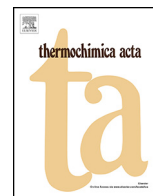




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Enthalpies of solution, enthalpies of fusion and enthalpies of solvation of polyaromatic hydrocarbons: Instruments for determination of sublimation enthalpy at 298.15 K

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ABSTRACT

In this work a simple method for calculation of solvation enthalpies of polyaromatic hydrocarbons (PAHs) in various solvents at 298.15 K was proposed. According to this method the enthalpy of solvation of any polyaromatic hydrocarbon in a particular solvent can be calculated on the basis of the general formula of the compound, the solvation enthalpy of benzene in the same solvent and parameter related to the contribution of hydrogen atom into solvation enthalpy. The validity of the proposed method was confirmed by the comparison of calculated and experimentally measured values of solvation enthalpies of PAHs in benzene, tetrahydrofuran and acetonitrile. This method was used for determination of the sublimation enthalpy of PAHs at 298.15 K based on the general relationship between the enthalpy of sublimation/vaporization of the compound of interest and its enthalpies of solution and solvation in the same solvent at 298.15 K. Enthalpies of solution at infinite dilution of several PAHs were measured in acetonitrile, benzene and tetrahydrofuran at 298.15 K. It was shown that solution enthalpies of PAHs in benzene at 298.15 K are approximately equal to their fusion enthalpies at the melting temperature. Solvation enthalpies of 15 PAHs at 298.15 K calculated according to the proposed method together with corresponding fusion enthalpy values (at the melting temperature) were used to calculate the sublimation enthalpy values at 298.15 K. Comparison of the obtained results with recommended values of sublimation enthalpy shows that fusion enthalpies at the melting temperature can be used instead of the solution enthalpies in benzene at 298.15 K for calculation of the sublimation enthalpy at 298.15 K.

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1. Introduction.

Many polyaromatic hydrocarbons (PAHs) possess carcinogenic properties. Significant amount of PAHs are entering the environment via high-temperature processes in chemical and petrochemical industries. Because of this, the research on thermodynamics of phase transitions of PAHs is a topic of constant interest. A number of studies on this problem were reported earlier [1–6]. Most comprehensive collections of data on enthalpies of vaporization and sublimation of PAHs are presented in [1,2,7].

A large number of methods for determining the enthalpy of vaporization and sublimation exist. All of them are based on different fundamental principles and have some strong and weak sides, which were discussed earlier [8]. In previous works [1,9–11] we

developed an approach for experimental determination of liquid-vapor and solid-vapor phase transition enthalpies using solution calorimetry technique at 298.15 K. It is based on the general relationship between the enthalpy of sublimation/vaporization of the compound of interest and its enthalpies of solution and solvation in the same solvent at 298.15 K. Enthalpy of solvation is calculated based on the linear correlation between molar refraction (determined from the experimental data of density and refractive index) and enthalpy of solvation [1,9,10,12,13] or using an additive scheme [11]. Enthalpy of solution is measured experimentally by direct solution calorimetry technique. This approach has some advantages. First, results are derived directly at the reference temperature 298.15 K (ambiguous temperature adjustment is not required) without transfer of molecule of interest to the gas phase. Second, it can be applied for studies of thermally unstable and/or explosive compounds. Third, solution calorimetry measurements are quick and less demanding as compared to conventional methods. In recent work [1], we applied this approach for

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Table 1
Enthalpy of solvation of benzene, one C–H fragment of benzene and “quasi” hydrogen atom (q_s) in various solvents at 298.15 K.

| Solvent S | $\Delta_{\text{solv}}H^{\text{C}_6\text{H}_6/\text{S}}(\text{kJ mol}^{-1})$ | $1/6 \cdot \Delta_{\text{solv}}H^{\text{C}_6\text{H}_6/\text{S}}(\text{kJ mol}^{-1})$ | q_s (kJ mol^{-1}) |
|-----------------|---|---|-----------------------------------|
| Acetonitrile | –32.2 | –5.37 | –0.66 |
| Benzene | –34.8 | –5.80 | –1.08 |
| Tetrahydrofuran | –36.3 | –6.05 | –0.68 |

determination of sublimation and vaporization enthalpies of aromatic and polyaromatic hydrocarbons based on their solution enthalpies at 298.15 K in benzene and their molar refractions. However, in some cases measurements of experimental data required for calculations of molar refraction of the compounds of interest were impossible due to poor solubility of polyaromatic compounds and/or highly colored solutions. The latter finding does not allow the correct refractive index determination. Therefore, it is difficult to access the enthalpy of solvation of the studied compound and consequently its enthalpy of sublimation. In present work, we propose another simple method for the calculation of enthalpy of solvation of PAHs in various solvents (for example, benzene, tetrahydrofuran or acetonitrile) at 298.15 K, which is based on the use of a simple additive scheme. We also found new relationships between values of solution enthalpy of PAHs in benzene at 298.15 K and their enthalpies of fusion at the melting temperature. All these findings were applied for development of the new less time consuming method for the determination of sublimation enthalpies of PAHs directly at 298.15 K without any adjustments. This method will be especially useful for the cases when solution enthalpy measurement is impossible.

2. Experimental part

2.1. Materials

All PAHs were of the commercial origin with the mass fraction better than 0.97 (Table S1). They were used without any purification. All solvents were carefully purified before usage (see Table S1). Benzene was purified by shaking with the concentrated H_2SO_4 , NaOH and water and distilled over the CaH_2 . Acetonitrile was dried with P_2O_5 and distilled afterward from anhydrous K_2CO_3 in order to remove traces of phosphorus oxide. Tetrahydrofuran was refluxed with and distilled from LiAlH_4 . Solvents purity was analyzed using Agilent 7890 B gas chromatograph (GC) equipped with the flame ionization detector. Water content in solvent studied was controlled by Karl Fisher titration technique.

2.2. Solution calorimetry

Solution enthalpies of PAHs in three solvents (benzene, acetonitrile and tetrahydrofuran) were measured using TAM III isothermal solution calorimeter. The procedure of measurements was described in detail previously [1,14]. Calorimeter was tested by determination of the solution enthalpy of potassium chloride in water ($\Delta_{\text{solv}}H^{\text{KCl}/\text{H}_2\text{O}} = 17.41 \pm 0.04 \text{ kJ mol}^{-1}$) at $T = 298.15 \text{ K}$. The resulting value was in good agreement with the standard literature value ($\Delta_{\text{solv}}H^{\text{KCl}/\text{H}_2\text{O}} = 17.47 \pm 0.07 \text{ kJ mol}^{-1}$) [15]. Masses of samples were determined using an analytical balance (Sartorius MSA225s-1ce-di) with a precision of 0.01 mg. Dissolution experiments were carried out for molalities of the solutes in the range from 1.22 to 20.64 mmol kg^{-1} . For each solute-solvent system solution enthalpies were measured at least 4 times (Table S2). Values of solution enthalpy in studied concentration range were practically constant which proves infinite dilution conditions.

3. Methodology

Method for determination of vaporization/sublimation enthalpies is based on the following principles and definitions. The enthalpy of solvation of solute A_i in the solvent S ($\Delta_{\text{solv}}H^{A_i/\text{S}}$) is the enthalpy of isothermal transfer of solute A_i from the ideal gas state to an infinitely diluted solution in solvent S at the 298.15 K and 0.1 MPa. The solution enthalpy of solute A_i in solvent S ($\Delta_{\text{solv}}H^{A_i/\text{S}}$) is the enthalpy of transfer of A_i from its standard state (solid, liquid or gas) to an infinitely diluted solution in solvent S at the 298.15 K and 0.1 MPa. Enthalpy of solvation and enthalpy of solution at 298.15 K of solid compound are related to the molar enthalpy of sublimation ($\Delta_{\text{cr}}^g H^{A_i}$) at 298.15 K as follows:

$$\Delta_{\text{cr}}^g H_{\text{m}}^{A_i}(298.15) = \Delta_{\text{solv}}H^{A_i/\text{S}}(298.15) - \Delta_{\text{solv}}H^{A_i/\text{S}}(298.15) \quad (1)$$

According to the Eq. (1) in order to determine sublimation enthalpy at 298.15 K one needs to obtain solution and solvation enthalpies of A_i in a solvent S at 298.15 K.

In this work we propose a new scheme for calculation of the solution enthalpy of PAHs in any solvent S, which is based on the following statements. The general formula of PAHs is C_nH_{n-y} , where n is a number of carbon atoms, y represents the difference between the quantity of carbon and hydrogen atoms. Simplest aromatic hydrocarbon is benzene. The enthalpy of solvation of benzene in any solvent can be represented as a sum of enthalpies of solvation of 6 C–H fragments. Thus, contribution of each C–H fragment is equal to one of sixth parts of its solvation enthalpy. Using the value of C–H fragment contribution into solvation enthalpy of benzene and the quantity of carbon atoms in other PAHs we can calculate corresponding solvation enthalpy. However, we need to take into account that in polycondensed compounds some of the carbon atoms are substituted completely and instead of C–H fragments, we deal with quaternary carbon atom. It can be done by the extraction of hydrogen atom contribution to the solvation enthalpy of C–H fragment. Consequently, Eq. (2) can be suggested for calculation of solvation enthalpy of any PAH:

$$\Delta_{\text{solv}}H^{\text{C}_n\text{H}_{n-y}/\text{S}} = n \cdot \frac{1}{6} \cdot \Delta_{\text{solv}}H^{\text{C}_6\text{H}_6/\text{S}} - q_s \cdot y \quad (2)$$

where n is a number of carbon atoms in PAH molecule; y is a difference between quantity of carbon and hydrogen atoms in PAH molecule; $\Delta_{\text{solv}}H^{\text{C}_6\text{H}_6/\text{S}}$ is the solvation enthalpy of benzene in solvent S; q_s is “quasi” enthalpy of solvation of hydrogen atom which was calculated by the optimization method using available experimental data of solvation enthalpies of PAHs in the solvent of interest.

We chose three solvents: acetonitrile, benzene and tetrahydrofuran in order to test the validity of Eq. (2). In Table 1 solvation enthalpies of benzene in these solvents along with calculated q_s values are presented. Detailed description of procedure for estimation of q_s values was added to the Supplementary material. It is evident from Table 1 that values of $\Delta_{\text{solv}}H^{\text{C}_6\text{H}_6/\text{S}}$ are differed depending the solvent.

Another term in Eq. (1) required for determination of sublimation enthalpy is enthalpy of solution. This value is usually determined experimentally by the solution calorimetry technique. But for some compounds it cannot be measured due to low solubility, especially for solid high molecular weight polyaromatic

Table 2Comparison of solution enthalpies of PAHs in benzene at 298.15 K ($\Delta_{\text{soln}}^{\text{H}^{\text{A}_i}/\text{C}_6\text{H}_6}$) and their fusion enthalpies ($\Delta_{\text{cr}}^{\text{H}^{\text{A}_i}}$) at melting temperature (T_m) and adjusted to 298.15 K.

| Compounds | $\Delta_{\text{soln}}^{\text{H}^{\text{A}_i}/\text{C}_6\text{H}_6}$ (kJ mol ⁻¹) | $\Delta_{\text{cr}}^{\text{H}^{\text{A}_i}}(T_m)$ (kJ mol ⁻¹) | T_m (K) | $\Delta_{\text{cr}}^{\text{H}^{\text{A}_i}}(298.15)^{\text{g}}$ (kJ mol ⁻¹) |
|--------------------------|--|--|--------------|--|
| Phenanthrene | 17.7 ± 0.1 ^a | 16.46 ^d | 347.5 | 12.9 ± 1.3 |
| Naphthalene | 17.7 ± 0.1 ^b | 19.06 ^d | 353.5 | 16.9 ± 0.7 |
| Azulene | 18.1 ± 0.2 ^a | 17.53 ^d | 373.0 | 14.54 |
| Fluoranthene | 18.1 ± 0.2 ^a | 18.73 ^d | 383.3 | 13.9 ± 1.6 |
| Pyrene | 16.3 ± 0.2 ^a | 17.36 ^d | 423.8 | 10.2 ± 2.3 |
| 1,2-Benzanthracene | 19.1 ± 0.1 ^a | 21.40 ^d | 434.3 | 12.9 ± 2.8 |
| Anthracene | 24.7 ± 0.3 ^b | 28.20 ± 0.01 ^e | 489.7 | 18.4 |
| Chrysene | 26.0 ± 0.1 ^c | 26.20 ^d | 531.4 | 14.8 ± 4.8 |
| 1,2,5,6-Dibenzanthracene | 28.1 ± 0.5 ^a | 28.40 ^f | 539.7 | 10.0 |

^a Solution enthalpy of PAHs in benzene taken from [1]. Uncertainties correspond to standard deviation.^b Solution enthalpy of PAHs in benzene taken from [12]. Uncertainties correspond to standard deviation.^c Solution enthalpy measured in this work. Uncertainties correspond to expanded uncertainties of the mean U (0.95 level of confidence, Student's *t* distribution 2.0).^d Recommended values of fusion enthalpy of PAHs at melting temperature in [7].^e Fusion enthalpy of anthracene at melting temperature measured in [17].^f Fusion enthalpy of 1,2,5,6-dibenzanthracene at melting temperature measured in [18].^g Enthalpies of fusion of PAHs adjusted to 298.15 K by Chickos et al. [19] method.

compounds. In these cases we need to replace this value in Eq. (1) on something else that can be measured experimentally.

Solution enthalpy of solid PAH at infinite dilution in benzene can be divided on three main terms: breaking of solute crystal lattice (endothermic), breaking of solute–solute intermolecular interactions (endothermic) and formation of solute–solvent intermolecular contacts (exothermic). PAHs contain only benzene fragments. Consequently, intermolecular interactions of PAHs molecules with each other or with benzene as a solvent should be similar. Summing up all these points we can conclude that the value of the solution enthalpy of any solid PAH in benzene is mainly determined by the contribution of the crystal lattice breaking. One can say that there is another thermochemical value which is responsible for the same process (breaking of crystal lattice). This is fusion enthalpy of PAH.

The relation between fusion and solution enthalpy of solute can be demonstrated as follows: in addition to the Eq. (1) sublimation enthalpy can be represented as a sum of fusion enthalpy ($\Delta_{\text{cr}}^{\text{H}^{\text{A}_i}}$) and vaporization enthalpy ($\Delta_{\text{l}}^{\text{H}^{\text{A}_i}}$) at 298.15 K (3):

$$\Delta_{\text{cr}}^{\text{H}^{\text{A}_i}}(298.15) = \Delta_{\text{cr}}^{\text{H}^{\text{A}_i}}(298.15) + \Delta_{\text{l}}^{\text{H}^{\text{A}_i}}(298.15) \quad (3)$$

Combination of Eqs. (1) and (3) gives Eq. (4):

$$\begin{aligned} \Delta_{\text{soln}}^{\text{H}^{\text{A}_i}/\text{S}}(298.15) - \Delta_{\text{soln}}^{\text{H}^{\text{A}_i}/\text{S}}(298.15) \\ = \Delta_{\text{cr}}^{\text{H}^{\text{A}_i}}(298.15) + \Delta_{\text{l}}^{\text{H}^{\text{A}_i}}(298.15) \end{aligned} \quad (4)$$

For solutes in liquid state vaporization enthalpy can be presented by Eq. (5):

$$\Delta_{\text{l}}^{\text{H}^{\text{A}_i}}(298.15) = \Delta_{\text{soln}}^{\text{H}^{\text{A}_i}/\text{S}}(298.15) - \Delta_{\text{soln}}^{\text{H}^{\text{A}_i}/\text{S}}(298.15) \quad (5)$$

If solute and solvent possess similar physical–chemical properties and structure (“like dissolves like”), then $\Delta_{\text{soln}}^{\text{H}^{\text{A}_i}/\text{S}}$ is close to zero, e.g. liquid *n*-hexadecane in *n*-heptane (0.46 kJ mol⁻¹ [16]) or 1-phenylnaphthalene in benzene (0.56 kJ mol⁻¹ [1]). In these cases solvation enthalpy of A_i in solvent S can be approximately equal to the vaporization enthalpy of A_i with opposite sign:

$$\Delta_{\text{soln}}^{\text{H}^{\text{A}_i}/\text{S}}(298.15) \approx -\Delta_{\text{l}}^{\text{H}^{\text{A}_i}}(298.15) \quad (6)$$

So, for similar solute and solvent molecules, e.g. aromatic hydrocarbons, we can convert Eq. (4) to the Eq. (7) taking into account Eq. (6):

$$\Delta_{\text{soln}}^{\text{H}^{\text{A}_i}/\text{S}}(298.15) \approx \Delta_{\text{cr}}^{\text{H}^{\text{A}_i}}(298.15) \quad (7)$$

Benzene is the simplest aromatic hydrocarbon and represents the best solvent for other aromatic hydrocarbons according to

“like dissolves like” principle. In Table 2 enthalpies of solution of a number of PAHs in benzene at 298.15 K are compared with the recommended literature values of fusion enthalpies of PAHs at the melting temperature and adjusted to 298.15 K. Values of $\Delta_{\text{cr}}^{\text{H}^{\text{A}_i}}$ were taken from comprehensive work [7] or from more recent papers [17,18]. Adjustment of the enthalpies of fusion at melting temperature to 298.15 K in work [7] and in this work was carried out by empirical procedure suggested by Chickos et al. [19]. The comparison shows that in most cases solution enthalpies of PAHs in benzene at 298.15 K are unexpectedly closer to the fusion enthalpies at melting temperature rather than to the fusion enthalpies empirically adjusted to 298.15 K. Differences between enthalpies of solution and enthalpies of fusion at the melting temperature is within (± 1.5 kJ mol⁻¹) in most cases. Only fusion enthalpies of anthracene and 1,2-benzanthracene differ on 3.5 and 2.3 kJ mol⁻¹, but in these cases solution enthalpies at 298.15 K are still closer to the fusion enthalpies at the melting temperature than to the fusion enthalpies extrapolated to 298.15 K.

According to the data in Table 2, fusion enthalpy of studied compounds at melting temperature is equal to the enthalpy of solution at 298.15:

$$\Delta_{\text{soln}}^{\text{H}^{\text{A}_i}/\text{S}}(298.15) \approx \Delta_{\text{cr}}^{\text{H}^{\text{A}_i}}(T_m) \quad (8)$$

Combination of Eqs. (7) and (8) gives Eq. (9):

$$\Delta_{\text{cr}}^{\text{H}^{\text{A}_i}}(298.15) \approx \Delta_{\text{cr}}^{\text{H}^{\text{A}_i}}(T_m) \quad (9)$$

Thus, fusion enthalpies of studied in this work compounds should not be substantially dependent on the temperature.

Eq. (1) therefore can be transformed into Eq. (10) where fusion enthalpy at the melting temperature ($\Delta_{\text{cr}}^{\text{H}^{\text{A}_i}}(T_m)$) is taken instead of solution enthalpy at 298.15 K ($\Delta_{\text{soln}}^{\text{H}^{\text{A}_i}/\text{S}}$):

$$\Delta_{\text{cr}}^{\text{H}^{\text{A}_i}}(298.15 \text{ K}) = \Delta_{\text{cr}}^{\text{H}^{\text{A}_i}}(T_m) - \Delta_{\text{soln}}^{\text{H}^{\text{A}_i}/\text{S}}(298.15 \text{ K}) \quad (10)$$

Certainly, for correct application of Eq. (10) all polymorphic transitions happening between 298.15 K and the melting temperature should be taken into account, because they will affect the equality between solution enthalpy in benzene at 298.15 K and fusion enthalpy at melting temperature. Therefore, additional terms corresponding to the enthalpies of polymorphic transitions between 298.15 K and T_m should be added to the fusion enthalpy ($\Delta_{\text{cr}}^{\text{H}^{\text{A}_i}}(T_m)$) in Eq. (10).

4. Results and discussion

In Table 3 solvation enthalpies of several PAHs in various solvents (benzene, acetonitrile, tetrahydrofuran) determined by

Table 3
Comparison between experimental and calculated solvation enthalpies of PAHs in various solvents at 298.15 K.

| Compounds | $-\Delta_{\text{sol}}H_{\text{int}}^{\text{A}_i}/S$ (exp) ^a (kJ mol ⁻¹) | $-\Delta_{\text{sol}}H_{\text{int}}^{\text{A}_i}/S$ (MR) ^b (kJ mol ⁻¹) | $-\Delta_{\text{sol}}H_{\text{int}}^{\text{A}_i}/S$ (Abr) ^c (kJ mol ⁻¹) | $-\Delta_{\text{sol}}H_{\text{int}}^{\text{A}_i}/S$ (Eq. (2)) ^d (kJ mol ⁻¹) |
|----------------------------|---|--|---|---|
| 1 | 2 | 3 | 4 | 5 |
| S – Benzene | | | | |
| Azulene | 56.1 | 55.2 | – | 55.8 |
| Naphthalene | 54.9 | 54.7 | 54.9 | 55.8 |
| Anthracene | 77.2 | 77.4 | 76.7 | 76.9 |
| Fluoranthene | 84.7 | 84.7 | 89.5 | 86.3 |
| 1,2-Benzanthracene | 97.1 | 97.1 | – | 97.9 |
| Pyrene | 87.5 | 87.5 | 89.8 | 86.3 |
| Chrysene | 97.4 | 97.5 | – | 97.9 |
| 1,2,5,6-Dibenzanthracene | 120.2 | 120.2 | – | 118.9 |
| S – Acetonitrile | | | | |
| Azulene | 51.7 | 52.0 | – | 52.3 |
| Naphthalene | 51.2 | 51.6 | 53.3 | 52.3 |
| Anthracene | 74.3 | 73.9 | 76.7 | 72.5 |
| Fluoranthene | 80.8 | 81.1 | 85.3 | 82.0 |
| 1,2-Benzanthracene | 91.7 | 93.3 | – | 92.6 |
| Pyrene | 83.3 | 83.8 | 90.9 | 82.0 |
| S – Tetrahydrofuran | | | | |
| Azulene | 59.0 | 59.8 | – | 59.1 |
| Naphthalene | 59.0 | 59.3 | 56.6 | 59.1 |
| Anthracene | 82.0 | 83.7 | 77.8 | 82.0 |
| Fluoranthene | 92.3 | 91.5 | 91.2 | 92.7 |
| 1,2-Benzanthracene | 105.0 | 104.9 | – | 104.8 |
| Pyrene | 94.3 | 94.6 | 91.2 | 92.7 |
| Chrysene | 103.5 | 105.4 | – | 104.8 |

^a Solvation enthalpy of PAHs in various solvents calculated from literature and experimental data of solution enthalpies (Table 2 and Table S2) and sublimation enthalpies (Table S3).

^b Solvation enthalpies of PAHs in various solvents calculated using molar refraction (Eq. (11)).

^c Solvation enthalpies of PAHs in various solvents calculated by Abraham-Acree multi-parameter model [21–25].

^d Solvation enthalpies of PAHs in various solvents calculated by Eq. (2).

different ways are presented. Enthalpy of solvation in column 2 was calculated from experimental data of solution enthalpy of PAHs in solvent S and sublimation enthalpy of PAHs (see Table S5). Enthalpy of solution of naphthalene in tetrahydrofuran (13.6 kJ mol⁻¹) was taken from [12]. Solution enthalpies of dibenz(a,h)anthracene and chrysene in acetonitrile and tetrahydrofuran were difficult to measure because of their low solubility in these solvents.

For calculations of solvation enthalpies of PAHs in solvent S we have also used linear correlations between molar refractions and solvation enthalpies in solvent S [1,11,20] described by Eq. (11) (column 3):

$$\Delta_{\text{sol}}H_{\text{int}}^{\text{C}_n\text{H}_{n-y}/S} = a_s + b_s \cdot MR^{\text{C}_n\text{H}_{n-y}} \quad (11)$$

where a_s and b_s are empirical coefficients specific for different solvents S; and Abraham-Acree multi-parameter LSER (linear solvation energy relationship) model [21–25] which based on Eqs. (12) and (13) (column 4):

$$\Delta_{\text{sol}}H_{\text{int}}^{\text{A}_i}/S = c_1 + e_1 \cdot \mathbf{E} + s_1 \cdot \mathbf{S} + a_1 \cdot \mathbf{A} + b_1 \cdot \mathbf{B} + l_1 \cdot \mathbf{L} \quad (12)$$

$$\Delta_{\text{sol}}H_{\text{int}}^{\text{A}_i}/S = c_v + e_v \cdot \mathbf{E} + s_v \cdot \mathbf{S} + a_v \cdot \mathbf{A} + b_v \cdot \mathbf{B} + v_v \cdot \mathbf{V} \quad (13)$$

where each term on the right-hand side of equations represents a different type of solute–solvent interaction contribution to the dissolution process; the upper case quantities denote the properties of the dissolved solute and lowercase alphabetic letters represent solvent properties.

The parameters of Eqs. (11)–(13) are presented in Supplementary material (Tables S3 and S6). Molar refraction values were taken from [1,12]. Accuracy of prediction of solvation enthalpy of PAHs in studied solvents by Eq. (11) (column 3, Table 3) is within 1 kJ mol⁻¹. For calculation of solvation enthalpies by Eqs. (12) and (13) (column 4, Table 3) we have used parameters obtained in [22–25] (Table S6). This method provides accuracy of solvation enthalpy calculations in studied solvents of about (2 kJ mol⁻¹) in accordance with [22–25].

The parameters of Eqs. (11)–(13) are presented in Supplementary material (Tables S3 and S6). Molar refraction values were taken from [1,12]. Accuracy of prediction of solvation enthalpy of PAHs in studied solvents by Eq. (11) (column 3, Table 3) is within 1 kJ mol⁻¹. For calculation of solvation enthalpies by Eqs. (12) and (13) (column 4, Table 3) we have used parameters obtained in [22–25] (Table S6). This method provides accuracy of solvation enthalpy calculations in studied solvents of about (2 kJ mol⁻¹) in accordance with [22–25].

Eq. (2) proposed in this work for calculation of solvation enthalpy does not require knowledge of any physical properties or empirical parameters of PAHs. Comparative analysis of data in Table 3 shows that the average difference between enthalpies of solvation of PAHs determined from experimental data and calculated by simple Eq. (2) is about (1 kJ mol⁻¹) for benzene and tetrahydrofuran as a solvents and (1.5 kJ mol⁻¹) – for acetonitrile, which is acceptable taking into account the uncertainties of experimental methods.

Solvation enthalpies of the same set of PAHs (Table 1) in additional 11 solvents were calculated using the linear dependences between the solvation enthalpy and molar refraction from work [12]. Based on obtained data, q_s values for these solvents were estimated. These values allow to calculate the solvation enthalpies of any PAHs in a wide range of solvents based just on their general formula. Details of determining the q_s and the calculated values of $\Delta_{\text{sol}}H_{\text{int}}^{\text{A}_i}/S$ are provided in the Supplementary Material (Table S4).

The next step after validation of Eq. (2) was to test the new scheme for determination of sublimation enthalpies based on Eq. (10). All required data for application of this scheme are presented in Table 4: enthalpies of solvation of PAHs in benzene at 298.15 K (column 2), enthalpies of fusion of PAHs at melting temperature (column 4) and quantity of carbon and hydrogen atoms in molecule of interest. Enthalpies of sublimation of 15 PAHs obtained by Eq. (10) are presented in column 6 of Table 4. Also Table 4 contains recommended values of sublimation enthalpies of studied PAHs

Table 4
Comparison of sublimation enthalpies of PAHs calculated by Eq. (10) (column 6) with recommended literature values at 298.15 K (column 7).

| Compounds | $-\Delta_{\text{sol}}H_{\text{m}}^{\text{A}}/\text{C}_6\text{H}_6$ (kJ mol ⁻¹) | T_{m} (K) | $\Delta_{\text{cr}}^{\text{A}}H_{\text{m}}^{\text{A}}(T)$ (kJ mol ⁻¹) | $\Delta_{\text{cr}}^{\text{A}}H_{\text{m}}^{\text{A}}(298.15)$ (kJ mol ⁻¹) | $\Delta_{\text{cr}}^{\text{A}}H_{\text{m}}^{\text{A}}(\text{Eq. (10)})$ (kJ mol ⁻¹) | $\Delta_{\text{cr}}^{\text{A}}H_{\text{m}}^{\text{A}}(\text{lit})$ (kJ mol ⁻¹) | Δ^{e} (kJ mol ⁻¹) | RE ^f % |
|---|---|-----------------------|--|---|--|---|--|----------------------|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| Acenaphthylene (C ₁₂ H ₈) | 65.3 | 362.6 | 7.8 ^a | 4.01 | 73.1 | 72.5 ± 1.2 | -0.6 | 0.8 |
| Biphenylene (C ₁₂ H ₈) | 65.3 | 385.4 | 22.6 ± 0.7 ^a | 18.7 ± 1.4 | 87.9 | 83.8 ± 0.6 | -4.1 | 4.9 |
| Naphthacene (C ₁₈ H ₁₂) | 97.9 | 623.0 | 36.9 ^a | 16.6 | 134.8 | 135.9 ± 5.1 | 1.1 | 0.8 |
| Triphenylene (C ₁₈ H ₁₂) | 97.9 | 471.0 | 24.74 ± 0.01 ^a | 13.9 ± 3.6 | 122.6 | 120.1 ± 3.3 | -2.5 | 2.1 |
| Corannulene (C ₂₀ H ₁₀) | 105.2 | 542.0 | 17.3 ± 1.2 ^a | 0.8 ± 5.6 | 122.5 | 119.4 ± 8.1 | -3.1 | 2.6 |
| Perylene (C ₂₀ H ₁₂) | 107.4 | 550.9 | 31.9 ± 0.1 ^a | 14.6 ± 5.7 | 139.3 | 135.9 ± 2.6 | -3.4 | 2.5 |
| Benzo[a]pyrene (C ₂₀ H ₁₂) | 107.4 | 454.0 | 17.3 ± 0.6 ^a | 6.7 ± 3.5 | 124.7 | 120.5 ± 2.7 | -4.2 | 3.5 |
| Benzo[e]pyrene (C ₂₀ H ₁₂) | 107.4 | 454.0 | 16.6 ± 0.8 ^a | 8.4 | 124.0 | 123.0 ± 1.8 | -1.0 | 0.8 |
| Benzo[k]fluoranthene (C ₂₀ H ₁₂) | 107.4 | 489.3 | 27.5 ± 0.1 ^a | 14.5 ± 4.3 | 134.9 | 133.8 ± 4.5 | -1.1 | 0.8 |
| Benzo[ghi]perylene (C ₂₂ H ₁₂) | 116.8 | 554.0 | 17.5 ± 0.2 ^a | -1.3 ± 6.3 | 134.3 | 132.9 ± 2.3 | -1.4 | 1.1 |
| Benzo[b]triphenylene (C ₂₂ H ₁₄) | 118.9 | 553.0 | 25.8 ± 0.1 ^a | 6.9 ± 6.2 | 144.8 | 145.9 ± 6.0 | 1.1 | 0.8 |
| Picene (C ₂₂ H ₁₄) | 118.9 | 637.0 | 35.2 ± 0.8 ^a | 10.1 ± 8.3 | 154.2 | 149.4 ± 2.9 | -4.8 | 3.2 |
| Benzo[b]chrysene (C ₂₂ H ₁₄) | 118.9 | 574.2 | 25.3 ± 3.1 ^b | 4.9 | 144.3 | 144.4 ± 2.5 | 0.1 | 0.1 |
| Coronene (C ₂₄ H ₁₂) | 126.2 | 710.0 | 19.6 ± 2.4 ^a | - | 145.8 | 142.6 ± 8.7 | -3.2 | 2.2 |
| 1,2:4,5-Dibenzopyrene (C ₂₄ H ₁₄) | 128.4 | 520.2 | 30.5 ± 1.1 ^a | 12.8 ± 5.9 | 158.9 | 155.2 | -3.7 | 2.4 |

^a Recommended fusion enthalpies of PAHs at melting temperature taken from [7].

^b Fusion enthalpy at melting temperature taken from [18].

^c Enthalpies of fusion of PAHs adjusted to 298.15 K by Chickos et al. [19] method.

^d Recommended sublimation enthalpies of PAHs at 298.15 K taken from [7].

^e Absolute difference between sublimation enthalpies taken from literature and obtained in this work (column 7 and 6).

^f Relative difference between sublimation enthalpies taken from literature and obtained in this work (column 7 and 6) in percentages.

(column 7) from the comprehensive survey on the thermodynamics of phase transitions of aromatic compounds [7]. These recommendations were made based on analysis of available experimental data obtained by different authors. Comparison between columns 6 and 7 in the Table 4 indicates that at the current level of the experimental accuracy Eq. (10) adequately predicts sublimation enthalpies of PAHs at 298.15 K based on solvation enthalpies calculated using Eq. (2) and fusion enthalpies at melting temperature or enthalpies of solution of PAHs in benzene.

Fusion enthalpies adjusted to the 298.15 K from [7] are also presented in Table 4 (column 5). It is evident, that if we use these values instead of the enthalpies of fusion at the melting temperature for calculations by Eq. (10), obtained data will significantly deviate from the recommended sublimation enthalpies.

5. Conclusion

In this work we proposed a simple method for calculation of solvation enthalpies of PAHs in various solvents. This method can greatly simplify determination of sublimation enthalpies of PAHs and their derivatives using solution calorimetry approach described in [1,9–11]. Sublimation enthalpies of 15 PAHs with different molecular sizes (from two to seven benzene rings) were determined directly at 298.15 K using this method. The average deviation of obtained results from the recommended literature sublimation enthalpies was about (2.4 kJ mol⁻¹).

We have found that solution enthalpies of PAHs in benzene at 298.15 K are approximately equal to their fusion enthalpies at melting temperature. In our following works, we will show that this finding is common to a wide variety of aromatic compounds.

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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.tca.2015.10.020>.

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