



Group contribution method: Surface tension of linear and branched alkanes



Alena Randová*, Lidmila Bartovská

University of Chemistry and Technology, Prague, Department of Physical Chemistry, Technická 5, 166 28 Prague 6, Czech Republic

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ABSTRACT

A group contribution method for predicting the surface tension of alkanes at various temperatures, based on Guggenheim-Katayama-van der Waals equation, has been developed. The constants of this equation evaluated from TRC Tables data for surface tension were used as a basis to determine contributions of structural units. With knowledge of critical temperature of the liquid alkane it is possible to predict value of its surface tension at various temperatures (from 273.15 to 333.15 K, or to temperature below the normal boiling point). The data for 50 compounds were processed: 30 of them to determine contributions of structural units (main set), and remaining 20 compounds (denoted as test set) to verify the proposed method. On the whole, 394 data points were used, 235 in the main set and 159 in the test set.

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1. Introduction

The efficient design of the processes in chemical, petroleum, pharmaceutical, or polymer industries can be performed if the values of the thermophysical, physicochemical, and/or thermodynamic properties of the involved liquids are available. One of these important physical properties is surface tension. Even though the experimental data for surface tensions are plentiful nowadays, the rapid development of industry needs large amounts of experimental data of surface tensions for a variety of substances at different temperatures. Therefore, it is very useful to develop estimating methods with a wide range of applicability and good prediction accuracy. This work pays attention to the prediction of surface tension of liquid alkanes by group contribution method.

1.1. Group contribution method (GCM)

Prediction/estimation of compound property is an important question in the industry (it is significant in simulation, modelling, and controlling factories). Many laboratories are concentrated on predicting properties of organic, inorganic, and biochemical compounds. One of the possibilities for prediction is a group

contribution method. Using group properties (assuming the structure of the molecule is known) to predict total property of a compound reduces the demand for experimental data considerably. The additive property may be calculated by summing up of the contributions corresponding to certain parts of the molecules, named units. A lot of GCM for a lot of properties has been already compiled. The most popular are critical properties [1–6] and enthalpy of vaporization [5,7–10]. Other examples are acentric factor [11], density [12,13], activity coefficient [14,15], normal boiling point [16], solvent activities in polymer solutions [17], gas permeability in glassy polymer [18], probability and rate of aerobic biodegradation [19], viscosity [20,21], Hansen solubility parameters [22], toxicity of organic chemicals [23], octane number [24], second virial coefficient [25], and least not last – surface tension, the subject of this work.

1.2. Surface tension

The boundary between a liquid phase and a gas phase can be considered a third phase with properties distinct from those of the liquid and gas – surface layer. The surface layer is in tension and tends to contract to the smallest area compatible with the mass of material, container restraints, and external forces, e.g., gravity. The surface tension (γ) is defined as the force exerted in the plane of the surface per unit length. The thermodynamics of surface layers presents an important and interesting part of science [26–32].

* Corresponding author.

E-mail addresses: randovaa@vscht.cz (A. Randová), bartovsl@vscht.cz (L. Bartovská).

1.3. Guggenheim-Katayama-van der Waals equation

The principle of corresponding states may be safely regarded as the most useful byproduct of van der Waals equation of state. This principle can be applied to a variety of properties, such as e.g. the critical state, the densities of coexistent phases, the vapour pressure of the liquid, the entropy of evaporation, the heat capacity of the liquid, and even to the temperature dependence of surface tension of the liquids. The surface tension decreases with increasing temperature, in the critical point the vapour-liquid interface disappears and the surface tension reaches zero.

Guggenheim [33] picked up the threads of van der Waals and Katayama works and presented the Guggenheim-Katayama-van der Waals equation:

$$\gamma = \gamma^0 \cdot \left(1 - \frac{T}{T_c}\right)^n \quad (1)$$

where γ^0 and n are constants, T is temperature in K, and T_c is critical temperature in K. Guggenheim's theoretically derived value of $n = 11/9$ holds true for ideal situation. In real systems the constant n takes various values, from $n = 1.16$ to $n = 1.5$ [34]. In recent years, equation (1) has been often used to correlation of surface tension and the constants γ^0 and n were determined for many compounds [35–38]. Equation (1) can be also used to estimation of critical temperature [26,39–41] from experimental data on temperature dependence of surface tension.

2. Developing of group contribution method

2.1. Definition of structural units

Various group contribution methods hitherto used either estimated directly the surface tension values [42,43], or the GCM were applied to determination of parachor [44–49] from which the surface tension was calculated.

The presented group contribution method is based on eq. (1), similarly as in the work of Wu et al. [38] for ionic liquids. But whereas they estimated only one of the constants, γ^0 , and the second constant, n , was assumed to have the Guggenheim's theoretical value of 11/9, our group contribution method is applied to determination of both constants. The definition of structural units and their description are presented in Table 1.

A detailed survey of all compounds together with their structural units is presented in Table 2. The principle of defining the structural units is demonstrated on two examples shown in Fig. 1.

2.2. Dividing of compounds into groups

The compounds included into our study were divided into eight groups: linear alkanes, alkylbutanes, alkylpentanes, alkylhexanes, alkylheptanes, alkyloctanes, alkylcyclopentanes, and alkylcyclohexanes (Table 2; each compound was assigned its serial number m).

Table 1
Structural units.

C-group units	
CH ₃	Group CH ₃ – (one single bond)
CH ₂	Group –CH ₂ – (two single bonds)
CH	Group > CH– (three single bonds)
C	Group > C< (four single bonds)
Geometry unit	
b	Number of C-bone units attached to the main skeleton or cycle of molecule
c	Cycle in the molecule (cyclopentane or cyclohexane)

Table 2
Characterization of compounds by structural units.

m	Compound	CH ₃	CH ₂	CH	C	b	c
Linear alkanes							
1	Hexane	2	4				
2	Heptane	2	5				
3	Octane	2	6				
4	Nonane	2	7				
5	decane	2	8				
6	Undecane	2	9				
7	Dodecane	2	10				
8	Tridecane	2	11				
Alkylbutanes							
9	2-methylbutane	3	1	1		1	
10	2,2-dimethylbutane	4	1		1	2	
11	2,3-dimethylbutane	4		2		2	
Alkylpentanes							
12	2-methylpentane	3	2	1		1	
13	2,2-dimethylpentane	4	2		1	2	
14	2,3-dimethylpentane	4	1	2		2	
15	2,2,3-trimethylpentane	5	1	1	1	3	
16	2-methyl-3-ethylpentane	4	2	2		3	
17	3-methyl-3-ethylpentane	4	3		1	3	
18	2,2-dimethyl-3-ethylpentane	5	2	1	1	4	
19	2,4-dimethyl-3-ethylpentane	5	1	3		4	
20	3,3-diethylpentane	4	4		1	4	
Alkylhexanes							
21	2-methylhexane	3	3	1		1	
22	2,2-dimethylhexane	4	3		1	2	
23	2,3-dimethylhexane	4	2	2		2	
24	3-ethylhexane	3	4	1		2	
25	2,2,3-trimethylhexane	5	2	1	1	3	
26	2-methyl-3-ethylhexane	4	3	2		3	
27	3-methyl-3-ethylhexane	4	4		1	3	
Alkylheptanes							
28	2-methylheptane	3	4	1		1	
29	2,2-dimethylheptane	4	4		1	2	
30	2,3-dimethylheptane	4	3	2		2	
Alkyloctanes							
31	2-methyloctane	3	5	1		1	
Alkylcyclopentanes							
32	Methylcyclopentane	1	4	1		1	1
33	Ethylcyclopentane	1	5	1		2	1
34	Propylcyclopentane	1	6	1		3	1
35	Decylcyclopentane	1	13	1		10	1
36	1,1-dimethylcyclopentane	2	4		1	2	1
37	Isobutylcyclopentane	2	5	2		4	1
Alkylcyclohexanes							
38	Methylcyclohexane	1	5	1		1	1
39	Ethylcyclohexane	1	6	1		2	1
40	Propylcyclohexane	1	7	1		3	1
41	Butylcyclohexane	1	8	1		4	1
42	Pentylcyclohexane	1	9	1		5	1
43	Hexylcyclohexane	1	10	1		6	1
44	Heptylcyclohexane	1	11	1		7	1
45	Octylcyclohexane	1	12	1		8	1
46	Nonylcyclohexane	1	13	1		9	1
47	Decylcyclohexane	1	14	1		10	1
48	1,1-dimethylcyclohexane	2	5		1	2	1
49	(1-methylpropyl)cyclohexane	2	6	2		4	1
50	(1,1-dimethylethyl)cyclohexane	3	5	1	1	4	1

The above listed compounds were divided in two sets: one, called “the main set”, comprising 30 members, from which the contributive values of structural units were determined, and the second, called “the test set”, comprising 20 members, serving to validation of the proposed procedure. The classification of individual compounds, identified by their serial numbers, into the main and test sets is shown in Table 3.

2.3. Errors

The contributions of the structural units were determined by

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