



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



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ABSTRACT

In the present work we demonstrate how the relationship between fusion enthalpies at the melting temperature of aromatic compounds and solution enthalpy values in benzene at 298.15 K values is affected by the fusion enthalpy temperature dependence and the solution enthalpy of hypothetical liquid in benzene. The fusion enthalpies at 298.15 K were independently calculated from the solution enthalpies in benzene and the fusion enthalpies at the melting temperatures according to Kirchhoff's law. Kirchhoff's law was applied for fusion enthalpy adjustment calculation, assuming that the heat capacities of the aromatic compounds studied in the molten state can be extrapolated down to 298.15 K. The fusion enthalpies at 298.15 K derived from the solution calorimetry and from the fusion enthalpies at the melting temperatures are in good agreement, including the compounds with significant fusion enthalpy adjustments, demonstrating the validity of the assumptions made.

The solution enthalpies of six aromatic compounds in benzene and the fusion enthalpy of dimethyl terephthalate were measured.

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1. Introduction

Fusion enthalpies of individual organic compounds are the source of information about solid-liquid equilibria in complex systems. Drug solubility [1] and phase diagram shape [2] may be predicted from the fusion enthalpies. However, accurate application of the fusion enthalpy measured at the melting temperature requires knowledge of the fusion enthalpy temperature dependence for prediction of solid-liquid equilibrium parameters. Neglecting fusion enthalpy temperature dependence of drugs leads to a significant error in estimation of their solubility at the ambient conditions [1,3]. On the other hand, fusion enthalpies at 298.15 K ($\Delta_{\text{cr}}^{\text{l}}H^{\text{Ai}}$ (298.15 K)) together with vaporization enthalpies at 298.15 K found from correlation gas chromatography [4] or melt vaporization studies [5] are used for calculation of sublimation enthalpy. Fusion enthalpy adjustments to 298.15 K can make a large contribution to resulting sublimation enthalpy values.

The enthalpy of solution of a solid compound may be represented as a sum of the enthalpy of its melting and solution of formed melt at the same conditions. In Refs. [6,7] it was shown that

the solution enthalpies of solid aromatic compounds not capable of self-association due to intermolecular hydrogen bonding in benzene at 298.15 K ($\Delta_{\text{soln}}H^{\text{Ai/C}_6\text{H}_6}$ (cr, 298.15 K)) are close to the fusion enthalpies at the melting temperatures ($\Delta_{\text{cr}}^{\text{l}}H^{\text{Ai}}(T_{\text{m}})$). This finding led to the development a new approach for estimating sublimation enthalpies of aromatic compounds based on fusion enthalpies at the melting temperatures and solvation enthalpies in benzene calculated according to a group-additivity scheme [6–8]. Since the solution enthalpies in benzene of liquid aromatic compounds not capable of self-association due to intermolecular hydrogen bonding are close to zero (for example, solution enthalpy of liquid 1-phenylnaphthalene in benzene at 298.15 K is 0.65 kJ mol^{-1} [9]), $\Delta_{\text{soln}}H^{\text{Ai/C}_6\text{H}_6}$ (cr, 298.15 K) should be close to $\Delta_{\text{cr}}^{\text{l}}H^{\text{Ai}}$ (298.15 K). Approximate equality between $\Delta_{\text{soln}}H^{\text{Ai/C}_6\text{H}_6}$ (cr, 298.15 K) and $\Delta_{\text{cr}}^{\text{l}}H^{\text{Ai}}(T_{\text{m}})$ led to conclusion that the fusion enthalpies of the studied compounds weakly depend on temperature [6]. Nevertheless, we also observed the compounds the solution enthalpies of which are notably lower than the fusion enthalpies at the melting temperature. In the case of anthracene, recommended value for $\Delta_{\text{cr}}^{\text{l}}H^{\text{Ai}}(T_{\text{m}})$ (29.4 kJ mol^{-1} [10]) exceeds the $\Delta_{\text{soln}}H^{\text{Ai/C}_6\text{H}_6}$ (cr, 298.15 K) (24.7 kJ mol^{-1} [11]) by 4.7 kJ mol^{-1} .

A quantitative approach to the analysis of a connection between fusion enthalpy at the melting temperature and solution enthalpy

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