A Note on the Relationship Between Organic Solid Density and the Liquid Density at the Triple Point

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ABSTRACT. A simple relationship between the solid density of organic compounds and the liquid density at the triple point is presented as an extension of a previous relationship used internally by the DIPPR 801 database project. The relationship allows estimation of solid density (of the solid phase most stable at the triple point) for organic compounds over a wide range of temperatures with an average uncertainty of approximately 6%.

KEYWORDS: Solid density, solid properties
We report in this short note a simple relationship between the liquid density of an organic liquid at its triple point and the density as a function of temperature for the solid phase. This relationship is an extension to what we believe is an unpublished relationship that has been used by the DIPPR 801 database project for estimation of solid densities at the triple point. We attribute the genesis of that first relationship to the early staff of the DIPPR 801 project\textsuperscript{1}, who required a reliable method for estimating the solid density (SDN) of compounds for which no experimental data were available. This was in keeping with the policy of the DIPPR 801 Pure Compound Database\textsuperscript{2} to provide values for the complete set of 44 properties tabulated in the database for each compound included. Organic compounds with low-temperature triple points therefore often required an estimation method for the solid density from more readily available data. As a reliable temperature-dependent correlation for saturated liquid density (LDN), based on the Rackett equation\textsuperscript{3}, is included in the DIPPR database, the value of LDN at the triple point was deemed to be readily available and it was found to correlate well with known values of SDN for the equilibrium solid phase at the triple point. A simple ratio of the two densities,

\[
\frac{\rho_S(T_t)}{\rho_L(T_t)} = 1.17
\]  

was found to be adequate and reliable for most organic compounds. Here $\rho_S$ is solid density, $\rho_L$ is liquid density, and $T_t$ is the triple point temperature.

In an effort to upgrade the methods used by the DIPPR database project for estimation of solid properties, we have reviewed the methods accepted by the DIPPR sponsors for prediction of solid heat capacity, solid vapor pressure, heat of fusion, heat of sublimation, melting point, and solid density. This review resulted in development of new group-contribution methods for solid heat capacity\textsuperscript{4}, solid vapor pressure\textsuperscript{5}, and heats of fusion\textsuperscript{5}. Current capabilities in the literature for estimating melting point were found to be adequate. However, few methods to estimate SDN were available in the literature, and Eq. (1)
appeared to be the most reliable. Although new analyses were performed on the SDN data available in the DIPPR database using group contributions and Quantitative Structure-Property Relationships (QSPR) with some 40 molecular descriptors, the resultant more complex forms were not as reliable as the simple ratio given in Eq. (1).

We were able, however, to extend Eq. (1) to include a temperature dependence for SDN from \( T_t \) to substantially lower temperatures. The extended relationship presented here is

\[
\rho_s(T) = 1.28 \times 0.16 \frac{T}{T_t} \rho_l(T_t). 
\]  

(2)

The training data set for developing this relationship consisted of 65 compounds from the DIPPR database with 303 temperature-dependent SDN values each having an evaluated uncertainty of less than 5% as reported in the DIPPR database. (Uncertainties in the DIPPR database are reported in distinct increments including 0.2%, 1%, 3%, 5%, 10%, 25%, etc.) The linear temperature dependence shown in Eq. (2) adequately represented all of the data within the limited training set available. Of the 54 compounds examined with more than two SDN values available at different temperatures, 28 yielded \( R^2 \) values greater than 99% and 43 gave \( R^2 \) values greater than 95% for the proposed linear relationship.

Equation 2 was evaluated using a test set of 117 additional compounds (170 SDN data points). The average absolute deviation (AAD) for this comparison was 0.560 kmol/m\(^3\), or an absolute average percent deviation (AAPD) of 6.28%. Figure 1 shows the estimated density obtained from Eq. (2) in comparison to the experimental density values for the combined training and test data sets.
Figure 1. Comparison of SDN values estimated (est) using Eq. (2) to experimental (exp) values for combined training and test data sets.

We found no other general methods for SDN estimation against which to compare the proposed correlation except for a purported “back of the envelope” method by Girolami. Little information is available about the specific temperature at which this method is valid, but we infer from the original paper that its intended application is room temperature. The Girolami method is an element-additive method (elements in the same row of the periodic table have the same additive contribution). In Table I, the results of applying the Girolami method for the 94 compounds from the combined training and test data sets for which data at room temperature were available are compared to the results from Eq. (2) for the same compounds. Table I also shows the results from Eq. (1) as applied to the 21 compounds from the combined data sets for which data were available at or near $T_i$, where this equation is applicable, compared to the
results obtained from Eq. (1) for the same compounds. The overall results obtained from Eq. (2) for the combined data sets at all available temperatures are also shown in Table I.

It is interesting that the new correlation gives a ratio of SDN to LDN at the triple point of 1.12 instead of the 1.17 value used in the original DIPPR correlation of Eq. (1). The improved AAD at the triple point shown in Table I for Eq. (2) relative to Eq. (1) suggests that the increased quantity of accurate SDN data now in the DIPPR database provides a better estimate of this ratio than could be obtained 20 years ago.

Table I. Deviations of solid density estimations from experimental data

<table>
<thead>
<tr>
<th></th>
<th>at various $T$</th>
<th>at $T_t$</th>
<th>at 298.15 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AAD/(kmol@m$^{-3}$)</td>
<td>AAPD/%</td>
<td>AAD/(kmol@m$^{-3}$)</td>
</tr>
<tr>
<td>Eq. (2)</td>
<td>1.10</td>
<td>5.6</td>
<td>1.36</td>
</tr>
<tr>
<td>Eq. (1)</td>
<td>NA</td>
<td>NA</td>
<td>1.80</td>
</tr>
<tr>
<td>Girolami</td>
<td>NA</td>
<td>NA</td>
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</tr>
</tbody>
</table>

Equation 2 represents a quick, useful method for predicting solid density. The only input information required is the triple point temperature (or in practice the normal melting point may be used) and the liquid density at that temperature. The method applies to the solid phase that is stable at the triple point, and our experience suggests that it may be applied from $T_t$ down to approximately 0.3$T_t$ or until there is solid phase transition. Figure 2 illustrates its use for three different compounds, comparing estimated values to experimental data.
Figure 2. SDN experimental values (points) compared to values estimated (lines) from LDN at the triple point (obtained from the DIPPR database) using Eq. (2) for neopentane (—), n-nonanoic acid (±), and n-hexadecanoic acid (+).

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LITERATURE CITED


