^S H_m^0$) enthalpies of 1-alkanethiols in $\text{kJ} \cdot \text{mol}^{-1}$ at 298.15 K.

Compound	$\Delta_{\text{soln}}H_m^{A_i/S}$ ^a	$-\Delta_{\text{soln}}H_m^{A_i/S}$	$\Delta_1^S H_m^0$
1	2	3	4
methanethiol (l)	5.7	18.7 ± 0.6	24.4 ± 0.8
ethanethiol (l)	3.2	23.6 ± 0.6	26.8 ± 0.8
1-propanethiol (l)	2.7	28.5 ± 0.6	31.2 ± 0.8
1-butanethiol (l)	2.3	33.4 ± 0.6	35.7 ± 0.8
1-octanethiol (l)	2.05 ± 0.01 ^b	53.1 ± 0.7	55.2 ± 0.7
1-nonanethiol (l)	1.4	58.0 ± 0.7	59.4 ± 0.9
1-decanethiol (l)	1.3	62.9 ± 0.7	64.2 ± 0.9
1-undecanethiol (l)	1.2	67.8 ± 0.7	69.0 ± 0.9
1-dodecanethiol (l)	1.1	72.7 ± 0.7	73.8 ± 0.9

^a Standard uncertainty of calculated solution enthalpy is $\pm 0.5 \text{ kJ} \cdot \text{mol}^{-1}$.

^b Taken from Table S1.

relationship was used to predict the solution enthalpies of *n*-heptane in the homologous series of 1-alkanethiols at 298.15 K, which are shown in Table 4.

For comparison, enthalpies of solution of *n*-heptane in alkanethiols were calculated by using Python Thermo [58] and UNIFAC (Dortmund) model [59]. As shown in Table 3, the solution enthalpies determined by the two different methods agree within $0.5 \text{ kJ} \cdot \text{mol}^{-1}$, which is generally a good result for solution enthalpy prediction methods.

3.3. Development of group contribution approach for estimation of solvation enthalpies of 1-alkanethiols

In the present work, the standard enthalpies of vaporization and measured enthalpies of solution of alkanethiols in *n*-heptane were used to improve the method for calculating the enthalpy of solvation. For this purpose, the experimental enthalpies of solvation of the alkanethiols in *n*-heptane were calculated using the following equation:

$$\Delta_{\text{soln}}H_m^{A_i/S} = \Delta_{\text{soln}}H_m^{A_i/S} - \Delta_1^S H_m^0 \quad (9)$$

The enthalpies of solvation for the four 1-alkanethiols in *n*-heptane calculated according to Eq. (9) are given in column 2 of Table 5.

The experimental solvation enthalpies were used to determine the magnitude of the contribution of the SH-group to the solvation enthalpy

in *n*-heptane. The $-\text{CH}_2-$ and $-\text{CH}_3$ group contributions into solvation enthalpy were found in the previous work [58] and are equal to $-4.91 \pm 0.03 \text{ kJ} \cdot \text{mol}^{-1}$ and $-5.83 \pm 0.13 \text{ kJ} \cdot \text{mol}^{-1}$, respectively. The value obtained for the SH group into the enthalpy of solvation in *n*-heptane was $12.88 \pm 0.5 \text{ kJ} \cdot \text{mol}^{-1}$. These group contributions were used to determine the enthalpy of solvation of other 1-alkanethiols, which are listed in Table 6.

The enthalpies of solution of the liquid 1-alkanethiols in *n*-heptane were determined using Python Thermo [58] and UNIFAC (Dortmund) model [59] and listed in Table 6. It can be concluded that the differences in the enthalpy of solution of 1-alkanethiols in *n*-heptane using the UNIFAC (Dortmund) method is of the level of $0.5 \text{ kJ} \cdot \text{mol}^{-1}$. This conclusion can be drawn from the comparison of the experimental and calculated enthalpies of solution of 1-pentanethiol, 1-hexanethiol, 1-heptanethiol and 1-octanethiol in *n*-heptane, which are summarized in Table S36. Thus, the enthalpies of solution determined by UNIFAC (Dortmund) model and solvation enthalpies of the 1-alkanethiols in *n*-heptane can be used to determine the enthalpies of vaporization at 298.15 K according to Eq. (9).

3.4. Standard molar enthalpies of formation of 1-alkanethiols at 298.15 K

Equilibrium structure, total electron energy (E_{total}) and enthalpy of formation from elementary substances at 298.15 K ($\Delta_f H_m^0(\text{g})$) for all selected compounds were obtained with functionals BMK, CAM-B3LYP, LC-wPBE, M06, wB97, wB97x with the triple-zeta basis set 6-311++G(3df,3pd) of spherical harmonics (5d 7f), as well as by the functionals M06 and wB97x with the quadruple-zeta basis set aug-cc-pvQZ 5d 7f in GAUSSIAN 09 software [60] (Table S2). The selection of the above-mentioned functionals has been previously carried out by us on compounds of different classes, which is described in details in [9,10]. Calculation with the quadruple-zeta basis set was applied to check the dependence of the value of $\Delta_f H_m^0(\text{g})$ (electron and vibrational contributions) on the size of the basis set. According to Table S2, this dependency can be neglected.

The following conditions were set for the optimization: convergence for the mean field energy (SCF) and the total electronic energy E_{total} not worse than $1 \cdot 10^{-8}$ a.u., for the forces $5 \cdot 10^{-6}$ a.u. bohr⁻¹ and the density matrix coefficients $5 \cdot 10^{-9}$.

A particularly large integration grid 250 radial shells per atom and 974 nodes in each atomic shell was used. The harmonic frequencies (ν_{harm}) were scaled (ω) by the equation of a cubic parabola passing through the origin (1), where the coefficients a , b and c for each DFT function used were selected from a comparison of the harmonic and well-defined experimental frequencies of normal alkanes:

$$\omega = a\nu_{\text{harm}}^3 + b10^{-6}\nu_{\text{harm}}^2 + c\nu_{\text{harm}} \quad (10)$$

For example, Eq. (10) for the basis set M06/6-311++G(3df,3pd) 5d 7f has the form (11):

$$\omega = -6.173 \times 10^{-9}\nu_{\text{harm}}^3 + 1.014 \times 10^{-5}\nu_{\text{harm}}^2 + 0.987\nu_{\text{harm}} \quad (11)$$

Table 7
Gas-phase enthalpies of formation $\Delta_f H_m^0$ (g) at $T = 298.15$ K ($p^\circ = 0.1$ MPa) for 1-alkanethiols (in $\text{kJ}\cdot\text{mol}^{-1}$).

basis set functional	G-n		aLL5	Benson [85]	reg ^a	exp	6-311++G(3df,3pd) 5d 7f		aug-cc-pvQZ5d 7f		$\Delta_{\text{mix}} H_m^0$ ^b Gn and aLL5	
	G3MP2	G4AMP2					G4	LC-wPBE	wB97	wB97x		wB97x
methanethiol	-24.6	-26.9	-22.6	-24.8	-22.7	-22.5	-24.8	-22.5	-22.8	-20.7	-20.5	0.0
ethanethiol	-50.4	-51.8	-47.6	-45.6	-46.4	-46.0	-45.6	-45.6	-47.4	-45.4	-43.5	0.4
1-propanethiol	-71.2	-72.4	-68.2	-66.4	-67.1	-67.7	-66.4	-68.2	-69.0	-67.2	-63.1	1.0
1-butanethiol	-91.7	-92.9	-88.7	-87.2	-87.8	-87.9	-87.2	-88.6	-89.8	-88.1	-82.1	1.6
1-pentanethiol	-112.3	-113.3	-109.1	-108.0	-108.5	-109.7	-108.0	-109.2	-110.6	-109.2	-101.2	2.6
1-hexanethiol	-132.8	-134.0	-129.9	-128.8	-129.2	-128.2	-128.8	-129.8	-132.9	-131.4	-120.2	3.4
1-heptanethiol	-153.4	-154.9	-150.5	-149.6	-149.9	-149.9	-149.6	-150.5	-154.6	-152.0	-139.5	4.4
1-octanethiol	-173.8	-175.3	-171.0	-170.4	-170.6	-170.4	-170.4	-171.1	-177.1	-172.7	-158.8	5.3
1-nonanethiol	-194.7	-196.2	-191.8	-191.2	-191.3	-191.2	-191.2	-191.5	-199.6	-193.6	-178.3	5.8
1-decanethiol	-215.7	-217.8	-212.9	-212.0	-212.0	-211.1	-212.0	-212.1	-221.9	-214.3	-197.3	6.3
1-undecanethiol	-237.1	-239.0	-234.3	-232.8	-232.8	-232.8	-232.8	-232.6	-243.9	-235.1	-214.5	7.0
1-dodecanethiol	-258.1	-259.9	-255.2	-253.6	-253.5	-253.6	-253.6	-253.1	-266.2	-256.3	-235.4	7.2
$\Delta\Delta H_{RMS}$	3.7	5.2	1.1	1.6	0.7	1.2	4.9	0.8	4.9	1.7	7.9	

^a $\Delta_f H^0$ (g, reg) is from interpolation (13) of experimental $\Delta_f H_m^0$ (g, exp).

^b the enthalpy correction for the equilibrium conformational mixture in gas phase.

(For a Cartesian basis set 6d 10f the coefficients in Eq. (11) will be slightly different). The enthalpies of formation, $\Delta_f H_m^0$ (g), of the analyzed substances were calculated using an anharmonic approximation ("rigid rotator – anharmonic oscillator" (RRAO) model). The vibration contribution is determined by direct summation of the energies of the levels of the individual modes (E_{anham}) which are located in non-parabolic potential wells. Energy E_{anham} (12) is found using the Dunham series, whose parameters are (n_{max} – number of levels in the well, $n_{max} > n$ – vibrational quantum number and $\chi_{i,i}$ – diagonal constant of the anharmonicity matrix) were obtained from two sets of frequencies (harmonic ν_{harm} and anharmonic ω).

$$E_{anham,i}(n) = hc\nu_{harm,i} \left(n + \frac{1}{2} \right) + hc\chi_{i,i} \left(n + \frac{1}{2} \right)^2 \quad (12)$$

The results of composite methods and aLL5 protocol were corrected accounting for the equilibrium mixture of conformers in the gas phase (Table 7). The uncertainty of the applied procedure was assumed to be equal of 10 % of the applied correction.

Based on the $\Delta_f H_m^0$ (g, exp) values from ethanethiol to 1-decanethiol, a linear approximation (13) and (Fig. S2) of the enthalpy of formation from the number of electrons in the molecule (N_{electr}) was derived:

$$\Delta_f H^0(\text{g, reg}) = (42.8 \pm 1.1) - (2.60 \pm 0.02) \times N_{electr} \quad (13)$$

with the correlation coefficient $R^2 = 0.9998$; residuals (RMS difference $\Delta\Delta H_{RMS}$ (13)) for all 1-alkanethiols and without methanethiol are equal to 1.2 and 0.9 $\text{kJ}\cdot\text{mol}^{-1}$, respectively.

$$\Delta\Delta H_{RMS} = \sqrt{\frac{\sum_{i=1}^n (\Delta_f H_m^0(\text{g, cal}) - \Delta_f H_m^0(\text{g, exp}))^2}{n}} \quad (14)$$

The linear approximation (13) only applies to the basic (gauche) conformers of alkanethiols. This dependence is not suitable for determining the enthalpies of formation of other structures. For these cases, the enthalpies of formation and other properties of conformers with higher energy can be determined by quantum chemical methods.

The $\Delta_f H_m^0$ (g) values obtained by RRAO method using CAM-B3LYP/6-311++G(3df,3pd) 5d 7f [86] ($\Delta\Delta H_{RMS} = 0.8$ $\text{kJ}\cdot\text{mol}^{-1}$, Table 7) are in good agreement with the $\Delta_f H_m^0$ (g, exp) values. Furthermore, these values do not differ significantly from the $\Delta_f H^0$ (g, reg) values. Thus, the CAM-B3LYP functional with the 6-311++G(3df,3pd) 5d 7f basis set best estimates the gas phase enthalpy of formation of alkanethiols in the gas phase and can be recommended for estimating the enthalpies of formation of other alkanethiols. The hybrid CAM-B3LYP functional comprises of 0.19 Hartree–Fock (HF) plus 0.81 Becke 1988 (B88) exchange interaction at short-range, and 0.65 HF plus 0.35 B88 at long-range. The intermediate region is smoothly described through the standard error function with parameter 0.33.

The fact that for the first terms of homologous series the enthalpy of formation (-22.5 $\text{kJ}\cdot\text{mol}^{-1}$) is often poorly predicted by a linear equation is not new. Interestingly, the enthalpy of formation of 1-pentanethiol (-108.0 $\text{kJ}\cdot\text{mol}^{-1}$) determined from the linear correlation differs slightly from the experimental value (-109.7 $\text{kJ}\cdot\text{mol}^{-1}$). At the same time, the results of at least three calculation methods (CAM-B3LYP 6-311++G(3df,3pd) 5d 7f, G4 and aLL5) are in excellent agreement with the experimental value for 1-pentanethiol.

Another interesting result is that it is desirable for G-n approaches to take the enthalpies of mixing into account. If this is not done, the deviations can be considerable, using 1-alkanethiols as an example. This is particularly pronounced for compounds with a large number of narrow energy conformers.

The enthalpies of formation of 1-alkanethiols were calculated using the Benson group scheme [85] and are given in Table 7. As can be seen, good agreement between the calculated and experimental values is observed.

In the present work, the enthalpies of formation in the gas phase of 1-octanethiol, 1-nonanethiol, 1-undecanethiol, and 1-dodecanethiol, for

Table 8

Standard enthalpies of formation ($\Delta_f H_m^o$) and vaporization ($\Delta_1^g H_m^o$) of 1-alkanethiols at 298.15 K (in kJ mol⁻¹).

Compound	$\Delta_f H_m^o$ (l) ^a	Ref.	$\Delta_1^g H_m^o$ ^b	$\Delta_f H_m^o$ (g) ^c
methanethiol	-46.4 ± 0.6	[87]	24.0 ± 0.1	-22.4 ± 0.6
ethanethiol	-73.3 ± 0.6	[87]	27.4 ± 0.1	-45.9 ± 0.6
1-propanethiol	-99.5 ± 0.6	[87]	31.9 ± 0.1	-67.6 ± 0.6
1-butanethiol	-124.3 ± 1.2	[87]	36.5 ± 0.2	-87.8 ± 1.2
1-pentanethiol	-150.9 ± 0.8	[87]	41.2 ± 0.3	-109.7 ± 0.8
1-hexanethiol	-175.0 ± 0.9	[87]	45.8 ± 0.4	-129.2 ± 1.1
1-heptanethiol	-200.1 ± 0.9	[87]	50.2 ± 0.6	-149.9 ± 1.3
1-octanethiol	-225.7 ± 2.2 ^d	this work	55.9 ± 1.3	-169.8 ± 1.5 ^e
1-nonanethiol	-250.7 ± 2.5 ^d	this work	60.4 ± 0.7	-190.3 ± 1.5 ^e
1-decanethiol	-276.4 ± 1.4	[87]	65.3 ± 0.4	-211.1 ± 1.5
1-undecanethiol	-300.0 ± 1.7 ^d	this work	69.0 ± 0.8	-231.0 ± 1.5 ^e
1-dodecanethiol	-324.9 ± 1.7 ^d	this work	73.2 ± 0.9	-251.7 ± 1.5 ^e

^a experimental enthalpies of formation of liquid thiols. Uncertainty in the table corresponds to standard uncertainty.

^b critically evaluated vaporization enthalpies at 298.15 K. Uncertainties of the vaporization enthalpies $U(\Delta_1^g H_m^o)$ are the expanded uncertainties (0.95 level of confidence).

^c calculated as a sum of enthalpy of formation and enthalpy of vaporization. Uncertainty in the table corresponds to standard uncertainty.

^d calculated as a difference of the gas-phase enthalpy of formation and enthalpy of vaporization.

^e calculated according to Eq. (13).

which there are no experimental data, were calculated using Eq. (13). The calculated enthalpies of formation and enthalpies of vaporization given in Table 2 were used to estimate the enthalpies of formation of 1-octanethiol, 1-nonanethiol, 1-undecanethiol and 1-dodecanethiol in the liquid state at 298.15 K. The standard thermochemical values for phase transitions and phase formation at 298.15 K were compiled in Table 8.

Enthalpies of formation and vaporization from Table 8 can be useful for calculating the material and heat balance of processes with these compounds.

4. Conclusions

In the present work, the vapor pressures and enthalpies of vaporization of 1-alkanethiols available in the literature have been critically reviewed. After, the reliable enthalpies of vaporization and the enthalpies of solution of 1-pentanethiol, 1-hexanethiol, 1-heptanethiol and 1-octanethiol in *n*-heptane measured in this work were used to determine the experimental enthalpies of solvation. The experimental values of the solvation enthalpy were used to develop a method for calculating the solvation enthalpy based on group additivity. Reliable values of the enthalpies of vaporization and enthalpies of formation in the condensed state were used to determine the experimental enthalpy of formation in the gas phase. Experimental enthalpies of formation in the gas phase were used to find the functional and basis set that best estimate the enthalpy of formation of alkanethiols in the gas phase. It has been shown that the CAM-B3LYP/6-311++G(3df,3pd) 5d 7f, G4 and aLL5 methods can be recommended as an accurate for estimating the enthalpies of formation of other alkanethiols. In the present work, the calculated enthalpies of formation and enthalpy of vaporization, which were also obtained by solution calorimetry, were used to estimate the enthalpies of formation of 1-octanethiol, 1-nonanethiol and 1-decanethiol and 1-dodecanethiol in the liquid state at 298.15 K.

CRedit authorship contribution statement

Ruslan N. Nagrimanov: Supervision, Methodology, Funding acquisition, Conceptualization. **Aliya R. Ibragimova:** Writing – review & editing, Visualization, Resources. **Dmitry A. Kornilov:** Writing – review & editing, Resources. **Aizat A. Samatov:** Writing – review & editing, Resources. **Boris N. Solomonov:** Project administration.

Dzmitry H. Zaitsau: Writing – review & editing, Investigation. **Vladimir V. Turovsev:** Writing – review & editing, Validation, Supervision, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.fluid.2025.114435.

Data availability

All data supporting the results reported in this paper are included in the main text and in the electronic supporting information.

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