

# A new group contribution method for the estimation of the surface tension of non-electrolyte organic compounds.



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## Introduction

- Surface tension is an important property in the chemical and process industries in many applications and operations.
- Current estimation methods require parameters that might not be widely available.
- A group contribution method for the estimation of surface tension was developed based on the preceding work and technology developed by Cordes et al. [1], Nannoolal et al. [2-5] and Moller et al. [6].
- Data from the Dortmund Data Bank (DDB) [7] was used to fit the group parameters.
- The DDB currently contains over 22000 surface tension data points for about 2200 compounds.
- Group contribution methods have the advantage that only molecular structure and easily obtainable data is required.

## Theory

- Surface tension is a property that arises at the vapour-liquid interface due to unbalanced forces acting on the molecules in the liquid surface layers.
- The molecules at the interface experience different interactions from the vapour and liquid phases which causes the surface to be in tension.
- The surface tension is related to the Gibbs free energy by Equation (1) [8].
- The surface tension of non-associating compounds follows an almost linear trend with temperature as can be seen in Figure 1.
- The surface tension of associating compounds follows a different trend as can be seen in Figure 2.
- The difference between these behaviours is due to dimerization of the compounds.

$$\sigma = \left( \frac{\partial G}{\partial A} \right)_{T, P, n} \quad (1)$$

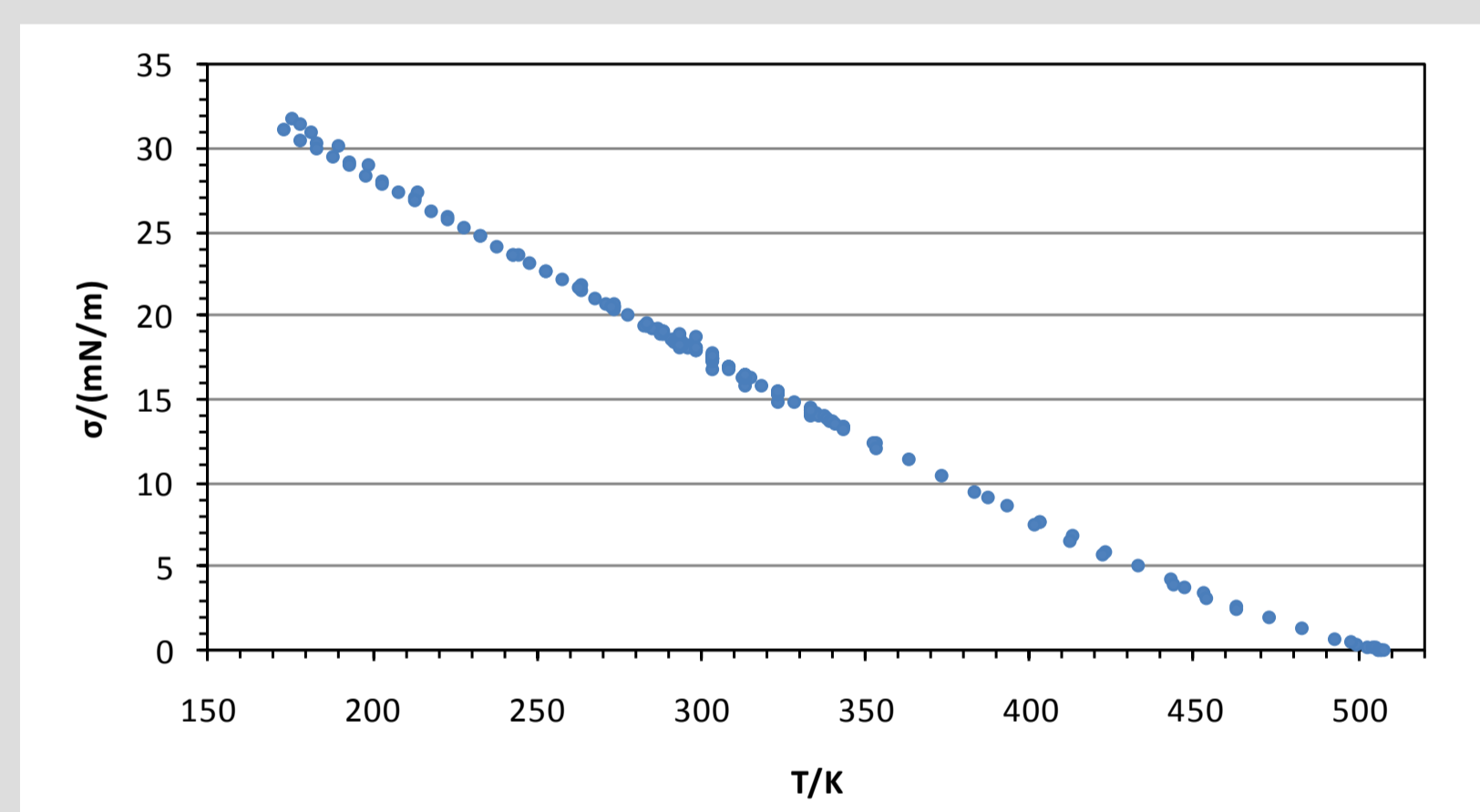


Figure 1. Surface tension of n-Hexane as a function of temperature. Data taken from DDB [7].

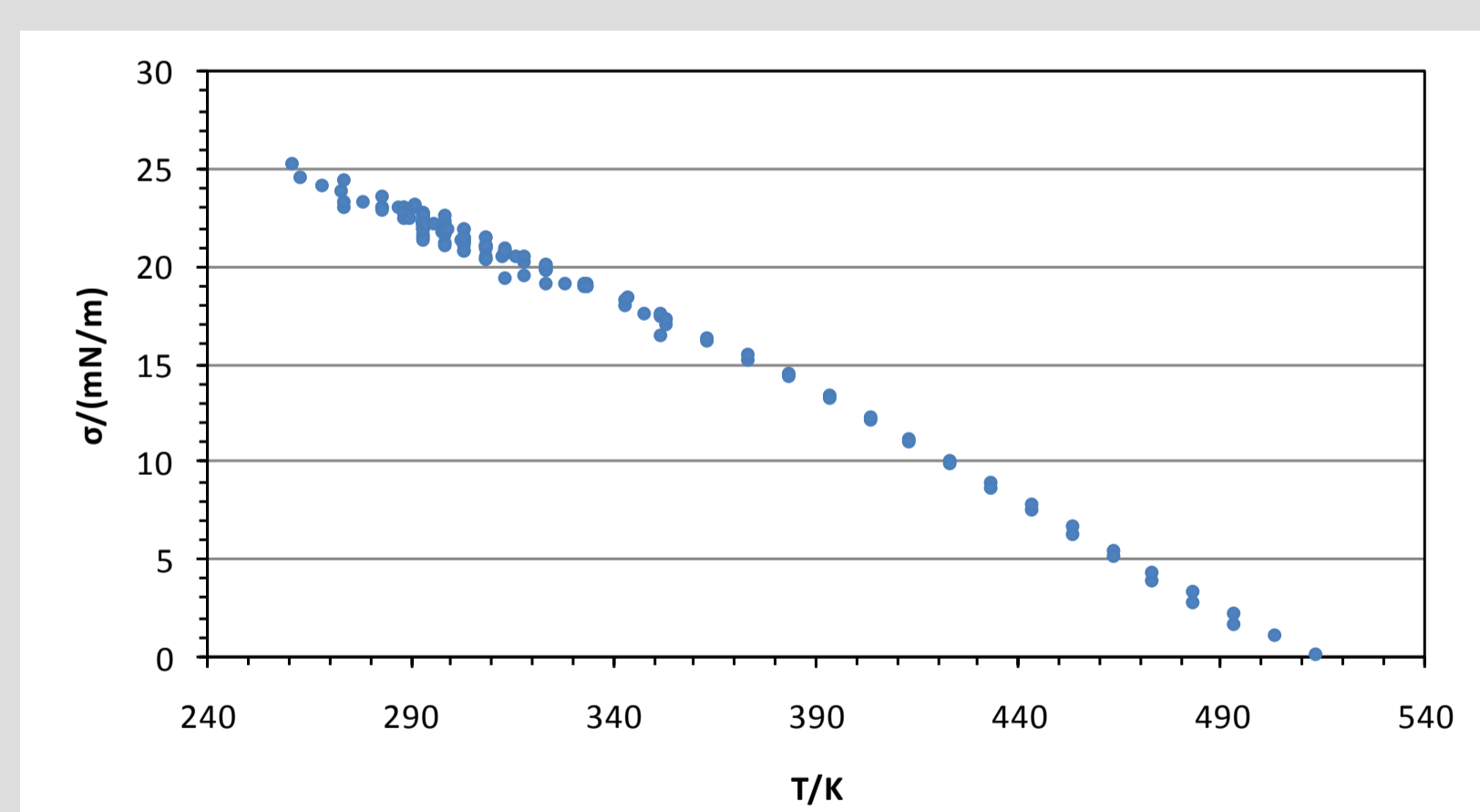


Figure 2. Surface tension of Ethanol as a function of temperature. Data taken from DDB [7].

## Model

- The proposed model is given by Equation (2).
- The normal boiling point is used as a reference temperature as this provides a better description over a larger reduced temperature range as opposed to using 298.15 K as the reference temperature. See Figure 3 and Figure 4.
- The a parameter was found to be non-linear with respect to the number of heavy atoms and is calculated using Equation (3). The trend can be seen in Figure 5.
- The b parameter was found to be non linear with respect to the number of heavy atoms and is calculated using Equation (4). The trend can be seen in Figure 6.

$$\sigma = \left( a + b \left( 1 - \frac{T}{T_b} \right) \right)^{\frac{11}{9}} \quad (2)$$

## Model (Continued)

$$a = \frac{\sum v_i C_i(a)}{n^d + e} + f \quad (3)$$

$$b = \frac{\sum v_i C_i(b)}{n^d + e} + f \quad (4)$$

- $C_i(a)$  and  $C_i(b)$  are parameters specific to each functional group.
- To ensure that the group values are physically realistic, and not just a fit to noise in the data, boundary conditions are introduced to enforce a specific relationship between the groups. See Figure 7.

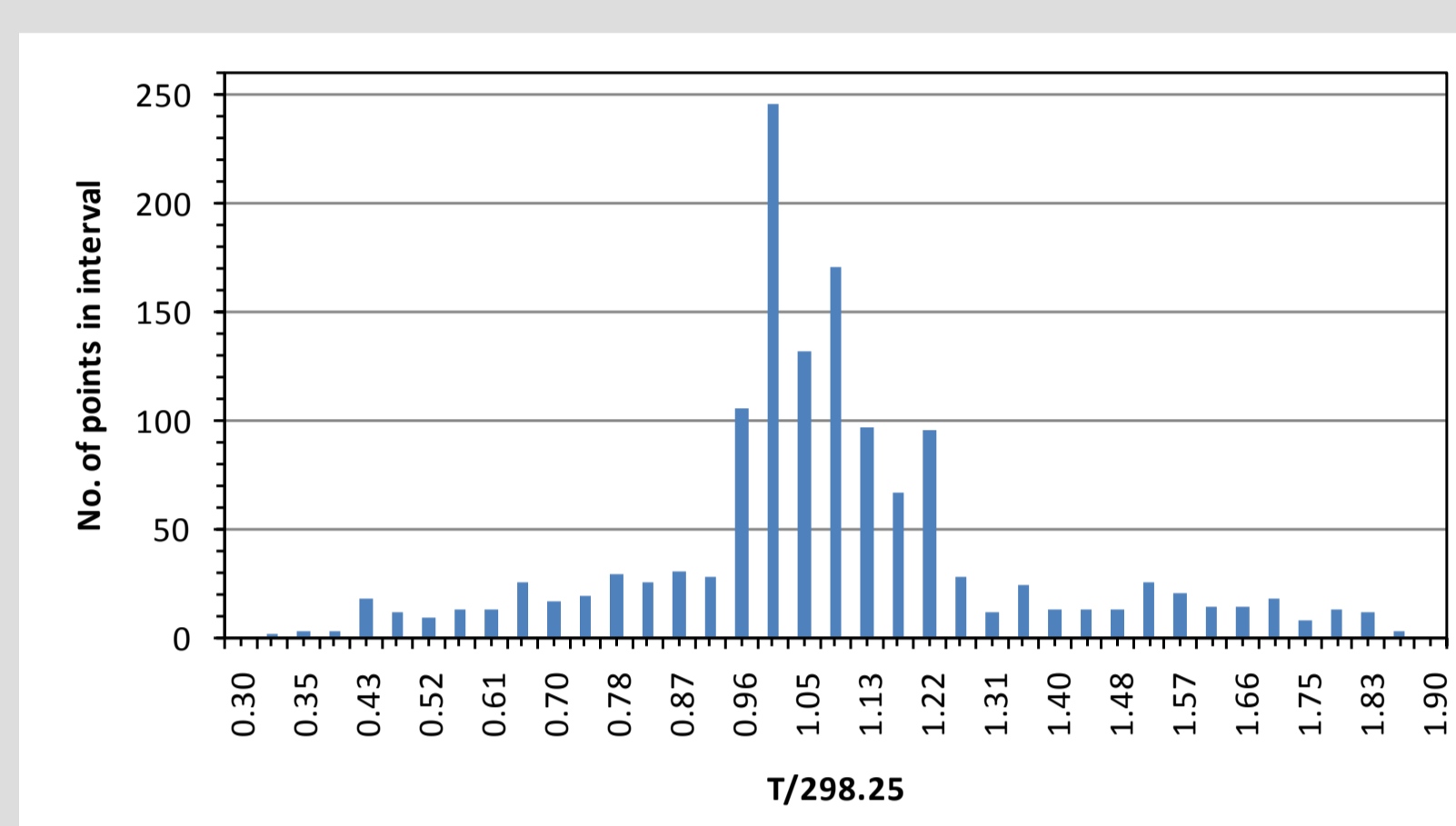


Figure 3. Distribution of data when using 298.15 K as a reference temperature for Equation (2).

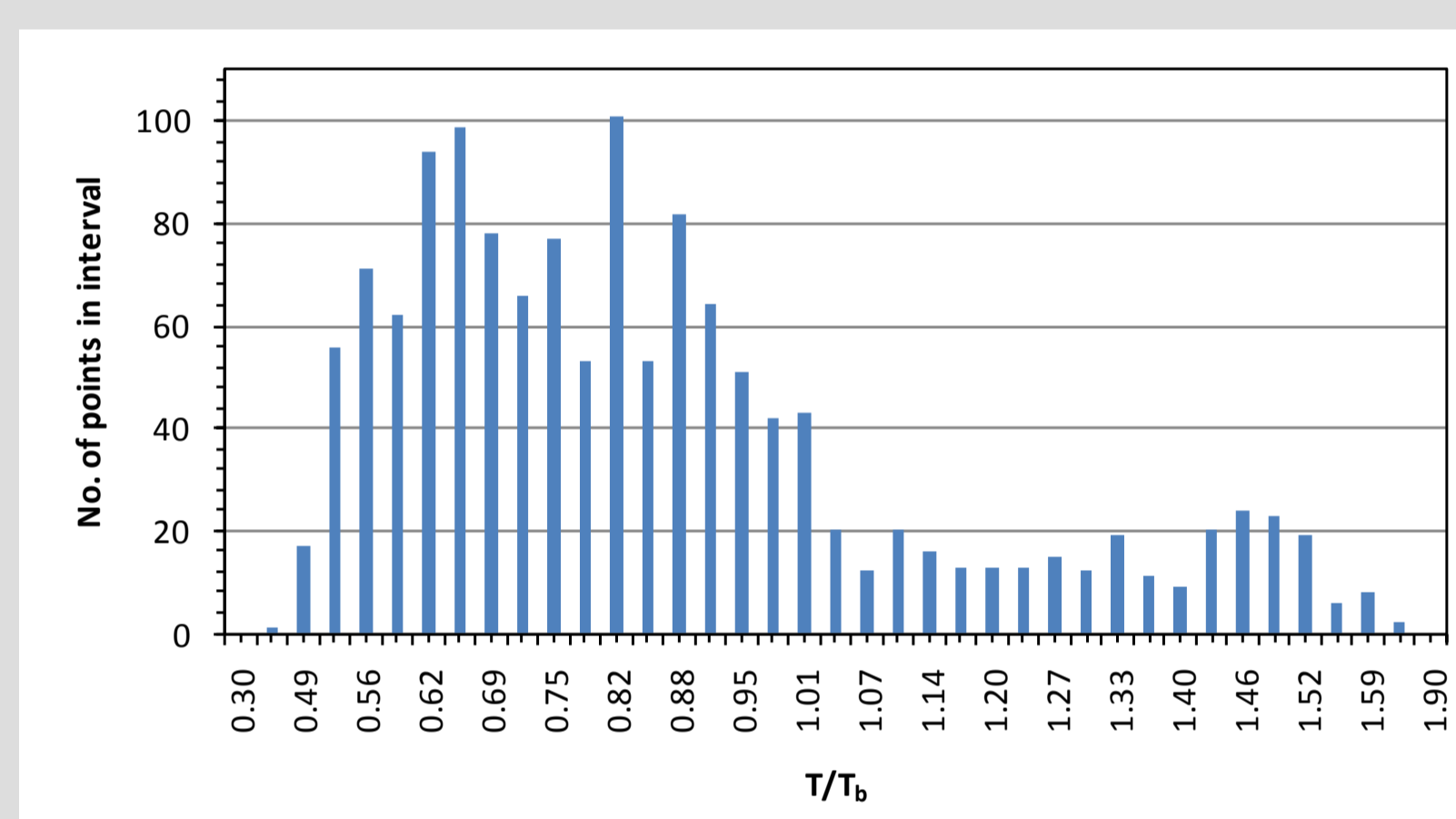


Figure 4. Distribution of data when using the normal boiling point as a reference temperature for Equation (2).

## Results

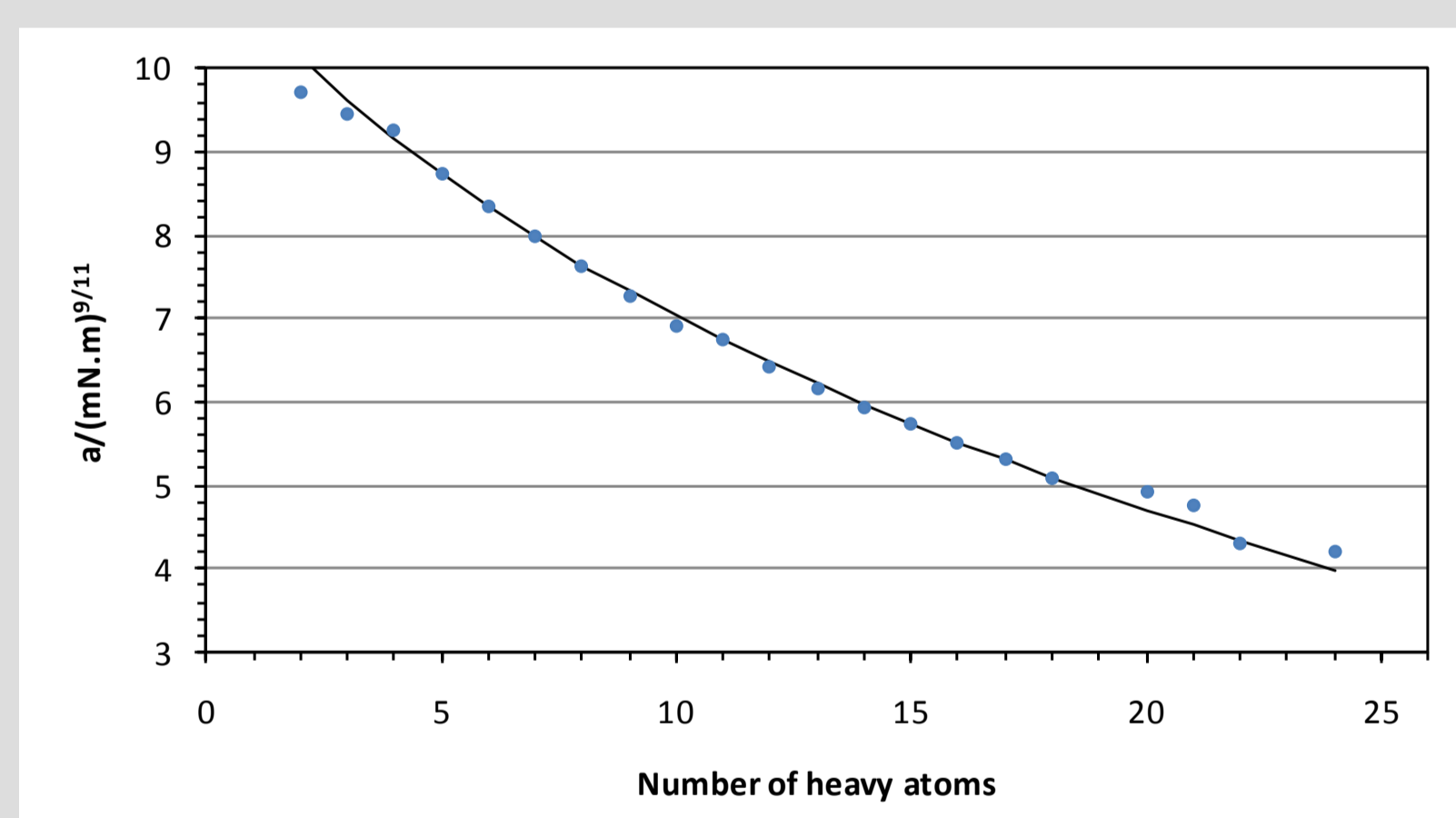


Figure 5. Parameter a from Equation 2 vs. the number of heavy atoms. (• Fitted to experimental data, — Predicted using Equation (3)).

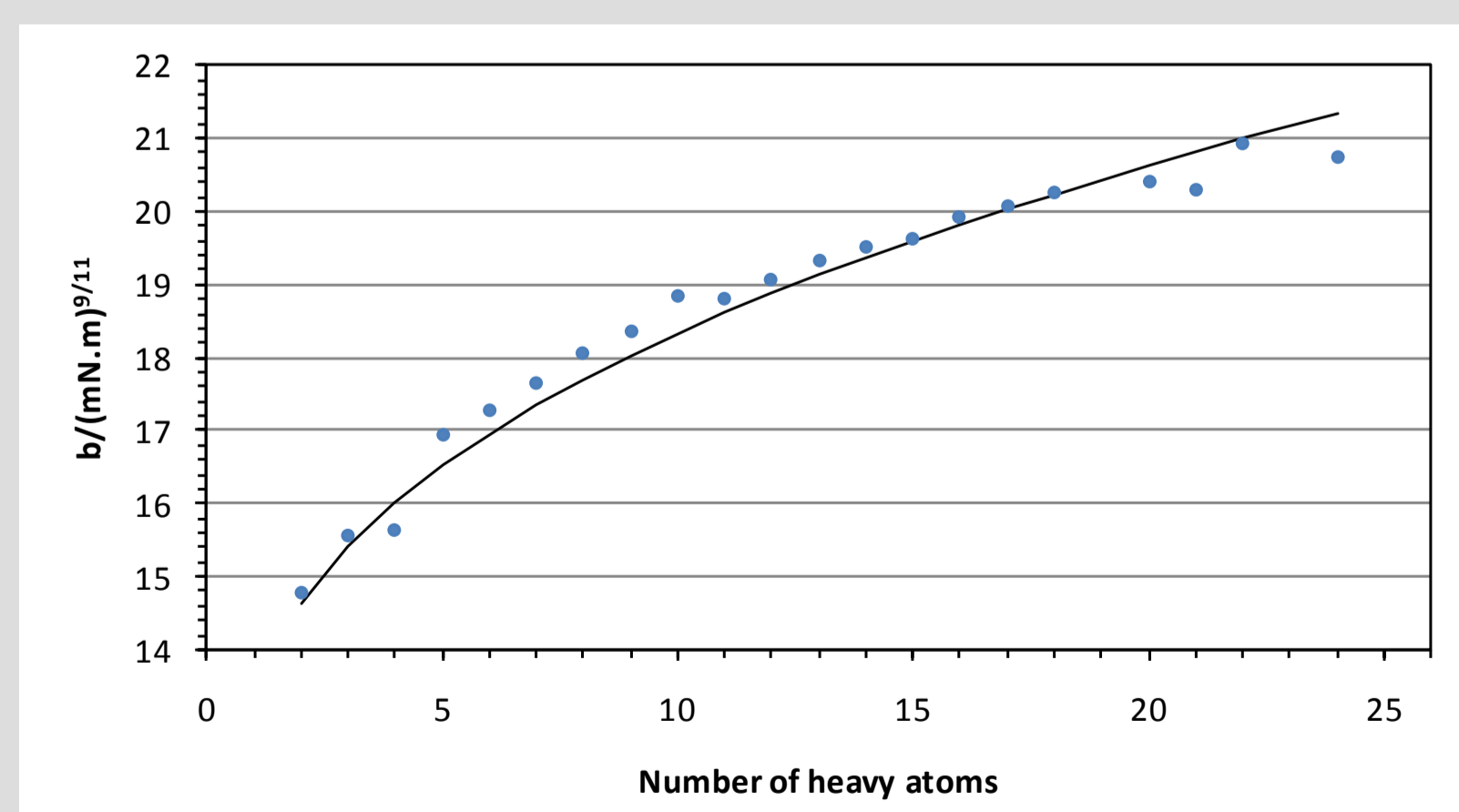


Figure 6. Parameter b from Equation 2 vs. the number of heavy atoms. (• Fitted to experimental data, — Predicted using Equation (4)).

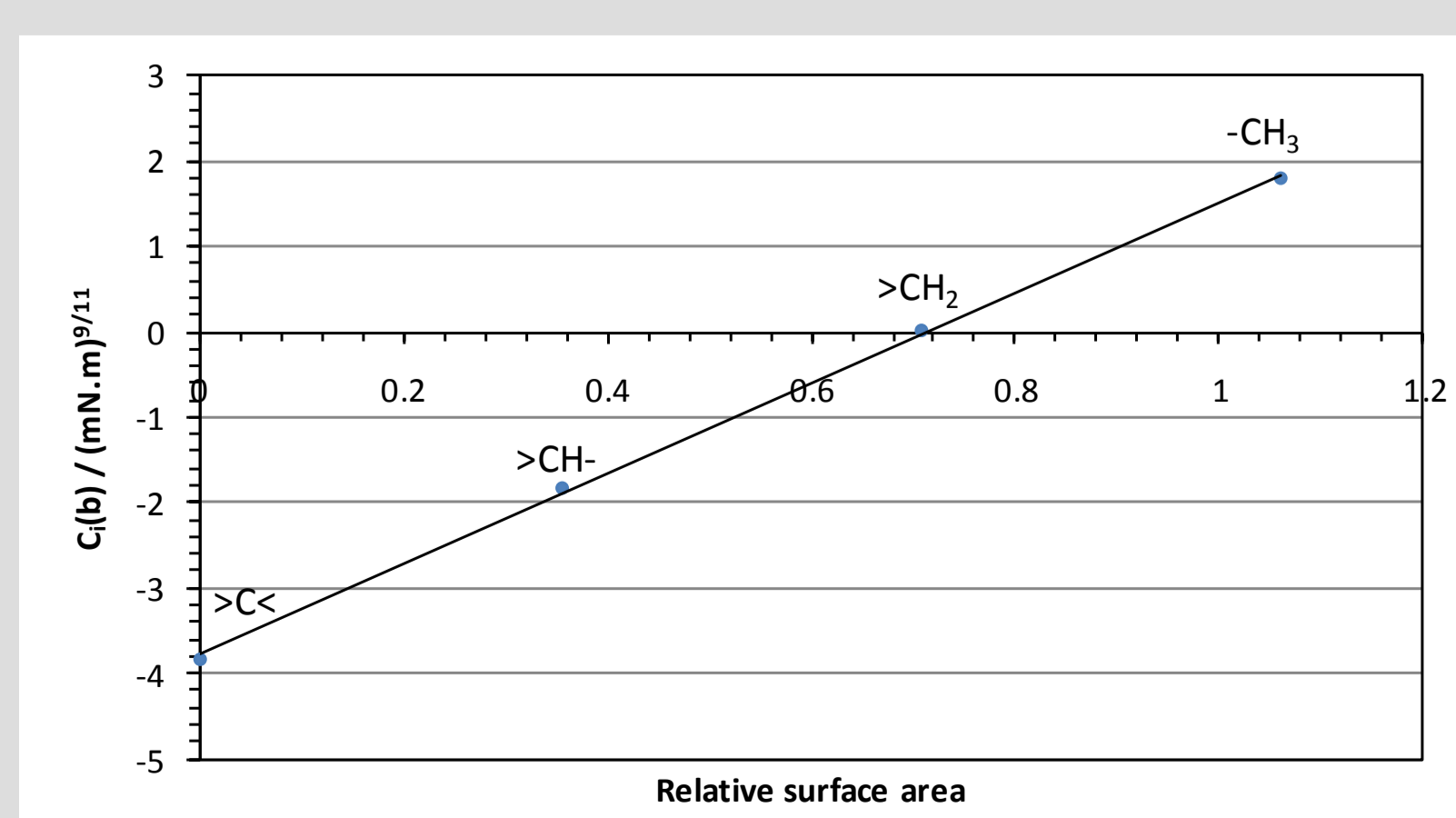


Figure 7. Group parameters for use in Equation (4) vs. the relative surface area. (• Fitted to experimental data, — linear fit).

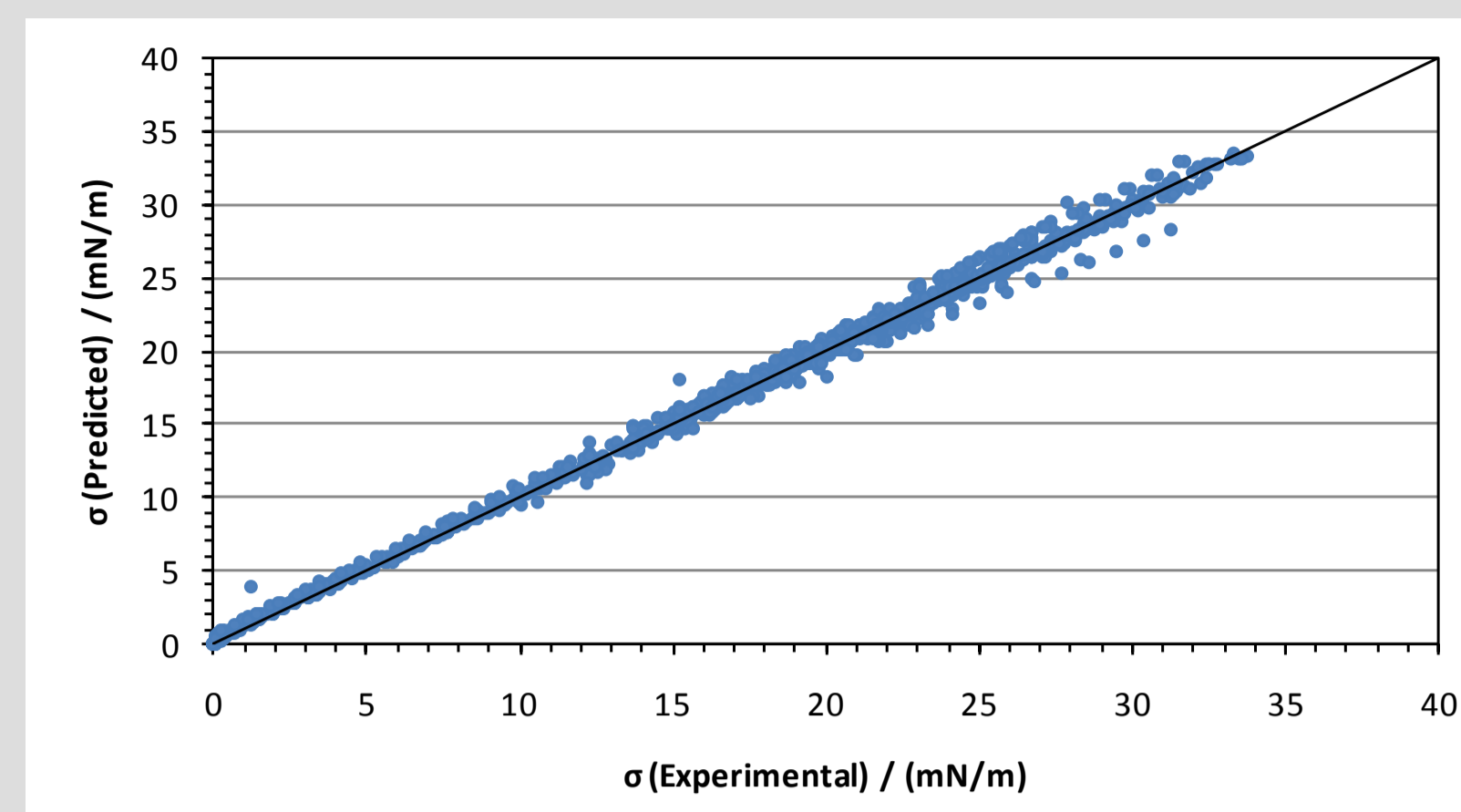


Figure 8. Surface tension predicted by Equation (2) vs. experimental data. Experimental data taken from DDB [7].

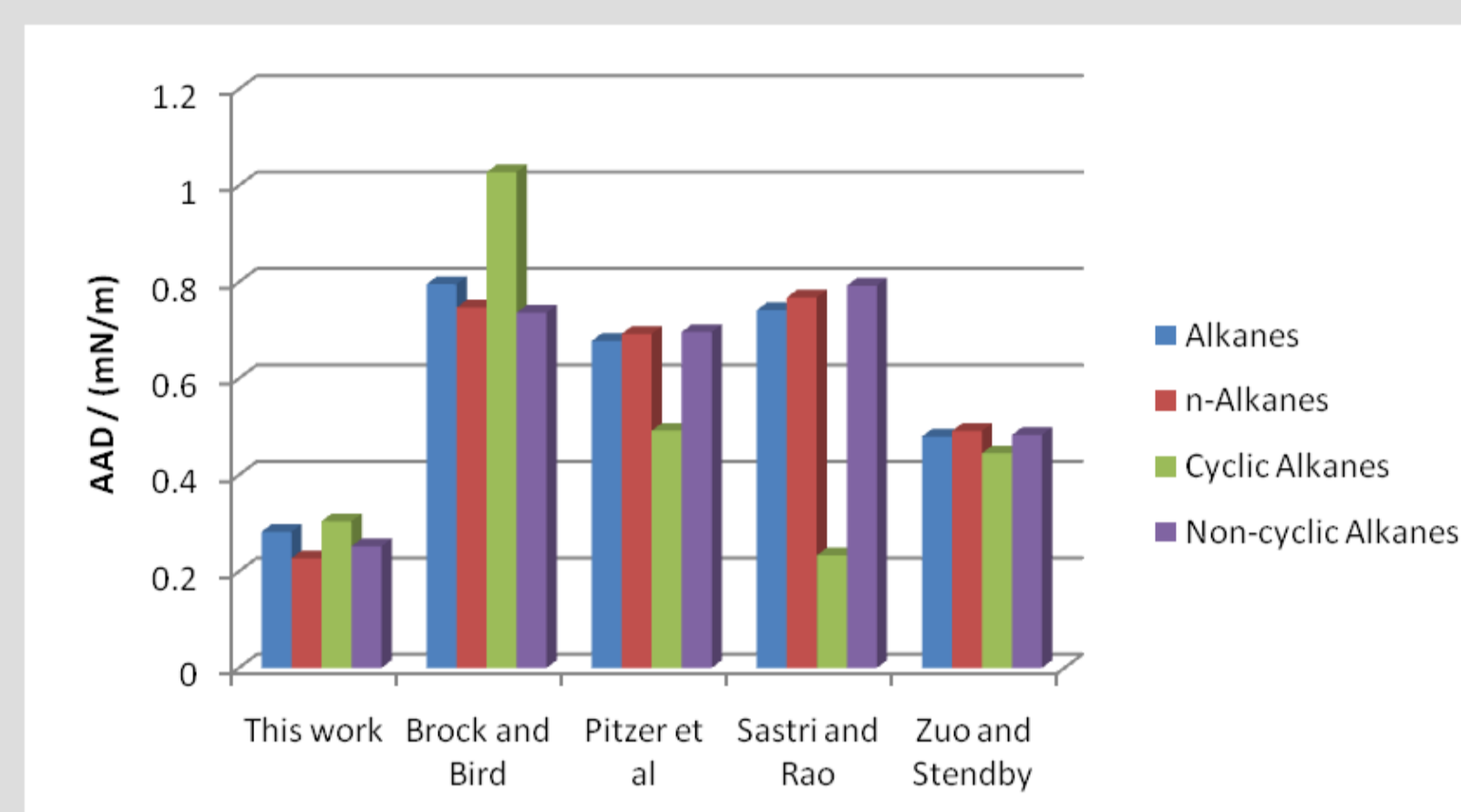


Figure 9. Absolute average deviation of different predictive methods for Alkanes.

## Discussion

- The proposed model, Equation (2), gives a correct description of the surface tension of non-associating compounds over a large range of molecular sizes.
- Both the a and b parameters in Equation (2) exhibit a non-linear dependence on the number of heavy atoms in the molecule.
- Only the molecular structure and the normal boiling point is required to predict the surface tension.
- The proposed method compares very favourably to methods that are currently available. See Figure 9.
- The proposed model can only describe the behaviour of associating compounds at higher temperatures. Work is underway to extend this method to lower temperatures by accounting for the formation of dimers.

## Conclusions

- A group contribution method has been developed for the prediction of surface tension of non-electrolyte organic compounds.
- The method compares favourably to predictive methods that are currently available.
- The method is being extended to predict the surface tension of other families of non-electrolyte organic compounds.

## Acknowledgements

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