Modified solution calorimetry approach for determination of vaporization and sublimation enthalpies of branched-chain aliphatic and alkyl aromatic compounds at T = 298.15 K

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ABSTRACT

The enthalpies of solution, solvation and vaporization/sublimation are interrelated values combined in the simplest thermodynamic circle. Hence, experimental determination of vaporization/sublimation enthalpy can be substituted by experimentally simpler determination of solution enthalpy when solvation enthalpy is known. Previously it was found that solvation enthalpies of a wide range of unbranched aliphatic and aromatic solutes in saturated hydrocarbons are in good linear correlation with their molar refraction values. This allows to estimate the vaporization/sublimation enthalpy of any unbranched organic compound from its solution enthalpy in saturated hydrocarbon and molar refraction. In the present work this approach was modified for determination of vaporization/sublimation enthalpy of branched-chain alkyl aromatic and aliphatic compounds. Group contributions to the enthalpy of solvation due to the branching of carbon chain were evaluated. Enthalpies of solution at infinite dilution of 18 branched-chain aliphatic and alkyl aromatic compounds were measured at T = 298.15 K. Vaporization/sublimation enthalpies for 35 branched aliphatic and alkyl aromatic compounds were determined by using modified solution calorimetry approach. These values are in good agreement with available literature data on vaporization/sublimation enthalpies obtained by conventional methods.

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1. Introduction

The enthalpies of "liquid–gas" and "solid–gas" phase transitions are fundamental characteristics of chemical compounds. Knowledge of these values is of great importance for different fields of chemistry and physics. They have practical application in separation processes, studies of solubility of substances and their distribution in environment. Vaporization/sublimation enthalpies also play an essential role in the analysis of intermolecular interactions in condensed phase. Numerous experimental techniques have been developed for determination of phase transitions enthalpies. Generally, conventional techniques can be divided into two groups: calorimetric techniques, in which the phase change enthalpy is measured directly, and techniques in which vapor pressure is measured directly or indirectly as a function of temperature. Also, some methods based on gas chromatography were developed to measure vaporization enthalpies. All these methods were applied for many years by different groups of authors for the determination of vaporization/sublimation

enthalpies of different series of compounds. The last compilation of vaporization/sublimation enthalpies was published by Acree and Chickos [1]. This database contains thousands of thermochemical values measured during the last two centuries. The analysis of this database shows, that despite the great amount of literature data for some compounds enthalpies of phase transitions are absent or in disarray, especially for large branched organic molecules, which are very often thermally unstable.

It is generally accepted that currently used methods for determination of the enthalpies of vaporization and sublimation are not universal. Their advantages and disadvantages are well documented in the literature [2]. Basically, conventional methods examine the transition of studied substances from a condensed phase to a gas phase at elevated temperatures. In this regard, the researchers who use these methods have problems with the study of low volatile and thermally unstable chemical compounds. Heat capacity difference between two equilibrium phases of a studied compound (solid and gaseous phases in case of sublimation, liquid and gaseous phases in case of vaporization) must be known in order to adjust experimental values by Kirchhoff's equation to the reference temperature which is usually 298.15 K. While the heat capacity in condensed phase can be measured experimentally,

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values of C_p^g are known only for very small molecules. So, various empirical correlations or quantum-chemical calculations are used for estimation of ΔC_p values [3]. Unfortunately, application of such methods for estimation of heat capacity difference makes it difficult to assess the uncertainties of obtained thermochemical data, especially for compounds with high average temperature of measurements (more than 400 to 500 K). Also, polymorphism, possible crystalline phase transitions, even small presence of impurities can affect the results of conventional methods and should be taken into account.

However, there is another way for determination of phase transitions enthalpies directly at $T = 298.15$ K without heating and transfer of compounds to the gas phase. In our previous works [4–6] we proposed the method of determination of vaporization/-sublimation enthalpy through the measurements of solution enthalpies of a studied compound in different solvents. The method is based on the general relationship (equations (1) and (2) depending on the standard state of a solute (liquid or crystal)) between vaporization/sublimation enthalpy of compound A_i, $\Delta_l^g H_m^{A_i}$ ($\Delta_{cr}^g H_m^{A_i}$), and its enthalpies of solution ($\Delta_{soln} H^{A_i/S}$) and solvation ($\Delta_{solv} H^{A_i/S}$) in solvent S.

$$\Delta_{solv} H^{A_i/S} = \Delta_{soln} H^{A_i/S} - \Delta_l^g H_m^{A_i}, \tag{1}$$

$$\Delta_{solv} H^{A_i/S} = \Delta_{soln} H^{A_i/S} - \Delta_{cr}^g H_m^{A_i}. \tag{2}$$

Enthalpy of solution can be measured experimentally using different experimental techniques (solution calorimetry, gas chromatography, etc.). Enthalpy of solvation in case of cyclohexane and other saturated hydrocarbon solvents can be calculated from the empirical linear dependence between these values and solute molar refractions [4]. Recently, solution calorimetry based approach was successfully applied for determination of phase transition enthalpies of aromatic and polyaromatic hydrocarbons [5] and their halogen derivatives [6]. Vaporization/sublimation enthalpies derived by using the proposed method were in good agreement (within experimental uncertainties) with those measured by conventional techniques. At the same time, solution calorimetry approach is less dependent on the purity of the studied compounds and less time consuming compared to the conventional methods. Unfortunately, it ought to be remarked that despite the excellent correlation between enthalpy of solvation and molar refraction for linear aliphatic or aromatic compounds, the solutes with branched-chain alkyl groups fallout from the common dependence [4]. In the present paper, we decided to analyze systematically these deviations. As a result of this analysis, the modified equation for calculation of solvation enthalpy of branched-chain alkyl aromatic and aliphatic compounds in cyclohexane was proposed. The new data on solution and solvation enthalpies of different branched-chain solutes (alkyl aromatic hydrocarbons, halogen derivatives, esters, alcohols, ketones, etc.) in cyclohexane were obtained. Vaporization/sublimation enthalpies of 35 branched-chain aliphatic and alkyl aromatic compounds were determined using modified solution calorimetry approach. These values were tested by the comparison with the available literature data obtained by conventional methods.

2. Experimental

2.1. Materials

Solvent (cyclohexane) and all solutes except for 3-*tert*-butylbiphenyl were high-purity commercial products. They are listed in table 1 with CAS registry numbers, molar masses, origins and commercial purity. 3-*tert*-butylbiphenyl was synthesized and kindly provided by the group of Dr. Tatyana N. Nesterova from Samara State Technical University. Its purity was found to be 0.988 as measured by gas chromatography method described in [7]. All solutes were used without further purification. Cyclohexane for calorimetric experiments was dried by the distillation over the sodium. The residual amount of water in cyclohexane determined by Karl Fischer titration method was less than 0.0001 mass fraction.

2.2. Solution calorimetry

Commercial TAM III precision solution/titration calorimeter (TA-Instruments) was used to measure the solution enthalpies. Experiments were performed at $T = (298.15 \pm 0.01)$ K in a 100 mL glass cell equipped with a gold stirrer. Solid samples were dissolved using the glass ampoule breaking accessory. Liquid solute samples were injected in solvent using the titration technique based on syringe pump. The performance and accuracy of the calorimetric system were tested by measuring the solution enthalpies of potassium chloride in water and of propan-1-ol in water. In both cases our experimental results $(\Delta_{soln} H^{KCl/H_2O}) = (17.41 \pm 0.04 \, kJ \cdot mol^{-1})$ and $(\Delta_{soln} H^{PrOH/H_2O}) = (-10.16 \pm 0.03 \, kJ \cdot mol^{-1})$ were in good agreement with recommended literature data $(\Delta_{soln} H^{KCl/H_2O}) = (17.47 \pm 0.07 \, kJ \cdot mol^{-1})$ [8] and $(\Delta_{soln} H^{PrOH/H_2O}) = (-10.16 \pm 0.02 \, kJ \cdot mol^{-1})$ [9]. The detailed description of the calorimetric experiment was published in previous works [10,11]. All experiments were carried out at infinite dilution conditions. It was confirmed by the constant value of solution enthalpy in the studied range of solute concentrations (see table S1). As an example, figure 1 shows dependence of solution enthalpy of 1,6-dimethylnaphthalene in cyclohexane on solute molality. The linear correlation presented on figure 1 is described by equation $\Delta_{soln} H^{A_i/S} = 5.9(0.1) + 0.01(0.007) \cdot b$. It is evident, that the slope of this dependence close to zero and $\Delta_{soln} H^{A_i/S}$ remains practically constant while the concentration of the solute is increased 6 times.

All experimental enthalpies of solution of studied compounds in cyclohexane measured in this work are listed in table S1 (supplementary material).

2.3. Molar refraction

Values of molar refraction (MR^{A_i}) for the majority of the liquid solutes were calculated using the Lorenz–Lorentz equation (3):

$$MR = \frac{M}{d} \cdot \frac{n^2 - 1}{n^2 + 2}, \tag{3}$$

where M is the molar mass of the solute; d is the density of the liquid solute; n is the refractive index ($\lambda = 589$ nm) of the solute. The latter two parameters for all solutes used in this work were taken from Reaxys database. The values of molar refraction and source data for its calculation are listed in table S2 (supplementary material). For some compounds we could find density and refractive index only at temperatures lower or higher than (298.15 K). We used these values for calculations, because molar refraction of each compound is usually the same at different temperatures. This fact was confirmed experimentally in previous works [6,12]. Also, molar refraction for some crystal solutes was calculated using density and refractive index measured at temperatures slightly higher than melting point due to the absence of experimental data at ($T = 298.15$ K). Additional values of molar refraction listed in table S3 were taken from the literature (on the basis of refractive indices and densities of solutions), or were calculated using the additive scheme.

TABLE 1
Specifications of chemicals studied, their CAS number, source, mass fraction purity, method of purification and final purity.

Chemical name[a]	CAS number	Source	Purity	Purification method	Final purity
sec-Butylbenzene (l)	135-98-8	Aldrich	$\geqslant 0.99$	None	
o-Xylene (l)	95-47-6	Aldrich	$\geqslant 0.99$	None	
m-Xylene (l)	108-38-3	Aldrich	$\geqslant 0.99$	None	
Mesitylene (l)	108-67-8	Aldrich	0.98	None	
1,2,4-Trimethylbenzene (l)	95-63-6	Aldrich	0.98	None	
1,2,4,5-Tetramethylbenzene (cr)	95-93-2	Aldrich	0.98	None	
Hexamethylbenzene (cr)	87-85-4	Aldrich	0.99	None	
Cyclohexylbenzene (l)	827-52-1	Aesar	$\geqslant 0.97$	None	
1-Methylnaphthalene (l)	90-12-0	Aesar	0.96	None	
1,6-Dimethylnaphthalene (l)	575-43-9	Aesar	0.98	None	
4-Methylbiphenyl (cr)	644-08-6	Aldrich	$\geqslant 0.98$	None	
3-tert-Butylbiphenyl (l)	2113-60-2	Synthesized		Distillation	0.988[b]
1,2-Diphenylethane (cr)	103-29-7	Aesar	0.98	None	
Triphenylmethane (cr)	519-73-3	Aldrich	0.99	None	
Tetraphenylmethane (cr)	630-76-2	Aldrich	0.97	None	
Acenaphthene (cr)	83-32-9	Aldrich	0.99	None	
Fluorene (cr)	86-73-7	Aesar	$\geqslant 0.98$	None	
Methyl isobutyrate (l)	547-63-7	Aldrich	0.99	None	
Methyl pivalate (l)	598-98-1	Aldrich	0.99	None	
Cyclohexane (l)	110-82-7	Aldrich	$\geqslant 0.99$	Distillation	0.999[b]

[a] Initial state of studied compounds (solid (cr) or liquid (l)) are denoted in parentheses.
[b] Final purity was analyzed by gas chromatography method.
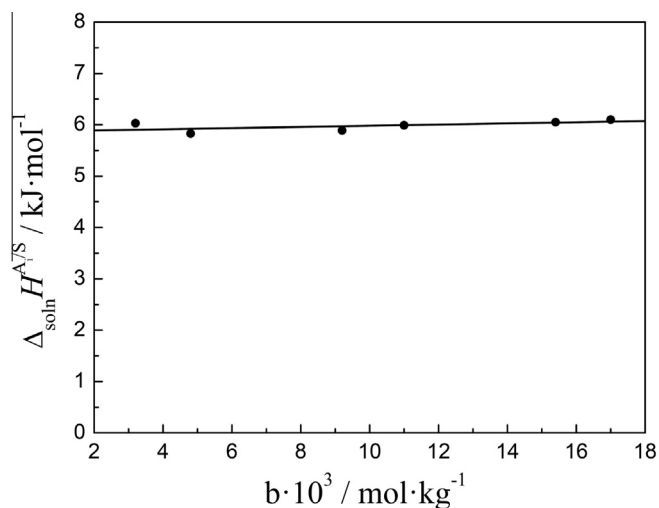
FIGURE 1. Comparison of solution enthalpy of 1,6-dimethylnaphthalene in cyclohexane, $\Delta_{solv}H^{A_i/Alk}$ (kJ · mol^{-1}), with the solute molality, b (10^3 · mol · kg^{-1}). Numeric data are presented in table S1 (supporting information).

3. Methodology

Our method is based on the following principles and definitions.
The molar enthalpy of solvation of solute A_i in the solvent S is the enthalpy change induced by isothermal transfer of solute A_i from the ideal gas state at 0.1 MPa and T = 298.15 K to the solvent S to give a solution of infinite dilution. The molar enthalpy of solution of solute A_i in the solvent S is the enthalpy change when 1 mole of solute A_i dissolves in sufficient amount of solvent S to give a solution of infinite dilution. Infinite dilution condition implies the absence of solute-solute intermolecular interactions in solution, only solute-solvent interactions are possible.

In accordance with equations (1) and (2), we need to know enthalpy of solvation and enthalpy of solution of solute A_i in solvent S in order to obtain enthalpy of vaporization or sublimation. Value of $\Delta_{soln}H^{A_i/S}$ can be measured experimentally at T = 298.15 K. It was shown in previous works [4,13,14] that the enthalpy of solvation in cyclohexane and other unsaturated hydrocarbons ($-\Delta_{solv}H^{A_i/Alk}$) linearly depends on the solute molar

refraction for the solutes with unbranched chain of carbon atoms. This empirical dependence was described by equation (4):

$$-\Delta_{solv}H^{A_i/Alk}/(kJ \cdot mol^{-1}) = 5.09 + 1.03 \cdot MR^{A_i}/(cm^3 \cdot mol^{-1})$$
$$(N = 102; R = 0.994; SD = 1.56 \text{ kJ} \cdot \text{mol}^{-1})$$

(4)

In present work, we recalculated this dependence using additional experimental values of solvation enthalpies in cyclohexane or other unsaturated hydrocarbon solvents [15–26] in addition to ones published in [4]. The experimental values of solvation enthalpy and molar refraction used for correlation are listed in table S4 (supplementary material). The resulting linear dependence is shown on figure 2. It is described by following equation (5):

$$-\Delta_{solv}H^{A_i/Alk}/(kJ \cdot mol^{-1}) = 4.95(0.21)$$
$$+ 1.035(0.006) \cdot MR^{A_i}/(cm^3 \cdot mol^{-1})$$

(5)

$$(N = 139; R = 0.997; SD = 0.91 \text{ kJ} \cdot \text{mol}^{-1})$$
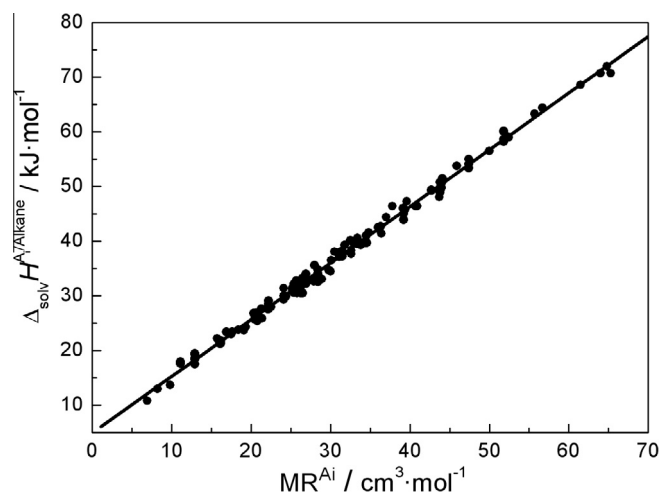
FIGURE 2. Correlation of solvation enthalpy of solute (A_i) in alkane (Alk), $\Delta_{solv}H^{A_i/Alk}$, and solute (A_i) molar refraction, MR^{A_i} (cm^3 · mol^{-1}). Numeric data are presented in table S4 (supporting information).

Actually, there is a good agreement between parameters of equations (4) and (5) within the calculated uncertainties of equation (5) (presented in parentheses) despite the significant increase of data set. Therefore, equation (5) is expected to provide reasonably accurate predictions of the solvation enthalpies for additional unbranched organic solutes whose molar refraction falls within the area of predictive space defined by the molar refractions used in deriving linear correlation.

According to equations (1), (2) and (5), enthalpy of vaporization ($\Delta_l^g H_m^{A_i}$) for liquid solutes and enthalpy of sublimation ($\Delta_{cr}^g H_m^{A_i}$) for solid solutes can be calculated using equations (6) or (7):

$$\Delta_l^g H_m^{A_i}/(kJ \cdot mol^{-1}) = \Delta_{soln}H^{A_i/Alk}/(kJ \cdot mol^{-1}) + 4.95 + 1.035 \cdot MR^{A_i}/(cm^3 \cdot mol^{-1}) \qquad (6)$$

$$\Delta_{cr}^g H_m^{A_i}/(kJ \cdot mol^{-1}) = \Delta_{soln}H^{A_i/Alk}/(kJ \cdot mol^{-1}) + 4.95 + 1.035 \cdot MR^{A_i}/(cm^3 \cdot mol^{-1}) \qquad (7)$$

These equations were successfully used to determine the thermochemical data of unbranched organic compounds. At the same time, solvation enthalpies calculated by equation (5) for branched solutes were always more exothermic than experimental values, and as a consequence, vaporization/sublimation enthalpies estimated by equations (6) and (7) differed from the results of conventional methods published in literature.

The deviations obtained for branched-chain compounds were induced by different dependence of molar refraction and thermochemical data upon structural isomerization of studied molecules. Experimental results show that molar refractions of structural isomers having the same composition are equal. At the same time, their enthalpies of phase transitions are significantly different [1].

We have calculated and systematically analyzed deviations of experimental solvation enthalpies and vaporization/sublimation enthalpies for branched organic compounds from the values determined by equations (5)–(7). We used linear alkanes and their structural isomers for this procedure. The next statements obtained in previous works served as the basis of our analysis:

– vaporization enthalpy of alkane is equal to the solvation enthalpy of alkane in itself with opposite sign [4,13];

$$-\Delta_{solv}H^{Alk_i/Alk} = \Delta_l^g H^{Alk_i} \; (\Delta_{soln}H^{Alk_i/Alk} = 0) \qquad (8)$$

– solvation enthalpies of various solutes in alkanes slightly depend on the nature and branching of alkane as a solvent [4];
– vaporization enthalpies of all alkanes can be considered as the solvation enthalpies of these alkanes in some averaged alkane solvent with opposite sign [13];
– vaporization enthalpies for alkanes of various branching were well determined in literature with high level of precision compared to other compounds [1].

In table S5 (supplementary material) molar refractions, enthalpies of vaporization calculated by equations (6) and (8), experimentally measured enthalpies of vaporization taken from Acree and Chickos database [1] and difference between them for branched-chain alkanes with one and two sp³ tertiary carbon atoms are presented. It is evident, that for all compounds in table S5 the difference between vaporization enthalpies is positive and practically the same for molecules with one and two tertiary carbon atoms independent of the size and composition of the alkane molecule (total number 22 compounds). Average group contribution for branching the alkyl group to each tertiary carbon atom is equal to (1.6 ± 0.3 kJ · mol⁻¹). This value can be used as additive

term in equations (6) and (7) for correct determination of vaporization/sublimation enthalpies of branched-chain molecules.

The same procedure was used for analysis of molecules with quaternary sp³ carbon atoms. Molar refractions, enthalpy values calculated by equations (6) and (8) and experimentally measured vaporizations enthalpies for these compounds are presented in table S6 (totally 10 compounds). For these systems the difference between enthalpy values in columns 3 and 4 in table S6 for alkanes with one quaternary sp³ carbon atom is practically the same and significantly larger than for molecules with tertiary sp³ carbon atom. So, in order to apply equations (6) and (7) for estimation of vaporization/sublimation enthalpy of branched-chain compounds with quaternary carbon atoms at $T = 298.15$ K, we need to use a group contribution term (4.1 ± 0.3 kJ · mol⁻¹). If a molecule has more than one quaternary carbon atom, the total correction term will be equal to a sum of group contributions due to each branching-chain carbon atom in the molecule. For example, in case of 2,2,4,4-tetramethylpentane, which has two quaternary carbon atoms, the correction term is equal (8.2 kJ · mol⁻¹) as expected (table S6).

Deviations of solvation and phase transition enthalpies calculated by equations (5)–(7) from the experimental values can be caused not only by the presence of the tertiary and quaternary sp³ carbon atoms. Similar consideration for alkenes and alkyl aromatic compounds showed, that branching at carbon-carbon double bond corresponds to the correction of (1.0 ± 0.3 kJ · mol⁻¹). This group contribution was evaluated from the comparison of experimental and calculated values of vaporization enthalpies in table S7.

According to the obtained group contributions for aliphatic and alkyl aromatic compounds with tertiary and quaternary sp³ and quaternary sp² carbon atoms, equations (5)–(7) can be transferred to the equations (8)–(10).

$$-\Delta_{solv}H^{A_i/Alk} = 4.95 + 1.035 \cdot MR^{A_i} - \sum Y_j \qquad (9)$$

$$\Delta_l^g H_m^{A_i} = \Delta_{soln}H^{A_i/Alk} + 4.95 + 1.035 \cdot MR^{A_i} - \sum Y_j \qquad (10)$$

$$\Delta_{cr}^g H_m^{A_i} = \Delta_{soln}H^{A_i/Alk} + 4.95 + 1.035 \cdot MR^{A_i} - \sum Y_j, \qquad (11)$$

where $\sum Y_j$ is the sum of group contributions for each type of branching in the solute molecule.

Step-by-step procedure of determination of vaporization enthalpies by modified equation (10) was described in supporting information section for compounds with two (2,3-dimethyl-1-butene) and four (2,2,3,3,4,4,5,5-octamethylhexane) branching carbon atoms. $\Delta_l^g H_m^{A_i}$ values obtained in this work and those from the literature are in excellent agreement.

Only two experimental parameters solution enthalpy and molar refraction are used in equations (9)–(11) for determination of vaporization/sublimation enthalpy. Molar refraction for liquid solutes can be determined using the Lorentz–Lorenz equation (3). This determination for crystal solutes can be performed in suitable solvents but it must be noted that in many cases the appropriate accuracy can be achieved using the simplest additive scheme for the determination of molar refraction. The determination of solution enthalpy in alkane is technically significantly simpler than the measurement of sublimation or vaporization enthalpy. Moreover, solution enthalpy can be measured directly at $T = 298.15$ K in the majority of cases. Value $\sum Y_j$ can be easily obtained from the knowledge of the type (figure 3) and number of branched carbon atoms in a molecule of a studied compound. Modified solution calorimetry approach can be used for determination of vaporization/sublimation enthalpies of branched-chain organic compounds at $T = 298.15$ K without heating of samples and heat capacity adjustments.
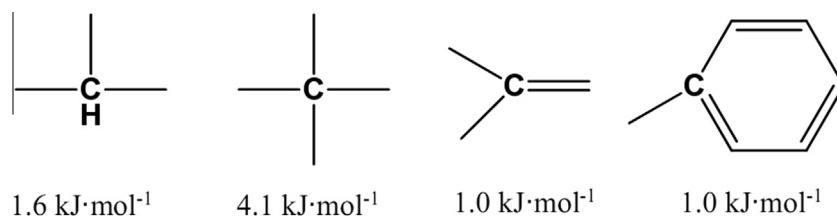
1.6 kJ·mol⁻¹   4.1 kJ·mol⁻¹   1.0 kJ·mol⁻¹   1.0 kJ·mol⁻¹

FIGURE 3. Group contributions, Y_j, to the solvation enthalpy calculated by equation (9) due to branching the carbon atoms.

TABLE 2

Molar refraction (MR^{A_i}), enthalpy of solution in cyclohexane ($\Delta_{soln}H^{A_i/Alk}$), sum of group contribution terms ($\sum Y_j$) due to each branching-chain carbon atom in molecule, enthalpy of solvation in cyclohexane ($\Delta_{solv}H^{A_i/Alk}$) and vaporization/sublimation enthalpy ($\Delta_{cr,l}^g H_m^{A_i}$) determined by equations (10) and (11) for the range of branched-chain alkyl aromatic and aliphatic compounds at T = 298.15 K and 0.1 MPa.[a]

Compound (A_i)[b]	MR^{A_i} cm³ · mol⁻¹	$\Delta_{soln}H^{A_i/Alk}$ kJ · mol⁻¹	$\sum Y_j$ kJ · mol⁻¹	$\Delta_{solv}H^{A_i/Alk}$ kJ · mol⁻¹	$\Delta_{cr,l}^g H_m^{A_i}$ [m] kJ · mol⁻¹
Toluene (l)	31.1	2.94 ± 0.03[c]	1.0	−36.1	39.1
sec-Butylbenzene (l)	45.0	2.34 ± 0.03	1.0 + 1.6	−48.9	51.3
tert-Butylbenzene (l)	45.0	2.18 ± 0.21[d]	1.0 + 4.1	−46.4	48.6
o-Xylene (l)	35.8	3.18 ± 0.05	2·1.0	−40.0	43.2
m-Xylene (l)	35.8	3.22 ± 0.04	2·1.0	−40.0	43.2
p-Xylene (l)	36.0	3.6 ± 0.1[e]	2·1.0	−40.2	43.8
Mesitylene (l)	40.7	3.92 ± 0.03 (4.1 ± 0.2)[f]	3·1.0	−44.1	48.0
1,2,4-Trimethylbenzene (l)	40.6	3.68 ± 0.04	3·1.0	−44.0	47.7
1,2,4,5-Tetramethylbenzene (cr)	45.4	25.4 ± 0.1	4·1.0	−47.9	73.3
Hexamethylbenzene (cr)	55.3	24.9 ± 0.3	6·1.0	−56.2	81.1
Cyclohexylbenzene (l)	51.8	2.31 ± 0.02	1.0	−57.6	59.9
1-Methylnaphthalene (l)	49.1	5.1 ± 0.2	1.0	−54.8	59.9
1,6-Dimethylnaphthalene (l)	53.8	5.98 ± 0.04	2·1.0	−58.6	64.6
4-Methylbiphenyl (cr)	56.7	21.5 ± 0.2	1.0	−62.6	84.1
3-tert-Butylbiphenyl (l)	71.2	4.09 ± 0.05	1.0 + 4.1	−73.5	77.6
9-Methylanthracene (cr)	69.6	24.4 ± 0.2[d]	1.0	−76.0	100.4
9,10-Dimethylanthracene (cr)	74.5	31.3 ± 0.8[g]	2·1.0	−80.1	111.4
1,2-Diphenylethane (cr)	60.4	27.1 ± 0.4	2·1.0	−65.5	92.6
Triphenylmethane (cr)	81.9	24.7 ± 0.1	3·1.0	−86.7	111.4
Tetraphenylmethane (cr)	106.7	28.9 ± 0.4	4·1.0	−111.4	140.3
Acenaphthene (cr)	52.0	26.05 ± 0.03	2·1.0	−56.8	82.8
Fluorene (cr)	54.7	25.01 ± 0.04	2·1.0	−59.6	84.6
2-Methylpropan-2-amine (l)	24.2	5.15 ± 0.13[d]	4.1	−25.9	31.0
2-Chloro-2-methylpropane (l)	25.5	2.26 ± 0.08[d]	4.1	−27.2	29.5
2-Bromo-2-methylpropane (l)	28.9	2.22 ± 0.13[d]	4.1	−30.8	33.0
2-Iodo-2-methylpropane (l)	34.8	2.01 ± 0.08[h]	4.1	−36.9	38.9
2-Methylpropane-2-thiol (l)	28.7	2.80 ± 0.13[d]	4.1	−30.6	33.4
3-Methylbutan-1-ol (l)	26.8	23.0 ± 0.4[d]	1.6	−31.1	54.1
3-Methylbutan-2-one (l)	25.6	7.53 ± 0.10[i]	1.6	−29.8	37.4
3,3-Dimethylbutan-2-one (l)	29.7	7.65 ± 0.09[i]	4.1	−31.6	39.3
2,2,4,4-Tetramethylpentan-3-one (l)	43.7	4.18 ± 0.13[j]	2·4.1	−42.0	46.2
Methyl isobutyrate (l)	26.9	6.47 ± 0.06 (6.47 ± 0.1)[i]	1.6	−31.2	37.7
Methyl pivalate (l)	31.5	6.50 ± 0.07 (6.50 ± 0.08)[i]	4.1	−33.5	40.0
m-Cresol (cr)	32.8	25.2 ± 0.7[k]	1.0	−37.9	63.1
2,6-Di-tert-butylphenol (cr)	65.6	19.7 ± 0.8[l]	2·(4.1 + 1.0)	−62.6	82.3

[a] Standard uncertainties u are $u(T)$ = 0.01 K, $u(p)$ = 10 kPa. Uncertainties of solution enthalpy correspond to the combined expanded uncertainty of the mean with a level of confidence 0.95.
[b] Initial state of studied compounds (solid (cr) or liquid (l)) are denoted in parentheses.
[c] Reference [27].
[d] Reference [4].
[e] Reference [28].
[f] Reference [29].
[g] Reference [30].
[h] Reference [31].
[i] Reference [17].
[j] Reference [32].
[k] Reference [33].
[l] Reference [34].
[m] Sublimation enthalpy, $\Delta_{cr}^g H_m^{A_i}$, is placed to this column for crystal substances and vaporization enthalpy, $\Delta_l^g H_m^{A_i}$, for liquid substances.

4. Results and discussion

Enthalpies of solution in cyclohexane for branched-chain alkyl aromatic and aliphatic compounds ($\Delta_{soln}H^{A_i/Alk}$) at T = 298.15 K measured in this work and taken from literature are listed in table 2. For mesitylene, methyl pivalate and methyl isobutyrate our calorimetric results are in good agreement with available literature values (see table 2). This fact confirms the reliability of our

experimental data. Values of $\Delta_{soln}H^{A_i/Alk}$ for all solutes are above zero. Consequently, the process of dissolution of studied compounds in cyclohexane is endothermic. Enthalpies of solution for liquid solutes are always less positive than for solid ones due to energy costs on breaking of crystal packing. Dissolution of liquid alkyl benzenes in cyclohexane induces practically the same enthalpy change (2 to 3 kJ · mol⁻¹) despite the different length, quantity and position of alkyl groups in a molecule. The same is true

TABLE 3

Comparison of average literature data on enthalpies of vaporization/sublimation, $\Delta_{cr,l}^{g}H_{m}^{A_i}$, of branched-chain alkyl aromatic and aliphatic compounds with the values obtained in this work.

Compound $(A_i)^a$	$\Delta_{cr}^{g}H_{m}^{A_i}$ for crystal and $\Delta_{l}^{g}H_{m}^{A_i}$ for liquid compounds (kJ · mol^{-1}, T = 298.15 K)		
	Average literature values^b	This work	Δ
Toluene (l)	38.0	39.1	1.1
sec-Butylbenzene (l)	48.8	51.3	2.5
tert-Butylbenzene (l)	48.1	48.6	0.5
o-Xylene (l)	43.2	43.2	0.0
m-Xylene (l)	42.7	43.2	0.5
p-Xylene (l)	42.5	43.8	1.3
Mesitylene (l)	47.4	48.0	0.6
1,2,4-Trimethylbenzene (l)	47.9	47.7	−0.2
1,2,4,5-Tetramethylbenzene (cr)	72.9	73.3	0.4
Hexamethylbenzene (cr)	84.2	81.1	−3.1
Cyclohexylbenzene (l)	60.4	59.9	−0.5
1-Methylnaphthalene (l)	61.2	59.9	−1.3
1,6-Dimethylnaphthalene (l)	63.6	64.6	1.0
4-Methylbiphenyl (cr)	81.5	84.1	2.6
3-*tert*-Butylbiphenyl (l)	77.1	77.6	0.5
9-Methylanthracene (cr)	101.8	100.4	−1.4
9,10-Dimethylanthracene (cr)	113.0	111.4	−1.6
1,2-Diphenylethane (cr)	91.5	92.6	1.1
Triphenylmethane (cr)	107.3	111.4	4.1
Tetraphenylmethane (cr)	140.0	140.3	0.3
Acenaphthene (cr)	84.0	82.8	−1.2
Fluorene (cr)	84.9	84.6	−0.3
Butan-2-amine (l)	32.7	33.6	0.9
2-Methylpropan-2-amine (l)	30.1	31.0	0.9
2-Chloro-2-methylpropane (l)	28.8	29.5	0.7
2-Bromo-2-methylpropane (l)	31.4	33.0	1.6
2-Iodo-2-methylpropane (l)	36.2	38.9	2.7
2-Methylpropane-2-thiol (l)	30.8	33.4	2.6
3-Methylbutan-1-ol (l)	54.1	54.1	0.0
3-Methylbutan-2-one (l)	36.9	37.4	0.5
3,3-Dimethylbutan-2-one (l)	38.1	39.3	1.2
2,2,4,4-Tetramethylpentan-3-one (l)	45.4	46.2	0.8
Methyl isobutyrate (l)	38.1	37.7	-0.4
Methyl pivalate (l)	39.5	40.0	1.2
m-Cresol (cr)	61.7	63.1	1.4
2,6-Di-*tert*-butylphenol (cr)	83.1	82.3	−0.8

^{a} Initial state of studied compounds (solid (cr) or liquid (l)) are denoted in parentheses.
^{b} Available literature data used for calculations of the average values are presented in Table S8 (Supporting Material) together with original references.
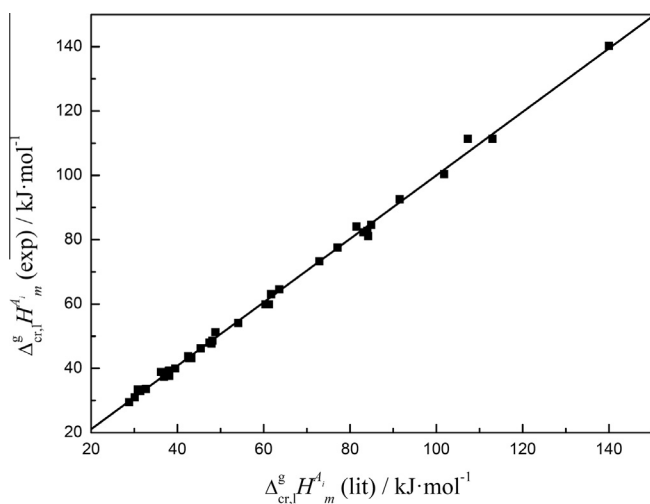
for alkyl naphthalenes, but enthalpy of solution for these compounds (5 to 6 kJ · mol^{-1}) is twice as large as that of alkyl benzenes. In case of aliphatic compounds, halogen alkanes have smaller values of $\Delta_{soln}H^{A_i/Alk}$ than ketones, acetates and amines. The most endothermic dissolution for liquid solutes was obtained for alcohols due to the breaking of their hydrogen bonded associative species in cyclohexane. Table 2 also contains values of solute molar refraction (MR^{A_i}). In this work, 35 branched chain alkyl aromatic and aliphatic compounds, which represent different classes of organic substances, were studied. For each compound the value of $\sum Y_j$ required for application of equations (9)–(11) was calculated on the basis of group contribution terms (figure 3) and quantity of tertiary or quaternary carbon atoms in molecule. These values are presented in table 2. The last two columns of table 2 contain values of solvation enthalpy ($\Delta_{solv}H^{A_i/Alk}$) calculated by equation (9) and values of vaporization/sublimation enthalpy ($\Delta_{cr,l}^{g}H_{m}^{A_i}$) calculated by equations (10) or (11). These data are referred directly to the reference temperature T = 298.15 K. Obtained enthalpies of vaporization of *ortho*-, *meta*- and *para*-xylenes are equal, as well as enthalpies of vaporization of mesitylene and 1,2,4-trimethylbenzene. It means that the position of alkyl group in aromatic ring does not affect the vaporization enthalpy.

Table 3 compares the vaporization/sublimation enthalpies obtained in the present work with the averaged values from the literature. The majority of literature data were taken from the most comprehensive collection of phase transition enthalpies [1]. Original references are collected in table S8 of supplementary material. We selected only data adjusted to the T = 298.15 K in the original papers. The difference (Δ) between averaged literature data and results obtained using modified solution calorimetry approach is shown in the last column of table 3. Generally, this deviation is quite comparable with the uncertainties ascribed to the experimental values. On figure 4 the graphical comparison is shown in order to better represent the good agreement between the literature and calculated vaporization/sublimation enthalpies. The average deviation for all 35 studied compounds is equal to (1.2 kJ · mol^{-1}). For more than half of the studied compounds, difference is less than (1.0 kJ · mol^{-1}). Such a good agreement between thermochemical data confirms the applicability of the modified solution calorimetry approach for determination of vaporization/sublimation enthalpies of branched chain aromatic and aliphatic compounds.

It must be kept in mind that calculation of averaged literature enthalpies was performed without any filtration of evidently dissimilar literature data. At the same time, the relatively higher deviations are observed for solid compounds with low vapor pressure such as hexamethylbenzene and triphenylmethane. But it should be noted that the difference between the results of conventional methods obtained by different authors for these compounds is also significantly higher. Consequently, modified solution calorimetry based approach can be used to resolve the contradiction within the available literature data.

5. Conclusion

We have expanded the applicability of our method for determination of vaporization and sublimation enthalpies through the determination of solution enthalpy in cyclohexane. This expansion was made by including the group contribution terms due to the definite type of branching in solute molecule into the enthalpy of solvation. We have demonstrated that the solution calorimetry based approach can be used for a quick and reliable evaluation of vaporization/sublimation enthalpies of branched-chain organic compounds. This method is less dependent on the purity of studied

FIGURE 4. Comparison of vaporization/sublimation enthalpies of alkyl aromatic compounds obtained in this work by solution calorimetry approach with average literature values (all values refer to T = 298.15 K).

compounds. In this work it was shown that the average deviation of $\Delta_l^g H_m$ and $\Delta_{cr}^g H_m$ values for 35 different branched chain alkyl aromatic and aliphatic compounds determined by SC method from the results of conventional methods is less than $1.2 \text{ kJ} \cdot \text{mol}^{-1}$. The modified solution calorimetry based approach has proved to be highly suitable for thermally unstable branched chain organic compounds and to provide the results directly at the reference temperature 298.15 K.

Acknowledgement

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jct.2015.07.037.

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