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SHORT COMMUNICATION

**Prediction of high pressure liquid heat capacities of organic compounds by a group contribution method**

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**Abstract:** A new method for estimating high pressure liquid heat capacities based on molecular structure and group contribution is proposed. A common set of structural groups was employed. The method was developed using 67 sets of 43 organic compounds with 3449 experimental heat capacity data. A small number of measured compounds, data points per compound and other comparable methods were observed. This is a simple first-order approximation with acceptable accuracy of 2.55 %.

**Keywords:** high pressure heat capacity; prediction; group contribution; liquid; pure compound.

INTRODUCTION

Heat capacity is a basic thermodynamic property, like a heat of vaporization.<sup>1</sup> It is used in chemical engineering calculations to obtain the differences in thermodynamic functions between two different temperatures. The heat capacity of liquids is often necessary information for chemical engineering calculation and design.<sup>2,3</sup> Experimental liquid heat capacity data are available for many substances,<sup>4–7</sup> but mostly at the saturation line, at atmospheric or low pressures. In addition, for only a small number of compounds do the extant data cover the temperature interval from melting point up to the critical temperature. A wide pressure interval of experimental data is even harder to find and data sets with both intervals are very rare.<sup>8</sup> Under such circumstances, prediction methods are an obvious choice for providing liquid heat capacities for compounds for which there is a

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complete lack of data or for which data are available only over limited temperature and/or pressure intervals.

Many methods for predicting liquid heat capacity data based only on temperature dependence<sup>9–39</sup> have been proposed. In this article, a new method is proposed with both temperature and pressure dependences.

#### METHOD DEVELOPMENT

Group contribution methods are among the simplest and easiest methods that apply techniques developed and tested for the estimation of various thermophysical properties. The aim of this article was to develop a simple group contribution estimation method using a consistent set of molecular groups that would cover a wide variety of organic compounds. We used the first order approximation (part of the Lydersen groups) because of insufficiency of experimental data and therefore inability to obtain reliable contributions for interactions between the groups and structurally dependent contributions. On the other hand, higher order contributions lead to significantly more complex estimation methods. After consideration and examination of many functional forms, as well as temperature and pressure influences, the following expression was developed:

$$c_{pl} = T^{0.5} \sum \Delta c + A + BT + CpT \quad (1)$$

The linear least squares method was used to calculate the group contributions  $\Delta c$ , and the adjustable parameters  $A$ ,  $B$ , and  $C$  in Eq. (1). The minimized objective function has the following form:

$$F = \sum_{i=1}^N (c_{pl,exp,i} - c_{pl,cal,i})^2 \rightarrow \min \quad (2)$$

Finally, the proposed equation for liquid heat capacity estimation at pressures up to 300 MPa and at temperatures up to  $0.9 T_r$  is as follows:

$$c_{pl} = T^{0.5} \sum \Delta c + 136.38 + 0.45419T - 0.00029936pT \quad (3)$$

Overall percent errors were calculated as follows:

$$P_{av} = \frac{\sum_{i=1}^N n_i AAPE_i}{\sum_{i=1}^N n_i} \quad (4)$$

$$AAPE = 100 \sum_{i=1}^n \frac{|c_{pl,exp,i} - c_{pl,cal,i}|}{c_{pl,exp,i}} \quad (5)$$

The literature experimental data used for the development of the method, covering 3449 data points in 67 data sets for 43 organic compounds, are given in Supplementary material.

#### RESULTS AND DISCUSSION

An extensive evaluation of the proposed method was conducted by comparing the estimated heat capacities with raw experimental data from the literature. The calculated group contribution values are presented in Table I. The proposed method is linear and an extrapolation can be made, however it fails in the vicinity

of the critical point where the heat capacity rises quickly and becomes indefinite at the critical point. For improvement and further development of the proposed method, more experimental data (more compounds and broad temperature and pressure intervals, particularly near critical temperature) are required.

Table I. Group contributions

Group	$\Delta c$
CH <sub>3</sub> -	-5.6218
-CH <sub>2</sub> -	1.7236
>CH-	8.7826
>C<	15.817
-CH <sub>2</sub> - (aromatic)	-1.2858
>CH- (aromatic)	5.7056
F-	-6.3816
Cl-	-6.1657
CN-	-5.7647
Br-	-6.6308
OH-	-3.0054
NH <sub>2</sub> -	-7.2171
Cyclic correction	-16.325

The results of the prediction for the liquid heat capacities are presented in Table I-S (Supplementary material). In the absence of any predictive method for high pressures, the results of the proposed method are presented with the results of the method developed by Kolská<sup>24</sup> for moderate pressures. The table includes a list of chemical compounds (literature references are given in column "Ref.", Table I-S), number of experimental points per set  $n$  (the second number in the fourth column is the number of data used in correlation – at pressures up to 300 MPa and at temperatures up to  $0.9 T_r$ ), temperature ranges (minimal  $T_{\min}$  and maximal  $T_{\max}$  temperature per set), critical temperatures  $T_c$ , pressure ranges (minimal  $p_{\min}$  and maximal  $p_{\max}$  pressure per set), and the average percent errors per set for both methods. As can be seen from Table I-S, the proposed method with an overall accuracy of 2.55 % has very wide applications.

Training and verification sets are not necessary in this case, since the new model is a group contribution model. The regression procedure of group contribution models should include as many experimental values as possible to cover the widest application and give safe extrapolations.<sup>11</sup>

#### CONCLUSIONS

A group contribution method for estimating high pressure liquid heat capacity, where the group identification was defined by Lydersen, has been proposed. This method provides satisfactory correlation accuracy over broad temperature and pressure ranges. The average percent error obtained for all investigated com-

pounds is around 2.5 %. For further method development, additional experimental data are necessary.

#### SUPPLEMENTARY MATERIAL

The literature experimental data used for the development of the method, covering 3449 data points in 67 data sets for 43 organic compounds, are available electronically at <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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#### NOMENCLATURE

$c_{pl}$	Liquid heat capacity, J mol <sup>-1</sup> K <sup>-1</sup>
$c_{pl,exp}$	Experimental liquid heat capacity, J mol <sup>-1</sup> K <sup>-1</sup>
$c_{pl,cal}$	Calculated liquid heat capacity, J mol <sup>-1</sup> K <sup>-1</sup>
$T$	Temperature, K
$p$	Pressure, MPa
$A, B, C$	Adjustable method parameters
$\Delta c$	Group contribution
$AAPE$	Average percent error, %
$P_{av}$	Overall percent error, %
$n$	Number of experimental data points
$N$	Number of compounds
$T_{max}$	Maximal temperature value per set, K
$T_{min}$	Minimal temperature value per set, K
$p_{max}$	Maximal pressure value per set, MPa
$p_{min}$	Minimal pressure value per set, MPa
$T_c$	Critical temperature, K
$T_r$	Reduced temperature $T/T_c$

#### ИЗВОД

#### ПРЕДСКАЗИВАЊЕ ТОПЛОТНОГ КАПАЦИТЕТА ОРГАНСКИХ ТЕЧНОСТИ НА ВИСОКОМ ПРИТИСКУ ПОМОЋУ МЕТОДЕ ДОПРИНОСА ГРУПА

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Предложен је нови метод за предсказивање вредности изобарског топлотног капацитета течности на високом притиску на основу молекулске структуре супстанце и вредности доприноса група у молекулу. Метод је развијен коришћењем 67 сетова експерименталних података за 43 различите органске супстанце са укупно 3449 података. Постојање експерименталних података за мали број различитих супстанци узроковао је ограничен број доприноса група. Предложени модел даје прихватљиво средње процентуално одступање од 2,55 %. У литератури није пронађен ни један метод за предсказивање вредности изобарског топлотног капацитета органских течности на високом притиску.

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