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New aspects of relationship between the enthalpies of fusion of aromatic compounds at the melting temperatures and the enthalpies of solution in benzene at 298.15 K. Part I

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ABSTRACT

In the present work the relationship between the enthalpies of fusion at the melting temperatures and the enthalpies of solution in benzene at 298.15 K of aromatic compounds is discussed in details. The difference between the fusion enthalpy at the melting temperature and the solution enthalpy at 298.15 K is determined by the temperature dependence of the fusion enthalpy, the solution enthalpy of the compound in the hypothetical liquid state at 298.15 K and the enthalpies of solid–solid phase transitions occurring between 298.15 K and the melting temperature. The latter contribution into the difference can be measured directly. The first two contributions were analyzed in a series of 17 aromatic compounds which do not exhibit solid-solid phase transitions between 298.15 K and the melting temperature. We calculated the fusion enthalpies at 298.15 K of these compounds in two different ways. On the one hand, they were derived from the fusion enthalpies at the melting temperature according to Kirchhoff's law using experimental data on solid and liquid heat capacities. It was assumed that the linear temperature dependence of melt heat capacity can be extrapolated down to 298.15 K. On the other hand, the fusion enthalpies at 298.15 K were calculated from the solution enthalpies in benzene at 298.15 K of the compounds in solid and hypothetical liquid states. Good agreement between the fusion enthalpies at 298.15 K calculated in different ways was demonstrated.

The solution enthalpies of eight solid and six liquid aromatic compounds in benzene at 298.15 K and the fusion enthalpies of two aromatic compounds were measured.

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1. Introduction

Thermodynamic properties of organic liquids below the melting point play significant role in estimation of phase equilibrium parameters. Particularly, the knowledge of temperature dependence of fusion enthalpy is necessary for the accurate calculation of the ideal solubility (activity in saturated solution) of solid compounds [1]. This dependence is determined from the isobaric heat capacities of liquid ($C_p^{A_i}$ (l, T)) and solid ($C_p^{A_i}$ (cr, T)) phases of the compound of interest. In most cases $C_p^{A_i}$ (l, T) below the melting temperature is unknown and can be hardly determined directly [2], especially for compounds which have high melting temperature (above 450 K) and decompose or evaporate during melting. Therefore, various methods of estimation of the difference $\Delta_{cr}^{l}C_p^{A_i}(T) = C_p^{A_i}$ (l, T) – $C_p^{A_i}$ (cr, T) have been tested in the last decades. Often the difference between the isobaric heat capacities of the liquid and solid phases is neglected [3–6]. Sometimes this difference is assumed to be close to fusion entropy [7–9] or to one-half of fusion entropy [10,11]. Such approximations lead to significant errors in solubility estimation when the melting temperature of the studied compound is high [1,12]. In the work [13] the molar heat capacity changes of dissolution in water at 298.15 K were used instead of the $\Delta_{cr}^{l}C_p^{A_i}(T)$ values for sugars and polyols. Empirical models also exist for estimation of the $\Delta_{cr}^{l}C_p^{A_i}(T)$ value [10,14]. However, the ambiguity in accounting the temperature dependence of fusion enthalpy remains.

Fusion enthalpy at 298.15 K ($\Delta_{cr}^{l}H^{A_i}$ (298.15 K)) together with vaporization enthalpy at 298.15 K obtained from the vapor pressure temperature dependencies [15] or determined using correlation gas chromatography [16] are used for estimation of sublimation enthalpy at the standard conditions. On the other hand, the vapor pressures of liquids at the standard conditions are required by the models describing the distribution of chemicals

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in the environment [17] and should be derived considering temperature dependence of vaporization enthalpy of the liquid below the melting temperature.

An interesting relation was observed between solution enthalpy of solid aromatic compounds in benzene at 298.15 K ($\Delta_{\mathrm{soln}}H^{\mathrm{A_i/C_6H_6}}$ (cr, 298.15 K)) and fusion enthalpy at the melting temperature ($\Delta_{\mathrm{cr}}^{\mathrm{l}}H^{\mathrm{A_i}}(T_{\mathrm{m}})$). The $\Delta_{\mathrm{soln}}H^{\mathrm{A_i/C_6H_6}}$ (cr, 298.15 K) value is close to $\Delta_{\mathrm{cr}}^{\mathrm{l}}H^{\mathrm{A_i}}(T_{\mathrm{m}})$ [18,19]. In addition, the studies [18–20] devoted to determination of sublimation enthalpy at 298.15 K of aromatic and heteroaromatic compounds and their derivatives through the solution calorimetry approach have shown that the fusion enthalpies of these compounds at the melting temperatures can be successfully used instead of the solution enthalpies in benzene at 298.15 K. This result also indirectly confirms the approximate equality between $\Delta_{\mathrm{soln}}H^{\mathrm{A_i/C_6H_6}}$ (cr, 298.15 K) and $\Delta_{\mathrm{cr}}^{\mathrm{l}}H^{\mathrm{A_i}}(T_{\mathrm{m}})$. Considering that the solution enthalpies of aromatic and heteroaromatic compounds and their derivatives in the liquid state in benzene ($\Delta_{\mathrm{soln}}H^{\mathrm{A_i/C_6H_6}}$ (l, 298.15 K)) should be close to zero (for example, the solution enthalpy of liquid 1-phenylnapthalene in benzene at 298.15 K is equal to 0.65 kJ mol^{-1} [21]), we proposed that such relation between $\Delta_{\mathrm{soln}}H^{\mathrm{A_i/C_6H_6}}$ (cr, 298.15 K) and $\Delta_{\mathrm{cr}}^{\mathrm{l}}H^{\mathrm{A_i}}(T_{\mathrm{m}})$ points to a weak temperature dependence of fusion enthalpy [18]. At least, the temperature dependences of the fusion enthalpies of studied compounds should be weaker than values adjusted by Chickos et al. scheme [22].

Generally a positive difference $\Delta_{\mathrm{cr}}^{\mathrm{l}}C_{\mathrm{p}}^{\mathrm{A_i}}$ is observed [23], e. g. $\Delta_{\mathrm{cr}}^{\mathrm{l}}H^{\mathrm{A_i}}$ (298.15 K) is less than $\Delta_{\mathrm{cr}}^{\mathrm{l}}H^{\mathrm{A_i}}(T_{\mathrm{m}})$ if $T_{\mathrm{m}} > 298.15$ K. Though for the most of the studied compounds [18,19] the $\Delta_{\mathrm{cr}}^{\mathrm{l}}H^{\mathrm{A_i}}$ (298.15 K) and $\Delta_{\mathrm{cr}}^{\mathrm{l}}H^{\mathrm{A_i}}(T_{\mathrm{m}})$ values are approximately equal, in the case of anthracene the fusion enthalpy at the melting temperature notably exceeds the solution enthalpy at 298.15 K [18].

Experimental data on isobaric heat capacities of liquid and solid phases are necessary for calculation of the $\Delta_{\mathrm{cr}}^{\mathrm{l}}C_{\mathrm{p}}^{\mathrm{A_i}}$ value. Heat capacities of aromatic compounds below and above the melting temperature were comprehensively studied in a series of works [24–44]. Collecting of the data on the solution enthalpies of aromatic and heteroaromatic compounds in benzene and further comparison of these values with the fusion enthalpies adjusted to 298.15 K using the experimental heat capacities has helped us to develop a general approach to the analysis of the relationship between $\Delta_{\mathrm{soln}}H^{\mathrm{A_i/C_6H_6}}$ (cr, 298.15 K) and $\Delta_{\mathrm{cr}}^{\mathrm{l}}H^{\mathrm{A_i}}(T_{\mathrm{m}})$. Here we focus on the case when the $\Delta_{\mathrm{cr}}^{\mathrm{l}}H^{\mathrm{A_i}}(T_{\mathrm{m}})$ value is equal within 2–3 kJ mol^{-1} to the $\Delta_{\mathrm{soln}}H^{\mathrm{A_i/C_6H_6}}$ (cr, 298.15 K) value.

2. Experimental part

2.1. Materials

Acenaphthene, 1,6-dimethylnaphthalene, 1,8-dimethylnaphthalene, 2,6-dimethylnaphthalene, 2,7-dimethylnaphthalene, *o*-, *m*- and *p*-xylenes, dimethyl phthalate, dimethyl isophthalate, 1-methylnaphthalene, 2-methylnaphthalene, 1,4-di-*tert*-butylbenzene, *E*-azobenzene, benzene and ethanol were of commercial origin with the mass fraction purities better than 0.97.

Benzene was purified before use according to [45]. Purity of benzene and other samples was analyzed using an Agilent 7820 B gas chromatograph (GC) equipped with a flame ionization detector. Water content was determined using Karl Fischer titration (see Table S1).

1-Methylnaphthalene was distilled under reduced pressure (1 Torr). 1,8-Dimethylnaphthalene, 2,6-dimethylnaphthalene and 2,7-dimethylnaphthalene were purified twice by fractional sublimation (1 Torr). 1,4-Di-*tert*-butylbenzene and *E*-azobenzene were recrystallized from ethanol. All operations with *E*-azobenzene were carried out in the dark. Acenaphthene, o-, m- and p-xylenes, 2-methylnaphthalene, 1,6-dimethylnaphthalene, dimethyl isophthalate, ethanol were used without further purification (see Table S1).

2.2. Solution calorimetry

The solution enthalpies of solid compounds (acenaphthene, 2-methylnaphthalene, 1,8-dimethylnaphthalene, 2,6-dimethylnaphthalene, 2,7-dimethylnaphthalene, dimethyl isophthalate, *E*-azobenzene, 1,4-di-tert-butylbenzene) in benzene were measured at 298.15 K in the concentration range from 3.08 to 21.04 mmol kg^{-1} using TAM III precision solution calorimeter. In the case of liquid compounds (1,6-dimethylnaphthalene, *o*-, *m*-, *p*-xylenes, dimethyl phthalate, 1-methylnaphthalene) the higher concentration range was chosen from 19.68 to 66.54 mmol kg^{-1}. Solid compounds were dissolved by breaking a glass ampule filled with 0.01–0.1 g of the studied sample in a glass cell containing 90 ml of pure solvent. Liquid compounds were injected in 25 μL portions using an electronically operated syringe equipped with a long gold cannula immersed in the solvent. The details on the solution calorimetry experimental procedure have been fully described elsewhere [46].

The average experimental solution enthalpies measured in this work are provided in Table 1.

2.3. Differential scanning calorimetry

The enthalpies and temperatures of fusion of 2,7-dimethylnaphthalene and dimethyl isophthalate were measured using the differential scanning calorimeter DSC 204 F1 Phoenix (Netzsch, Germany) as described previously [47]. Samples of about (5–15) mg were placed in a 40 μL aluminum crucible and closed with a lid having a hole of 0.5 mm diameter. Experiments were performed in the argon dynamic atmosphere (150 mL·min^{-1}) with the heating/cooling rate of 10 K·min^{-1}. The measurements on two samples were performed for each compound. Two cycles of "heating-cooling" runs from room temperature up to temperature on 40 K higher than melting point and back were carried out in the

Table 1
Average experimental solution enthalpies of aromatic compounds in benzene measured in this work at 298.15 K and 0.1MPa[a].

Solute	$\Delta_{\mathrm{soln}}H^{\mathrm{A_i/C_6H_6}}$ kJ mol^{-1}
Acenaphthene	20.82 ± 0.18
1,8-Dimethylnaphthalene	16.42 ± 0.16
2,6-Dimethylnaphthalene	23.99 ± 0.14
2,7-Dimethylnaphthalene	22.90 ± 0.15
1,6-Dimethylnaphthalene	1.46 ± 0.02
1-Methylnaphthalene	0.78 ± 0.03
2-Methylnaphthalene	12.64 ± 0.08
Dimethyl phthalate	1.86 ± 0.04
Dimethyl isophthalate	25.17 ± 0.20
1,4-Di-*tert*-butylbenzene	24.61 ± 0.19
o-Xylene	0.93 ± 0.01
m-Xylene	1.07 ± 0.02
p-Xylene	0.79 ± 0.02
E-azobenzene	22.17 ± 0.15

[a] The detailed compilation of the experimental solution enthalpies measured at different solute concentrations for each compound is listed in Table S2. Uncertainties correspond to expanded uncertainties of the mean U (0.95 level of confidence. Student's t distribution 2.0).

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