A Note on the Relationship between Organic Solid Density and Liquid Density at the Triple Point[†]

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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%.

Introduction

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 This relationship is an extension to what we believe is an unpublished relationship that has been used by the DIPPR 801 database project for the estimation of solid densities at the triple point.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,[1] who required a reliable method for estimating the solid density of compounds for which no experimental data were available. This was in keeping with the policy of the DIPPR 801 Pure Compound Database[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, based on the Rackett equation,[3] is included in the DIPPR database, liquid densities at the triple point were deemed to be readily available, and they were found to correlate well with known density values for the equilibrium solid phase at the triple point. A simple ratio of the two densities

$$\frac{\rho_S(T_t)}{\rho_L(T_t)} = 1.17 \qquad (1)$$

was found to be adequate and reliable for most organic compounds. Here ρ_S is solid density, ρ_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,[4] solid vapor pressure,[5] and heats of fusion.[5] Current capabilities in the literature for estimating the melting point were found to be adequate. However, few methods for estimating solid density were available in the literature, and eq 1 appeared to be the most reliable. Although new analyses were performed on the solid density 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 solid density from T_t to substantially lower temperatures. The extended relationship presented here is

$$\rho_S(T) = \left(1.28 - 0.16\frac{T}{T_t}\right)\rho_L(T_t) \qquad (2)$$

The training data set for developing this relationship consisted of those compounds in the DIPPR database with experimental data available at more than two temperatures and for which the reported uncertainty of the data was less than 5%. (Uncertainties in the DIPPR database are reported in distinct increments, including 0.2%, 1%, 3%, 5%, 10%, 25%, etc.) These selection criteria resulted in a training set of 65 compounds with 303 temperature-dependent solid density values. The standard deviation for the fit of eq 2 to this training set was 1.13 kmol/m^3 or 5.6%. The linear temperature dependence shown in eq 2 adequately represented all of the data within the accuracy of the limited training set available. Of the 54 compounds examined with more than two density 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.

Extension of DIPPR 801 Method

Equation 2 was evaluated using a test set of 117 additional compounds (170 solid-density data points). These additional data were also obtained from the DIPPR database using those compounds with a reported uncertainty of less than 5% but for which only one or two solid density values were available. The average absolute deviation (AAD) for this comparison was 0.560 kmol/m^3 or an absolute average percent deviation (AAPD) of 6.3%. As used in this work, these comparative statistics are defined as

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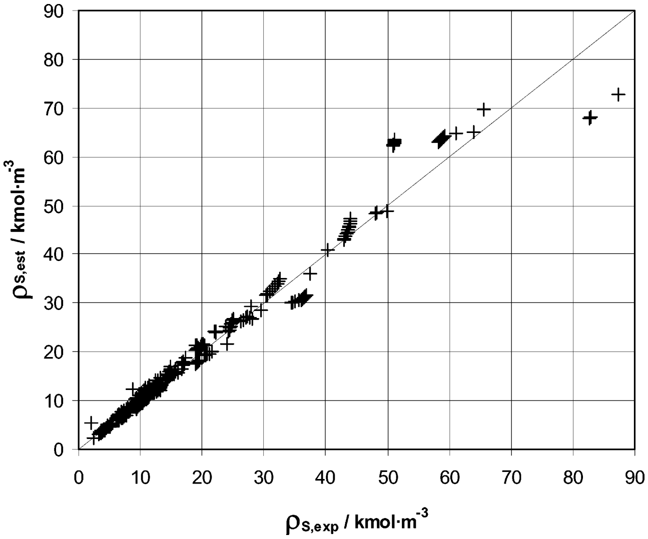

Figure 1. Comparison of solid densities estimated using eq 2, $\rho_{S,est}$, to experimental values, $\rho_{S,exp}$, for combined training and test data sets.

$$\mathrm{AAD} = \sum_{i=1}^{N} |\rho_{S,calc} - \rho_{S,exp}|$$

$$\mathrm{AADP} = \sum_{i=1}^{N} \left|\frac{\rho_{S,calc} - \rho_{S,exp}}{\rho_{S,exp}}\right| \times 100\% \qquad (3)$$

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.

There are very few methods for predicting solid density in the literature. Horvath[6] reviews several very approximate methods of considerably lower accuracy than eq 2. He also includes in the review some methods found in earlier reviews.[7-9] Many of these methods apply to a narrow range of chemical types, such as a group additivity of atomic volumes suggested by Tarver[10] for explosives and an additivity of molar volume increments by Nielsen[11] for fuels and explosives. Of these early methods, the more general method suggested by Immirzi and Perini[12] was recommended by both Horvath and Lyman et al.[9] The Immirzi and Perini method assumes additivity of tabulated volume increments, v_i, for common elements and ions to obtain the solid density from

$$\rho_S = \frac{1.66M}{\sum_{i}^{N} v_i} \qquad (4)$$

where M is molecular weight. The volume increments were regressed from a training set of 53 crystalline organic compounds. The method is restricted to compounds that are solids at room temperature that contain only the elements H, C, O, N, S, F, Cl, Br, I, Na, K, and Rb, and its applicability to cyclic compounds is limited to derivatives of benzene and naphthalene.

The only other reasonably accurate, general method for estimating solid density that we found in the literature was a purported "back of the envelope" method by Girolami.[13] Little information is available about the specific temperature at which this method is valid, but we infer from the original paper that, like the Immirzi–Perini method, its intended application is room temperature. The Girolami method is also an element-additive method (elements in the same row of the periodic table have the same additive contribution). In Table 1, 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 1 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_t, where this equation is applicable, compared to the results obtained from eq 2 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 1. Also shown in Table 1 are the results obtained from the Immirzi–Perini method for a subset of the test data containing 70 compounds to which it could be applied. For this same group of compounds at room temperature, eq 2 produced an AAD of 0.48 kmol/m^3 showing considerable improvement over the element additive methods that produced AADs of 1.02 kmol/m^3 and 1.10 kmol/m^3 for the Girolami and Immirzi–Perini methods, respectively.

It is interesting that the new correlation gives a ratio of solid to liquid density at the triple point of 1.12 instead of the 1.17 value used in the original DIPPR correlation, eq 1. The improved AAD at the triple point shown in Table 1 for eq 2 suggests that the increased quantity of accurate solid densities now in the DIPPR database provides a better estimate of this ratio than could be obtained 20 years ago. 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 $0.3T_t$ or until there is a solid–solid-phase transition. Figure 2 illustrates its use for three different compounds, comparing estimated values to experimental data.

Conclusion

In this short note, 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 new relationship allows estimation of solid density (of the solid phase most stable at the triple point)

Table 1. Deviation Statistics (see Equation 2 for Definitions) for ρ_S

	at various *T*		at T_t		at 298.15 K	
	AAD/kmol·m^{-3}	AAPD/%	AAD/kmol·m^{-3}	AAPD/%	AAD/kmol·m^{-3}	AAPD/%
eq 2	1.10[c]	5.6[c]	1.36[a]	4.8[a]	0.60;[b] 0.48[d]	6.7;[b] 6.2[d]
eq 1	NA	NA	1.80[a]	6.4[a]	NA	NA
Immirzi–Perini[12]	NA	NA	NA	NA	1.10[d]	14.4[d]
Girolami[13]	NA	NA	NA	NA	0.95;[b] 1.02[d]	10.7;[b] 12.4[d]

[a] 21 compounds. [b] 94 compounds. [c] 182 compounds. [d] 70 compounds.

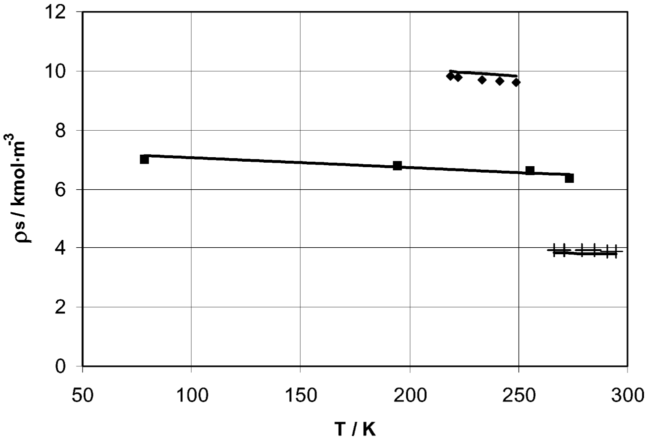

Figure 2. Experimental solid densities (points) compared to values estimated (lines) from liquid densities at the triple point (obtained from the DIPPR database) using eq 2. ◆, neopentane; ■, *n*-nonanoic acid; +, *n*-hexadecanoic acid.

for organic compounds over a wide range of temperatures with an estimated average uncertainty of about 6%, and it fills a void in available estimation techniques for solid properties.

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