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A similarity variable for estimating the heat capacity of solid organic compounds Part II. Application: Heat capacity calculation for ill-defined organic solids

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ABSTRACT

A correlation for the constant pressure specific heat capacity, c_p, valid from 50 K to the fusion temperature for pure crystalline organic solids was presented recently [V. Laštovka, J.M. Shaw, J. Chem. Eng. Data 52 (2007) 1160–1164]. The predictive correlation includes seven universal coefficients. The variables are temperature and a similarity variable, α, which possesses a value proportional to the number of atoms in a molecule divided by molecular mass. This similarity variable, identified in the first paper of this series [V. Laštovka, N. Sallamie, J.M. Shaw, Fluid Phase Equilib. 268 (2008) 51–60] is more robust than molecular structure or composition as a descriptor for heat capacity for solid hydrocarbons. In this contribution the correlation is applied to the estimation of solid-state heat capacities, identification of temperature ranges where phase transitions arise, and the enthalpy associated with such phase transitions for poorly defined mixed organic solids. Agreement between predicted and measured c_p values is within anticipated error bounds [V. Laštovka, J.M. Shaw, J. Chem. Eng. Data 52 (2007) 1160–1164]. Illustrative examples include polymers, charge transfer complexes, and hydrocarbon resource fractions such as asphaltenes, where the role of the correlation as a baseline for solid behavior was found to be particularly useful. This general purpose correlation can also be used as a basis for the development of high precision predictive equations tailored to specific compounds or mixtures where limited experimental heat capacity data are available.

1. Introduction

In the petroleum industry, the thermophysical properties such as heat capacities for solid hydrocarbons and mixtures in temperature ranges arising in production, transport and refining are of growing interest in themselves and as a means to detect phase transitions. Hydrocarbons of industrial interest are frequently ill-defined structurally and their mean molar masses are not known a priori. Thus heat capacity estimation methods requiring such inputs are not readily applied. In the polymer and petrochemical industries new products and formulations present additional ongoing needs for thermophysical property data for solids of varying degrees of definition. In the current contribution, the suitability of a predictive heat capacity correlation for such applications, based solely on elemental composition, is evaluated.

2. Predictive heat capacity correlation development

Briard et al. [3] established a four-parameter equation to correlate the temperature dependence of molar heat capacity, C_p, for n-alkanes:

$$C_p(\mathrm{J\,K^{-1}\,mol^{-1}}) = 3AR\left(\frac{\theta}{T}\right)^2 \frac{\exp(\theta/T)}{[\exp(\theta/T)-1]^2} + c\left(\frac{T}{K}\right) + d\left(\frac{T}{K}\right)^2 \tag{1}$$

where the parameters A, θ, c and d are functions of the number of carbons in the alkane chain, and R is the ideal gas constant, 8.314472 J K^{-1} mol^{-1}. The adjustable parameters in Eq. (1) were optimized for 17 n-alkanes individually by fitting this equation to experimental heat capacities between 0 K and the first transition temperature. According to the authors [3], the first term takes into account only the contribution of group vibrations within the molecule, while the second and third terms, derived from Benson's method of group contribution, represent the contribution of the skeletal vibrations (stretching, bending, wagging, twisting and rocking). In two recent publications [1,2], we show that there is a similarity variable linking heat capacity for all crystalline organic solids and illustrate how to extend correlations such as Eq. (1) and

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Table 1
Universal coefficients appearing in Eq. (2) [1]

Parameters	
A_1	0.013183
A_2	0.249381
θ	151.8675
C_1	0.026526
C_2	−0.024942
D_1	0.000025
D_2	−0.000123

render them predictive. The resulting expression, Eq. (2):

$$c_p\ (\mathrm{J\,K^{-1}\,g^{-1}}) = 3(A_1\alpha + A_2\alpha^2)R\left(\frac{\theta}{T}\right)^2 \frac{\exp(\theta/T)}{[\exp(\theta/T)-1]^2} + (C_1\alpha + C_2\alpha^2)\left(\frac{T}{K}\right) + (D_1\alpha + D_2\alpha^2)\left(\frac{T}{K}\right)^2 \qquad (2)$$

includes seven universal coefficients (A_1, A_2, θ, C_1, C_2, D_1 and D_2) and the parameter α which can be evaluated from elemental composition as illustrated with Eq. (3) for n-alkanes with the formula C_nH_{2n+2}. v_i is the stoichiometric coefficient for element i in a compound consisting of N atoms, n is the number of elements in the compound and M_i is the molar mass of the element i (g mol^{-1}):

$$\alpha = \frac{\sum_{i=1}^{n} v_i}{\sum_{i=1}^{n} v_i M_i} = \frac{v_C + v_H}{v_C \cdot 12.0107 + v_H \cdot 1.00794} = \frac{v_C + (2v_C + 2)}{v_C \cdot 12.0107 + (2v_C + 2)\cdot 1.00794} \qquad (3)$$

Evaluation of α for all organic compounds or ill-defined organic materials comprising carbon, hydrogen and hetero-atoms such as nitrogen, oxygen and sulfur is performed analogously, based on elemental composition.

Elemental composition measurements are reliable and commonly available even for ill-defined organic industrial materials. The seven universal coefficients, appearing in Eq. (2), were obtained and their validity was tested using a heat capacity database comprising more than 160 organic compounds with diverse elemental compositions and molar masses. The values of α for pure compounds in the database range from 0.1 mol g^{-1} for sulfur and oxygen substituted aromatics to approximately 0.22 mol g^{-1} for n-alkanes. Temperatures range from 5 K to the temperatures of the first phase transition T_{trs}. These data were culled from the literature. Much of the data in the database has been critically reviewed [4]. The heat capacity data in temperature ranges where solid–solid transitions or premelting effects were observed were not included in the parameter regression calculations. This is a common approach and the one used for example by Briard et al. [3].

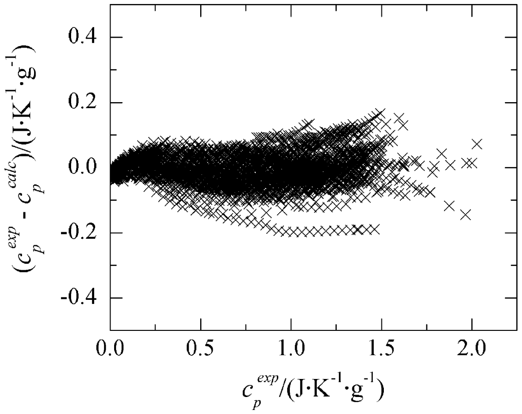

Fig. 1. Absolute deviation of the predicted heat capacity values from the experimental values for the pure-solid training data set.

The values of the coefficients appearing in Eq. (2) are listed in Table 1. Statistical overviews for a pure crystalline training data set and a predictive test set from 50 K to the first transition temperature are shown in Table 2. The number of compounds, the number of data points, the average standard deviation of the fit (σ_F), average standard deviation (σ), average absolute deviation (ε) and average relative deviation (δ) are listed for both data sets. A detailed statistical overview of results for the pure compounds used in the training and test data sets was published previously [1]. A summary is presented in Table 2, and the absolute error for data in the training and test data sets is illustrated in Figs. 1 and 2, respectively. Both data sets comprise compounds with diverse elemental compositions (including the elements carbon, hydrogen, nitrogen, oxygen

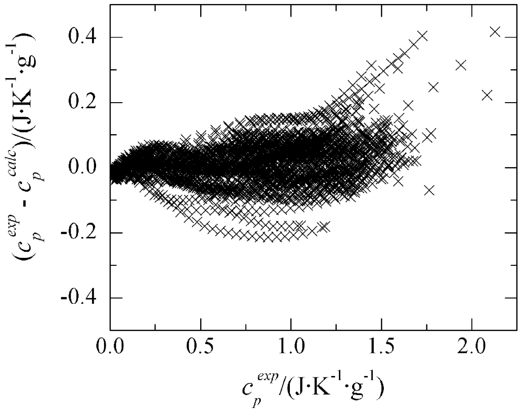

Fig. 2. Absolute deviation of the predicted heat capacity values from the experimental values for pure-solid test data set.

Table 2
Statistical overview for data sets from 50 K to the first transition temperature

	Pure solid training set [1]	Pure solid test set [1]	Polymer data set[a]	Molecular complexes[a]
Number of compounds	72	93	29	8
Number of c_p values	1621	2080	617	129
σ (J K^{-1} g^{-1})	0.059[b]	0.065	0.059	0.137
ε (J K^{-1} g^{-1})	0.040	0.058	0.050	0.129
100δ	5.36	6.80	5.59	18.0

[a] A detailed statistical breakdown by component is available in Appendix A.

[b] Average standard deviation of the fit σ_F, $\sigma_F = (1/m)\sum_{i=1}^{m}\sqrt{\sum_{j=1}^{n}(c_p^{\mathrm{exp}} - c_p^{\mathrm{calc}})_j^2/(n-p)}$; $\sigma = (1/m)\sum_{i=1}^{m}\sqrt{\sum_{j=1}^{n}(c_p^{\mathrm{exp}} - c_p^{\mathrm{calc}})_j^2/(n-1)}$; $\varepsilon = (1/m)\sum_{i=1}^{m}\left[\sum_{j=1}^{n}\sqrt{(c_p^{\mathrm{exp}} - c_p^{\mathrm{calc}})_j^2/n}\right]$; $\delta = (1/m)\sum_{i=1}^{m}\left\{\sum_{j=1}^{n}\sqrt{[(c_p^{\mathrm{exp}} - c_p^{\mathrm{calc}})/c_p^{\mathrm{exp}}]_j^2/n}\right\}$, where m denotes the number of compounds, n represents the number of experimental heat capacity values for a compound and p is the number of fitted parameters.