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Group Contribution Methods for Estimation of Selected Physico-Chemical Properties of Organic Compounds

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1. Introduction

Thermodynamic data play an important role in the understanding and design of chemical processes. To determine values of physico-chemical properties of compounds we can apply experimental or non-experimental techniques. Experimental techniques belong to the most correct, accurate and reliable. All experimental methods require relevant technical equipment, time necessary for experiment, sufficient amount of measured compounds of satisfactory purity. Compound must not affect technical apparatus and should not be decomposed during experiment. Other aspect is a valid legislation, which limits a usage of dangerous compounds by any users.

If due to any of these conditions mentioned above causes the experiment cannot be realized, some non-experimental approaches can be applied.

2. Non-experimental approaches to determine physico-chemical properties of compounds

If due to any of conditions results in that experimental determination cannot be realized and data on physico-chemical property are necessary, we have to employ some non-experimental approaches, either calculation methods or estimation ones. Due to the lack of experimental data for several industrially important compounds, different estimation methods have been developed to provide missing data. Estimation methods include those based on theory (e.g. statistical thermodynamics or quantum mechanics), various empirical relationships (correlations of required property with variable, experimentally determined compound characteristics, e.g. number of carbon atoms in their molecule, molecular weight, normal boiling temperature, etc.), and several classes of “additivity-principle” methods

(Baum, 1989; Pauling et al., 2001). Estimation methods can be divided into several groups from many aspects, e.g. into methods based on theoretical, semi-theoretical relations and the empirical ones. Books and papers of last decades divide estimation methods depending on the required input data into QPPR or QSPR approaches (Baum, 1989). QPPR methods (Quantity-Property-Property-Relationship) are input data-intensive. They require for calculation of searched value property knowledge of other experimental data. We can use them successfully only when we have input data. On the other hand QSPR (Baum, 1989) methods (Quantity-Structure-Property-Relationship) need only knowledge of the chemical structure of a compound to predict the estimated property. QSPR methods use some structural characteristics, such as number of fragments (atoms, bonds or group of atoms in a molecule), topological indices or other structural information, molecular descriptors, to express the relation between the property and molecular structure of compound (Baum, 1989; Pauling et al., 2001; Gonz  les et al., 2007a). Empirical and group contribution methods seem to be the most suitable (Pauling et al., 2001; Majer et al., 1989) due to their simplicity, universality and fast usage.

2.1. Group contribution methods

Group contribution methods are presented as empirical QSPR approaches. The easiest models were based on study of property on number of carbon atoms n_C or methylen groups n_{CH_2} in molecules of homological series. In Fig. 1 is presented dependence of normal boiling temperature T_b on number of carbon atoms n_C (bottom axis) or methylen groups n_{CH_2} (top axis) in molecules of homological series n -alkanols C_1 - C_{12} (Majer & Svoboda, 1985; NIST database). As we can see, this dependence is clearly linear in some range of $n_C=C_2$ - C_{10} . But increasing discrepancy is evident either for low number of carbon atoms C_1 or for higher one $n_C>C_{10}$. Due to these departures from linear behaviour some parameters covering structural effects on property were inclusive to these easy models (e.g. Chickos et al., 1996). From these approaches structural fragments and subsequently group contribution methods have been established.

Group contribution methods are based on the so called “additive principle”. That means any compound can be divided into fragments, usually atoms, bonds or group of atoms, etc. All fragments have a partial value called a contribution. These contributions are calculated from known experimental data. Property of a compound is obtained by a summing up the values of all contributions presented in the molecule. Example of division of molecule of ethanol into atomic, bond and group fragments is presented in Fig. 2. When we divide this molecule into atomic fragments, the total value of property X of ethanol is given by summing up the values for two carbon atom contributions $X_{(C)}$, six hydrogen atom contributions $X_{(H)}$ and one oxygen atom contribution $X_{(O)}$. The second way is the division of ethanol molecules into the following bond fragments with their contribution: $X_{(C-C)}$, $X_{(C-O)}$, $X_{(C-H)}$ and $X_{(O-H)}$. Due to increasing quality and possibility of computer technique a fragmentation into more complex group structural fragments is applied in present papers (Baum, 1989; Pauling et al., 2001). Some of ways to divide the molecule ethanol into group structural fragments are presented in Fig. 2. Ethanol molecule can be divided either into: (i)

CH₃-, -CH₂- and -OH, or: (ii) CH₃- and -CH₂OH. More complex compounds are described by more complex structural fragments.

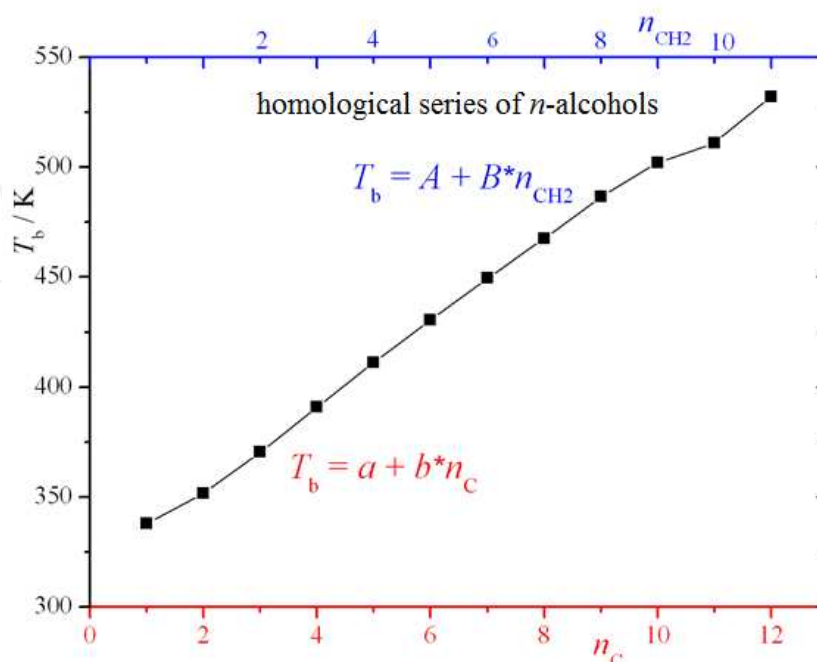


Figure 1. Dependence of normal boiling temperature of *n*-alkanols in homological series C₁-C₁₂

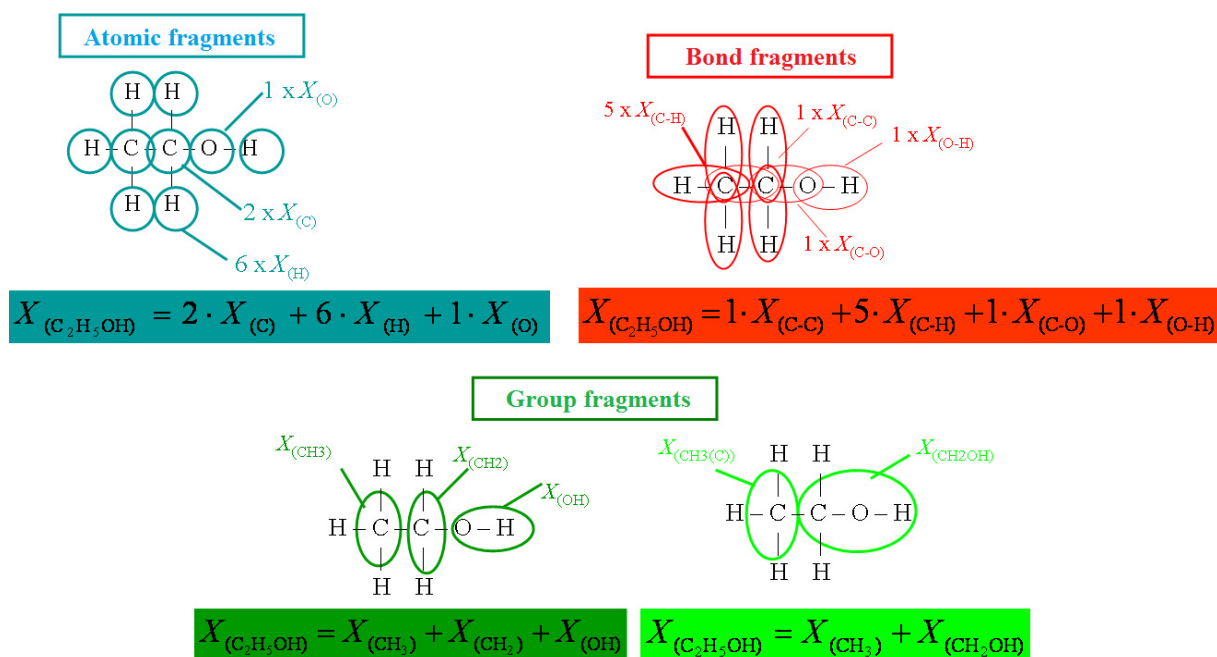


Figure 2. Example of division of ethanol molecule into atomic, bond and group structural fragments

Group contribution methods are essentially empirical estimation methods. A large variety of these models have been designed during last centuries, differing in a field of their applicability and in the set of experimental data. They were developed to estimate, e.g. critical properties (Lydersen, 1955; Ambrose, 1978; Ambrose, 1979; Joback & Reid, 1987;

Gani & Constantinou, 1996; Poling et al., 2001; Marrero & Gani, 2001; Brown et al., 2010; Monago & Otobrise, 2010; Sales-Cruz et al., 2010; Manohar & Udaya Sankar, 2011; Garcia et al., 2012), parameters of state equations (Pereda et al., 2010; Schmid & Gmehling, 2012), acentric factor (Constantinou & Gani, 1994; Brown et al., 2010; Monago & Otobrise, 2010), activity coefficients (Tochigi et al., 2005; Tochigi & Gmehling, 2011), vapour pressure (Poling et al., 2001; Miller, 1964), liquid viscosity (Joback & Reid, 1987; Conte et al., 2008; Sales-Cruz et al., 2010), gas viscosity (Reichenberg, 1975), heat capacity (Joback & Reid, 1987; Ruzicka & Domalski, 1993a; Ruzicka & Domalski, 1993b; Kolská et al., 2008), enthalpy of vaporization (e.g. Chickos et al., 1995; Chickos & Wilson, 1997; Marrero & Gani, 2001; Kolská et al. 2005, etc.), entropy of vaporization (Chickos et al., 1998; Kolská et al. 2005), normal boiling temperature (Joback & Reid, 1987; Gani & Constantinou, 1996; Marrero & Gani, 2001), liquid thermal conductivity (Nagvekar & Daubert, 1987), gas thermal conductivity (Chung et al., 1984), gas permeability and diffusion coefficients (Yampolskii et al., 1998), liquid density (Campbell & Thodos, 1985; Sales-Cruz et al., 2010; Shahbaz et al., 2012), surface tension (Brock, 1955; Conte et al., 2008; Awasthi et al., 2010), solubility parameters of fatty acid methyl esters (Lu et al., 2011), flash temperatures (Liaw & Chiu, 2006; Liaw et al., 2011). Large surveys of group contribution methods for enthalpy of vaporization and liquid heat capacity have been presented in references (Zábranský et al., 2003; Kolská, 2004; Kolská et al., 2005; Kolská et al., 2008; Zábranský et al., 2010a). Group-contribution-based property estimation methods can be also used to predict the missing UNIFAC group-interaction parameters for the calculation of vapor-liquid equilibrium (González et al., 2007b).

Group contribution methods can be used for pure compounds, even inorganic compounds (e.g. Williams, 1997; Briard et al., 2003), organometallic compounds (e.g. Nikitin et al., 2010) and also for mixtures (e.g. Awasthi et al., 2010; Papaioannou et al., 2010; Teixeira et al., 2011; Garcia et al., 2012). Also e.g. estimation of thermodynamic properties of polysaccharides was presented (Lobanova et al., 2011). Discussion about determination of properties of polymers has been also published (Satyanarayana et al., 2007; Bogdanic, 2009; Oh & Bae, 2009). Property models based on the group contribution approach for lipid technology have been also presented (Díaz-Tovar et al., 2007).

During last years also models for ionic liquids and their variable properties were developed, e.g. for density, thermal expansion and viscosity of cholinium-derived ionic liquids (Costa et al., 2011; Costa et al., 2012), viscosity (Adamová et al., 2011), the glass-transition temperature and fragility (Gacino et al., 2011), experimental data of mixture with ionic liquid were compared with group contribution methods (Cehreli & Gmehling, 2010) or thermophysical properties were studied (Gardas et al., 2010).

Some of these group contribution methods were developed for only limited number of compounds, for some family of compounds, e.g. for fluorinated olefins (Brown et al., 2010), hydrocarbons (Chickos et al., 1995), fatty acid methyl esters (Lu et al., 2011), etc., most of approaches were established for a wide range of organic compounds.

2.1.1. Group contribution methods by Marrero-Gani

In this chapter for most of estimations the modified group contribution method by Marrero and Gani (Marrero & Gani, 2001; Kolská et al., 2005; Kolská et al. 2008) was applied, which has been originally developed for estimation of different thermodynamic properties at one temperature only (Constantinou & Gani, 1996; Marrero & Gani, 2001). Determination of group contribution parameters is performed in three levels, primary, secondary and third. At first, all compounds are divided into the primary (first) order group contributions. This primary level uses contributions from simple groups that allow description of a wide variety of organic compounds. Criteria for their creation and calculation have been described (Marrero & Gani, 2001; Kolská et al., 2005; Kolská et al., 2008). The primary level groups, however, are insufficient to capture a proximity effect (they do not implicate an influence of their surroundings) and differences between isomers. Using primary level groups enables to estimate correctly properties of only simple and monofunctional compounds, but the estimation errors for more complex substances are higher. The primary level contributions provide an initial approximation that is improved at the second level and further refined at the third level, if that is possible and necessary. The higher levels (second and third) involve polyfunctional and structural groups that provide more information about a molecular structure of more complex compounds. These higher levels are able to describe more correctly polyfunctional compounds with at least one ring in a molecule, or non-ring chains including more than four carbon atoms in a molecule, and multi-ring compounds with a fused or non-fused aromatic or non-aromatic rings. The differences between some isomers are also able to distinguish by these higher levels. Complex polycyclic compounds or systems of fused aromatic or nonaromatic rings are described by the third order contributions. They are still bigger and more complex than the first, even the second order ones. The multilevel scheme enhances the accuracy, reliability and the range of application of group contribution method for an almost all classes of organic compounds.

After these all three levels the total value of predicted property X is obtained by the summing up of all group contributions, which occur in the molecule. First order groups, second and third order ones, if they are in.

$$X = x_0 + \sum_{i=1}^n N_i C_{xi} + \varpi \sum_{j=1}^m M_j D_{xj} + z \sum_{k=1}^o O_k E_{xk} \quad (1)$$

where X stands the estimated property, x_0 is an adjustable parameter for the relevant property, C_{xi} is the first-order group contribution of type i , D_{xj} is the second-order group contribution of type j , E_{xk} is the third-order group contributions of the type k and N_i , M_j , O_k denote the number of occurrences of individual group contributions. The more detail description of parameters calculation is mentioned in original papers (Marrero & Gani, 2001; Kolská et al., 2005; Kolská et al., 2008)

To develop reliable and accurate group contribution model three important steps should be realized: (i) to collect input database, rather of critically assessed experimental data, from which parameters, group contributions, would be calculated; (ii) to design structural

fragments for description of all chemical structures for compounds of input database; (iii) to divide all chemical structures into defined structural fragments correctly. It can be realized either manually, when databases of chemical structures and structural fragments inclusive several members only, either via computer program, when databases contain hundreds of compounds and structural fragments are more complex. To calculate group contribution parameters for thermophysical properties the ProPred program has been used (Marrero, 2002). Description and division chemical structures for other estimations have been made handy. Molecular structures for electronical splitting of all compounds from the basic data set were input in the Simplified Molecular Input Line Entry Specification, so-called the SMILES format (Weininger et al., 1986; Weininger, 1988; Weininger et al., 1989; Weininger, 1990).

For more universal usage of computer fragmentation a suitable computer program has been developed (Kolská & Petrus, 2010). The main goal of the newly developed program is to provide a powerful tool for authors using group contribution methods for automatic fragmentation of chemical structures.

2.2. Estimation of selected physico-chemical properties of compounds

The models for estimation of several physical or physico-chemical properties of pure organic compounds, such as enthalpy of vaporization, entropy of vaporization (Kolská et al., 2005), liquid heat capacity (Kolská et al., 2008) and a Nafion swelling (Randová et al, 2009) is presented below. Most of them are developed to estimate property at constant temperature 298.15 K and at normal boiling temperature (Kolská et al., 2005; Kolská et al., 2008; Randová et al., 2009), liquid heat capacity as a temperature dependent (Kolská et al., 2008). Hitherto unpublished results for estimation of a flash temperature or organic compounds and for determination of reactivation ability of reactivators of acetylcholinesterase inhibited by inhibitor are presented in this chapter.

2.2.1. Enthalpy of vaporization and entropy of vaporization

Enthalpy of vaporization, ΔH_v , entropy of vaporization, ΔS_v are important thermodynamic quantities of a pure compound, necessary for chemical engineers for modelling of many technological processes with evaporation, for extrapolation and prediction of vapour pressure data, or for estimation of the other thermodynamic properties, e.g. solubility parameters. It can be also used for extrapolation and prediction of vapour pressure data.

There are several methods to determine these properties, experiment-based and model-based. Experiment-based methods, such as calorimetry or gas chromatography, provide generally reliable data of good accuracy. In the case of model-based methods, we can distinguish several groups of methods on the basis of the input information they require. Methods based on the Clausius-Clapeyron equation and vapour pressure data, variable empirical correlations, methods based on the tools of statistical thermodynamics or quantum mechanics. During last decades the group contribution methods are widely used

for their universality and simplicity. More rich survey of estimation methods for enthalpy of vaporization is presented in papers (Kolská, 2004; Kolská et al., 2005).

Large databases of critically assessed data have been used for group contribution calculations: data for 831 compounds have been used for estimations at 298.15 K, and data for 589 compounds have been used for estimations at the normal boiling temperature. Organic compounds were divided into several classes (aliphatic and acyclic saturated and unsaturated hydrocarbons, aromatic hydrocarbons, halogenated hydrocarbons, compounds containing oxygen, nitrogen or sulphur atoms and miscellaneous compounds). Especially calorimetrically measured experimental data from the compilation (Majer & Svoboda, 1985) and data from some other sources mentioned in original paper (Kolská et al., 2005) were employed.

Results for estimations of these three properties are presented in the following Tables, Table 1 for enthalpy of vaporization at 298.15 K, Table 2 for enthalpy of vaporization at normal boiling temperature and Table 3 for entropy of vaporization at normal boiling temperature, *NC* means a number of compounds used for development of model and contributions calculation, *NG* is number of applied structural fragments (groups), *AAE* is absolute average error and *ARE* is average relative error (Kolská et al., 2005).

Table 1 shows that values for 831 compounds were used for estimation of enthalpy of vaporization at 298.15 K. When only first level groups were used, the prediction was performed with the *AAE* and the *ARE* of 1.3 kJ/mol and 2.8%, resp. Values of 116 group contributions were calculated at this step. Then, 486 compounds were described by the second order groups. Prediction of these compounds improved after the use of these contributions from the value of 1.3 kJ/mol to 0.8 kJ/mol (from 2.8% to 1.8%) in comparison when using only the first level groups. At the end only 55 compounds were suitable for refining by the third order groups. The results were refined from the values of 1.4 kJ/mol to 1.1 kJ/mol (from 2.5% to 2.1%). The total prediction error was cut down from the value of 1.3 kJ/mol to 1.0 kJ/mol for *AAE* and from 2.8% to 2.2 % for *ARE* after usage of all three-level groups, as it is obvious from this table. A similar pattern of results for other predicted properties are presented in Tables 2 and 3.

Estimation level	<i>NC</i>	<i>NG</i>	<i>AAE</i> / kJ/mol	<i>ARE</i> / %
FIRST	831	116	1.3	2.8
SECOND	486	91	0.8	1.8
486 compounds	after only the FIRST		(1.3)	(2.8)
THIRD	55	15	1.1	2.1
55 compounds	After FIRST + SECOND		(1.4)	(2.5)
ALL LEVELS	831	222	1.0	2.2

Table 1. Results for estimation of enthalpy of vaporization at 298.15 K (Kolská et al., 2005)

Estimation level	NC	NG	AAE / kJ/mol	ARE / %
FIRST	589	111	1.2	3.2
SECOND	377	100	0.9	2.5
377 compounds	after only the FIRST		(1.2)	(3.4)
THIRD	23	14	1.1	2.1
23 compounds	After FIRST + SECOND		(1.3)	(2.7)
ALL LEVELS	589	225	0.9	2.6

Table 2. Results for estimation of enthalpy of vaporization at normal boiling temperature (Kolská et al., 2005)

Estimation level	NC	NG	AAE / J/(K·mol)	ARE / %
FIRST	589	111	2.1	2.2
SECOND	377	100	1.8	1.9
377 compounds	after only the FIRST		(2.3)	(2.4)
THIRD	23	14	1.9	1.9
23 compounds	After FIRST + SECOND		(2.5)	(2.5)
ALL LEVELS	589	225	1.7	1.8

Table 3. Results for estimation of entropy of vaporization at normal boiling temperature (Kolská et al., 2005)

As an example of the use of all three levels we have chosen the molecule of 1,1,4,7-tetramethylindane. Its chemical structure is shown in Fig. 3 and its division into individual first, second and third order groups with the result for vaporization enthalpy at 298.15 K is presented in Table 4. When we sum up all group contribution of the first level, we have got value of 64.48 kJ/mol. The first level provides an initial approximation with the relative error of estimated value exceeding 5 % in comparison with experimental value 61.37 kJ/mol. Estimated value of vaporization enthalpy at 298.15 K is then improved at the second level and further refined at the third level, after those the relative error reduced to 1.2 %.

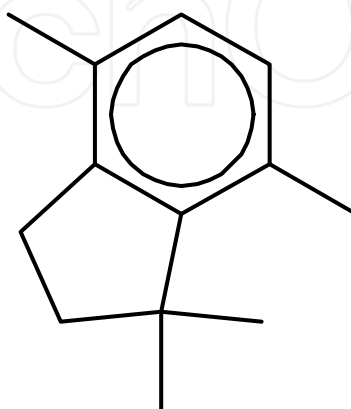


Figure 3. Chemical structure of 1,1,4,7-tetramethylindane

Estimation level	Group fragment no.	Group fragment definition	Its frequency	Group contribution value for ΔH_v at 298.15 K / kJ/mol
FIRST	x_0	Adjustable parameter	1	9.672
	1	CH3	2	2.266
	13	aCH	2	4.297
	15	aC fused with nonaromatic subring	2	6.190
	18	aC-CH3	2	8.121
	107	CH2 (cyclic)	2	4.013
	109	C (cyclic)	1	3.667
Estimated value				64.48
SECOND	55	Ccyc-CH3	2	-1.355
Estimated value				63.59
THIRD	6	aC-CHncyc (fused rings) (n in 0..1)	2	0.279
	19	AROM.FUSED[2]s1s4	1	-0.615
Estimated value				62.13

Table 4. Results for estimation of enthalpy of vaporization at 298.15 K for 1,1,4,7-tetramethylindane, aC means carbon atom in aromatic ring, abbreviation cyc is used for cycle (Kolská et al., 2005)

Group contribution methods by Ducros (Ducros et al., 1980; Ducros et al., 1981; Ducros & Sannier, 1982; Ducros & Sannier, 1984), by Chickos (Chickos et al., 1996), the empirical method, equations nos. 6 and 7 by Vetere (Vetere, 1995) and method by Ma and Zhao (Ma & Zhao, 1993) were used for comparison of results obtained in this work for estimation at 298.15 K and at normal boiling temperature, resp. While the new approach (Kolská et al., 2005) was applied for enthalpy of vaporization at 298.15 K for 831 organic compounds with the ARE of 2.2 %, the Ducros's method could be applied to only 526 substances with the ARE of 3.1 % and the Chickos's one for 800 compounds with the ARE of 4.7 %. For comparison of the results of estimation at the normal boiling temperature the new model provided for 589 compounds, the ARE was 2.6 % for enthalpy of vaporization and 1.8 % for entropy of vaporization (Kolská et al., 2005), the Vetere's method was capable of estimating the values of for the same number of compounds with the following results: 4.6 % (Eq. 6, Vetere, 1995) and 3.4 % (Eq. 7, Vetere, 1995), model by Ma and Zhao (Ma & Zhao, 1993) for 549 compounds with the ARE of 2.5 %. The error for the enthalpy of vaporization, based on an independent set of various 74 compounds not used for correlation, has been determined to be 2.5%. Group contribution description and values for next usage of readers are presented in original paper (Kolská et al., 2005).

2.2.2. Liquid heat capacity

Isobaric heat capacity of liquid C_p^l is an important thermodynamic quantity of a pure compound. Its value must be known for the calculation of an enthalpy difference required

for the evaluation of heating and cooling duties. Liquid heat capacity also serves as an input parameter for example in the calculation of temperature dependence of enthalpy of vaporization, for extrapolation of vapour pressure and the related thermal data by their simultaneous correlation, etc.

In work (Kolská et al., 2008) the three-level group contribution method by Marrero and Gani (Marrero & Gani, 2001) mentioned above, which is able to calculate liquid heat capacity at only one temperature 298.15 K, was applied, and this approach has been extended to estimate heat capacity of liquids as a function of temperature. Authors have employed the combination of equation for the temperature dependence of heat capacity and the model by Marrero and Gani to develop new model (Kolská et al., 2008).

For parameter calculation 549 organic compounds of variable families of compounds were taken. In Table 5 are presented results of this estimation. *NG* means number of applied structural groups and *ARE* is the average relative error. More detailed results are presented in original paper (Kolská et al., 2008).

Estimation level	<i>NG</i>	<i>ARE</i> / %
First	111	1.9
Second	88	1.6
Third	25	1.5

Table 5. Results for estimation of liquid heat capacity in temperature range of pure organic compounds (Kolská et al., 2008)

Also these estimated values were compared with results obtained by other estimation methods (Zábranský & Růžička, 2004; Chickos et al., 1993) for the basic dataset (compounds applied for parameter calculation) and also for 149 additional compounds not used in the parameter calculation (independent set). The first method (Zábranský & Růžička, 2004) was applied for all temperature range, the method proposed by Chickos (Chickos et al., 1993) was only used for temperature 298.15 K with the following results: new model was applied for 404 compounds with *ARE* of 1.5 %, the older method by Zábranský (Zábranský & Růžička, 2004) for the same number of compounds with the *ARE* of 1.8 % and the Chickos's one for 399 compounds with the *ARE* of 3.9 %.

For the heat capacity of liquids authors used recommended data from the compilations by (Zábranský et al., 1996; Zábranský et al., 2001). Because the experimental data are presented permanently, it is necessary to update database of critically assessed and recommended data. Therefore authors's work has been also aimed at updating and extending two publications prepared earlier within the framework of the IUPAC projects (Zábranský et al., 1996; Zábranský et al., 2001). These publications contain recommended data on liquid heat capacities for almost 2000 mostly organic compounds expressed in terms of parameters of correlating equations for temperature dependence of heat capacity. In new work (Zábranský et al., 2010b) authors collected experimental data on heat capacities of pure liquid organic and inorganic compounds that have melting temperature below 573 K published in the primary literature between 1999 and 2006. Data from more than 200 articles are included

into the database. Compounds were divided into several families, such as hydrocarbons (saturated, cyclic, unsaturated, aromatic), halogenated hydrocarbons containing atoms of fluorine, chlorine, iodine, bromine, compounds containing oxygen (alcohols, phenols, ethers, ketones, aldehydes, acids, esters, heterocycles, other miscellaneous compounds), compounds containing nitrogen (amines, nitriles, heterocycles, other miscellaneous compounds), compounds containing sulphur (thioles, sulphides, heterocycles) and compounds containing silicon. Also data of organometallic compounds, compounds containing atoms of phosphorus and boron as well as some inorganic compounds were included. Also the list of families of compounds has been extended by a new group denoted as ionic liquids due to an increased interest in physical-chemical properties of these compounds in recent years. Data for approximately 40 ionic liquids were included. Altogether new data for almost 500 compounds, out of them about 250 compounds were not covered in previous works (Zábranský et al., 1996; Zábranský et al., 2001), were compiled and critically evaluated.

2.2.3. Nafion swelling

Prediction of the physical and chemical properties of pure substances and mixtures is a serious problem in the chemical process industries. One of the possibilities for prediction of the properties is the group contribution method. The anisotropic swelling of Nafion 112 membrane in pure organic liquids (solvents) was monitored by an optical method. Nafion is a poly(tetrafluoroethylene) (PTFE) polymer with perfluorovinyl pendant side chains ended by sulfonic acid groups. The PTFE backbone guarantees a great chemical stability in both reducing and oxidizing environments. Nafion membrane is important in chemical industry. It is used in fuel cells, membrane reactors, gas dryers, production of NaOH, etc. (Randová et al., 2009). In many applications Nafion is immersed in liquid, which significantly affects the membrane properties, namely swelling and transport properties of permeates (Randová et al., 2009). The change in the size of the membrane sample is taken as a measure of swelling. All experimental data were presented (Randová et al., 2009) and these results were used as a basis for application of the group contribution method to the relative expansion in equilibrium. From a total of 38 organic liquids under study, 26 were selected as an evaluational set from which the group and structural group contributions were assigned. The remaining 12 compounds were used as the testing set.

Due to limited number of compounds the more complex and known group contribution methods could not be taken. Authors have to develop new group structural fragments. The proposed method utilizes the four kinds of the structural units: constants, C-backbone, functional groups, and molecular geometry (Randová et al., 2009). Constants were presented as alcohols, ketones, ethers, esters, carboxylic acids. As C-backbone were taken groups CH_3 , $-\text{CH}_2-$ and $>\text{CH}-$. Functional groups as hydroxyl $\text{OH}-$, carbonyl $-\text{C}=\text{O}$ and ether $-\text{O}-$ and fragments for molecular geometry for cycles and branched chains were taken. The relative expansions A_{exp} (for the drawing direction) and/or B_{exp} (for the perpendicular direction) were calculated from the side lengths of the dry membrane sample (a_{10} , a_{20} , b_{10} , b_{20}) and the side lengths of the swelled membrane sample in equilibrium (a_1 , a_2 , b_1 , b_2) according to the eq. (3). Description of mentioned sizes is presented in Fig. 4.

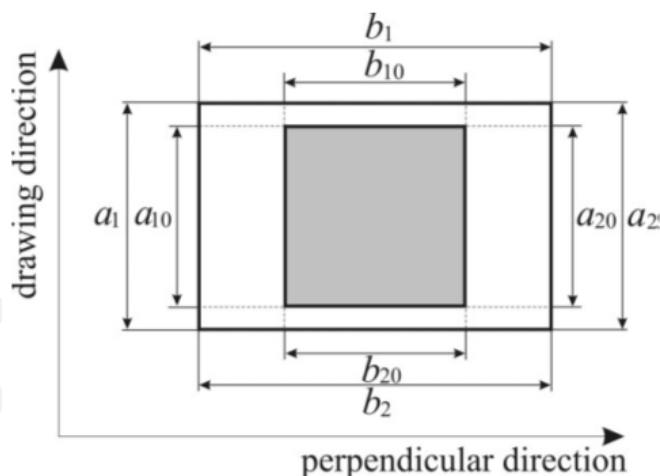


Figure 4. Description of membrane dimensions a_{10} , a_{20} , b_{10} , b_{20} side lengths of the dry membrane and a_1 , a_2 , b_1 , b_2 side lengths of the swelled membrane in equilibrium (Randová et al., 2009)

$$u_{a1} = \frac{a_1 - a_{10}}{a_{10}} \quad , \quad u_{a2} = \frac{a_2 - a_{20}}{a_{20}} \quad , \quad u_{b1} = \frac{b_1 - b_{10}}{b_{10}} \quad , \quad u_{b2} = \frac{b_2 - b_{20}}{b_{20}} \quad (3)$$

Calculation approach is presented in original paper (Randová et al., 2009). Value of $\pm 1.5\%$ in relative expansions was determined to be the experimental error. Maximum differences between the experimental and calculated relative expansions in both sets did not exceed the value of $\pm 3\%$ (Randová et al., 2009).

The values of 13 contributions for individual membrane relative expansions were determined on the basis of experimental data on relative expansion of Nafion membrane. Obtained results are in good agreement with experimental data. Maximum differences between experimental and calculated values are nearly the same, only twice greater than the experimental error.

2.2.4. Flash temperature of organic compounds

The flash temperature T_f and lower flammability limit (LFL) are one of the most important variables to consider when designing chemical processes involving flammable substances. These characteristics are not fundamental physical points. Flash temperature is one of the most important variables used to characterize fire and explosion hazard of liquids. The flash temperature is defined as the lowest temperature at which vapour above liquid forms flammable mixture with air at a pressure 101 325 Pa. Usual approach for flash temperature estimation is linear relationship between flash temperature T_f and normal boiling temperature T_b (Dvořák, 1993). Some models for flash temperature were presented earlier (Liaw & Chiu, 2006; Liaw et al., 2011).

In this work to estimate flash temperature of organic compound authors applied the modified group contribution method (Kolská et al., 2005) and calculate group contribution values data for 186 compounds (Steinleitner, 1980) were used. The database for calculation of parameters contains data for aliphatic and acyclic saturated and unsaturated

hydrocarbons, aromatic hydrocarbons, alcohols, halogenated hydrocarbons, compounds containing oxygen, nitrogen or sulphur atoms and miscellaneous compounds. To collect more data for development of reliable method was not able due to that all databases collect some values obtained via closed cup type measuring method and others measured by open cup one and data both of methods vary.

Flash temperature was calculated by relationship (4) similar to eq. (1):

$$T_f = T_f^{\circ} + \sum_{i=1}^n N_i C_i + \varpi \sum_{j=1}^m M_j D_j + z \sum_{k=1}^o O_k E_k \quad (4)$$

where T_f° is an adjustable parameter, C_i is the first-order group contribution of type i , D_j is the second-order group contribution of type j , E_k is the third-order group contribution of the type k and N_i , M_j , O_k denote the number of occurrences of individual group contributions. Determination of contributions and of adjustable parameters was performed by a three-step regression procedure (Marrero & Gani, 2001). To evaluate the method error the following statistical quantities for each compound, absolute error AE (eq. 5) and relative error ARE (eq. 6) were used:

$$AE[T_f] = \left| (T_f)_{\text{exp}} - (T_f)_{\text{est}} \right| \quad (5)$$

$$RE[T_f] = \left(\frac{\left| (T_f)_{\text{exp}} - (T_f)_{\text{est}} \right|}{(T_f)_{\text{exp}}} \right) \cdot 100 \quad (6)$$

where subscripts "exp" and "est" mean experimental and estimated value of the flash temperature. 186 compounds from the basic data set were described by the first level group contributions (Kolská et al., 2005). From this large database only 114 compounds could be selected to be described by the original second level groups as defined earlier (Kolská et al., 2005). The total absolute and the relative average errors for all 186 compounds were equal to 6.3 K and 2.0 %. Results for individual estimation levels are presented in Table 6.

Estimation level	NC	AAE / K	ARE / %
FIRST	186	7.9	2.4
SECOND	105	5.7	1.8
THIRD	11	2.9	0.8
ALL LEVELS	186	6.5	2.0

Table 6. Results for Estimation of flash temperature, NC is number of compounds

Individual calculated structural fragments of the first, second and third estimation levels are presented in Tables 7-9, resp.

Structural fragment	Contribution / K	Structural fragment	Contribution / K	Structural fragment	Contribution / K
T_f^p	194.35	aCH	12.39	aC-OH	85.26
CH ₃	5.38	aC	21.15	CH ₂ Cl	45.56
CH ₂	13.28	aC	26.84	CHCl	42.83
CH	15.77	aC	31.53	CCl	37.51
C	13.59	aN	25.51	CHCl ₂	67.42
CH ₂ =CH	11.51	aC-CH ₃	28.32	CCl ₃	100.38
CH=CH	34.57	aC-CH ₂	37.11	aC-Cl	50.70
CH ₂ =C	19.63	aC-CH	37.38	aC-F	53.47
CH=C	27.52	aC-C	19.88	aC-Br	64.97
C=C	29.27	aC-CH=CH ₂	50.66	-I	78.85
CH#C	14.94	OH	64.22	-Br	59.25
C#C	15.04	-SH	55.62	CH=CH	18.21
-F	2.99	CH ₂	10.89	CH=C	37.59
-Cl	29.32	CH	22.89	N	52.99
CH ₂ SH	56.33	C	-9.50	O	-3.39

Table 7. Group contribution of the first level for estimation of flash temperature

Structural fragment	Contribution / K	Structural fragment	Contribution / K	Structural fragment	Contribution / K
(CH ₃) ₂ CH	-1.45	CH _m =CH _n -Cl (m,n in 0..2)	-0.50	CH _{cyc} -OH	-1.31
(CH ₃) ₃ C	-3.98	aC-CH _n -X (n in 1..2) X: Halogen	1.04	C _{cyc} -CH ₃	-0.23
CH(CH ₃)CH(CH ₃)	7.68	aC-CH _n -OH (n in 1..2)	5.51	>N _{cyc} -CH ₃	-1.11E-17
CH(CH ₃)C(CH ₃) ₂	22.69	aC-CH(CH ₃) ₂	1.80	AROMRINGS1s2	-2.24
CH _n =CH _m -CH _p =CH _k (k,m,n,p in 0..2)	0.53	aC-CF ₃	0.13	AROMRINGS1s3	1.72
CH ₃ -CH _m =CH _n (m,n in 0..2)	-2.01	(CH _n =C) _{cyc} -CH ₃ (n in 0..2)	0.46	AROMRINGS1s4	-0.84
CH ₂ -CH _m =CH _n (m,n in 0..2)	2.23	CH _{cyc} -CH ₃	-5.70	AROMRINGS1s2s4	-2.84
CH _p -CH _m =CH _n (m,n in 0..2; p in 0..1)	3.78	CH _{cyc} -CH ₂	17.80	AROMRINGS1s2s4s5	6.22
CHOH	-3.92	CH _{cyc} -CH=CH _n (n in 1..2)	8.52	PYRIDINES3s5	9.98E-18
COH	-4.98	CH _{cyc} -C=CH _n (n in 1..2)	-1.20	(CH=CHOCH=CH) _{cyc}	-4.24
CH _m (OH)CH _n (OH) (m,n in 0..2)	13.41	CH _{cyc} -Cl	1.59	(3 F)	-0.13
				(perFlouro)	2.66E-17

Table 8. Group contribution of the second level for estimation of flash temperature

Structural fragment	Contribution / K	Structural fragment	Contribution / K	Structural fragment	Contribution / K
OH-(CH _n) _m -OH (m>2, n in 0..2)	-33.36	CH _{cyc} -CH _{cyc} (different rings)	-1.87	AROM.FUSED[2]	8.69
aC-aC (different rings)	-6.04	CH multiring	0.98	AROM.FUSED[4a]	-26.07
aC-CH _n cyc (fused rings) (n in 0..1)	-4.34	aC-CH _m -aC (different rings) (m in 0..2)	12.92		

Table 9. Group contribution of the third level for estimation of flash temperature

2.2.5. Reactivation ability of some reactivators of acetylcholinesterase

In the last years regarding to valid legislation on dangerous compounds it is necessary to know many of important characteristics of chemical compounds. Due to this new models for their estimation were developed. New models for estimation of reactivation ability of reactivators for acetylcholinesterase inhibited by (i) chlorpyrifos (*O,O*-diethyl *O*-3,5,6-trichloropyridin-2-yl phosphorothioate) as a representative of organophosphate insecticide and by (ii) sarin ((*RS*)-propan-2-yl methylphosphonofluoridate) as a representative of nerve agent is now presented. Both of these family compounds, organophosphate pesticide and nerve agent, are highly toxic and have the same effect to living organisms, which is based on an inhibition of acetylcholinesterase (AChE). New compounds able to reactivate the inhibited AChE, so-called reactivators of AChE, are synthesized. Reactivation ability of these reactivators is studied using standard reactivation *in vitro* test (Kuča & Kassa, 2003). Reactivation ability of reactivators means the percentage of original activity of AChE (Kuča & Patočka, 2004). New models for determination values of reactivation ability of reactivators AChE inhibited by (i) chlorpyrifos and (ii) sarin have been developed. Concentration of reactivators was $c=1 \cdot 10^{-3}$ mol·dm⁻³. In comparison with previous cases (estimations of thermophysical properties) authors have only less experimental data for development of model (about 20 for each of cases). Due to their long names and complex chemical structures these compounds in this chapter only are presented as their codes taken from original papers (Kuča & Kassa, 2003; Kuča et al., 2003a; Kuča et al., 2003b; Kuča et al., 2003c; Kuča & Patočka, 2004; Kuča & Cabal, 2004a; Kuča & Cabal, 2004b; Kuča et. al., 2006. Data of reactivation ability for these reactivators were given by the mentioned author team (Kuča et al.). Classical group contribution method includes groups describing some central atom, central atom with its bonds, or central atom with its nearest surrounding. However these models commonly used experimental data of hundreds or thousands compounds for parameters calculation. Due to for much small database in these cases it was necessary to design new fragments depending on the molecular structures available compounds. Structural fragments in this work cover larger and more complex part of molecules in comparison with other papers focused to group contribution methods. Reactivation potency is given in the group contribution method by the following relation, eq. 7:

$$R_p = \sum_{i=1}^n x_i \cdot R_{pi} \quad (7)$$

where R_{pi} is value of individual fragment i presented in molecule by which it contributes to total value of R_p , x is number of frequency of this fragment i in molecule. Parameters R_{pi} were obtained by minimization function S_{Rp} , eq. 8:

$$S_{Rp} = \sum_{i=1}^m (R_{pi,calc} - R_{pi,exp})^2 \quad (8)$$

where suffix $_{exp}$ presents experimental data and suffix $_{calc}$ the calculated values of R_p , m is number of compounds in dataset. The results obtained by this new approach were compared with experimental data using the following statistical quantities - an absolute error of individual compounds AE (eq. 9) and the average absolute error of dataset AAE (eq. 10):

$$AE_i = R_{pi,calc} - R_{pi,exp} \quad (9)$$

$$AAE = \sum_{i=1}^m \left(\frac{|R_{pi,calc} - R_{pi,exp}|}{m} \right) \quad (10)$$

Parameters of new model were calculated from the experimental data of the basic dataset. For model for reactivators AChE inhibited by chlorpyrifos the input database included data of reactivation ability R_p for 24 reactivators (K 135, K 078, TO 096, TO 100, K 076, TO 094, TO 063, TO 097, TO 098, K 347, TO 231, K 117, K 074, K 033, K 106, K 107, K 110, K 114, HI-6, K 282, K 283, K 285, K 129, K 099) of concentration $c=1 \cdot 10^{-3}$ mol·dm⁻³. Values for 17 groups with the AAE of 1.85 % of R_p were calculated. Designed groups with their calculated values of R_{pi} are presented in Table 10. These calculated parameters were tested on the test set of 5 independent compounds (TO 238, K 111, K 113, Methoxime, K 280) of which experimental data were not applied to group contributions determination. The AAE of R_p prediction for this test-set was 1.45 %. Table 11 presents experimental data and predicted values for these 5 independent compounds. Also illustration of usage of this method for two compounds from this test set is added below.

As it is clear from Table 10 the highest values of contributions are given for fragments P_3 , P_7 for monoaromatic reactivators and P_{11} , P_{12} and P_{14} for two aromatic rings in reactivator molecule. On the other hand the smallest contribution (the negative ones) to total value of reactivation ability yields fragments P_5 a P_6 for monoaromatic compounds and P_{16} and P_{17} for two aromatic ring reactivators. These values resulted in fact that reactivation ability of new reactivators for reactivation AChE inhibited by chlorpyrifos should be increased by presence of the following functional groups in molecules: another quarternary nitrogen atom in aliphatic ring bonded to aromatic quarternary nitrogen atom, the oxime groups in *para*- or *meta*- positions and presence of other aliphatic rings bonded to aromatic ring in other position than quarternary nitrogen and oxime groups. In all cases it is clear that reactivation ability decreases with presence of cycle ring, double bond and also in a less range with the presence of oxygen atoms presented in molecules. Also *ortho*- position of oxime group does not contribute positively.

no.	Fragment description	R_{pi} / %	no.	Fragment description	R_{pi} / %
P ₁	Oxime group (=NOH) in position <i>o</i> - due to a quarternary nitrogen N ⁺ atom in aromatic ring	26.365	P ₉	two oxime groups in positions <i>o</i> - due to a quarternary nitrogen atom in aromatic ring	26.580
P ₂	Oxime group (=NOH) in position <i>p</i> - due to a quarternary nitrogen N ⁺ atom in aromatic ring	15.365	P ₁₀	two oxime groups in positions <i>m</i> - due to a quarternary nitrogen atom N ⁺ in aromatic ring	15.737
P ₃	Other quarternary nitrogen atom N ⁺ with 4 CH _x - groups in molecule, in aliphatic ring bonded to nitrogen atom N in aromatic ring	46.792	P ₁₁	two oxime groups in positions <i>p</i> - due to a quarternary nitrogen atom N ⁺ in aromatic ring	47.105
P ₄	Number of members bonded in aliphatic ring after the group P ₃	-1.047	P ₁₂	two oxime groups, one in position <i>o</i> -, other in position <i>m</i> - due to a quarternary nitrogen atom N ⁺ in aromatic ring	52.105
P ₅	Cycle ring bonded to nitrogen atom N in aromatic ring	-10.365	P ₁₃	two oxime groups, one in position <i>o</i> -, other in position <i>p</i> - due to a quarternary nitrogen atom N ⁺ in aromatic ring	25.842
P ₆	Oxygen atom O bonded in aliphatic ring bonded to one aromatic ring	-32.437	P ₁₄	two oxime groups, one in position <i>m</i> -, other in position <i>p</i> - due to a quarternary nitrogen atom N ⁺ in aromatic ring	56.105
P ₇	Presence of other aliphatic ring bonded to aromatic one	88.073	P ₁₅	Oxygen atom O bonded in aliphatic ring between two aromatic rings	-5.842
P ₈	Number of members bonded in aliphatic ring following group N-CH _x - (nitrogen atom N is a part of aromatic ring), (which are not included in other groups)	-2.344	P ₁₆	Cycle between two aromatic rings	-10.474
			P ₁₇	Double bond between two aromatic rings	-22.105

Table 10. List of structural fragments and their values for estimation of reactivation ability of reactivators for acetylcholinesterase inhibited by chlorpyrifos

Reactivator	$R_{p,exp} / \%$	$R_{p,calc} / \%$	Deviation / %
TO 238	48.00	49.55	1.55
K 111	8.00	5.26	-2.74
K 113	37.00	36.63	-0.37
Methoxime	45.00	47.11	2.11
K 280	4.00	4.48	0.48

Table 11. Results for estimation of reactivation ability of the test dataset of 5 reactivators of acetylcholinesterase inhibited by chlorpyrifos

Illustration of new method for reactivation ability prediction of two reactivators (TO 238 and K 280) of which experimental data were not used for parameters calculation follows.

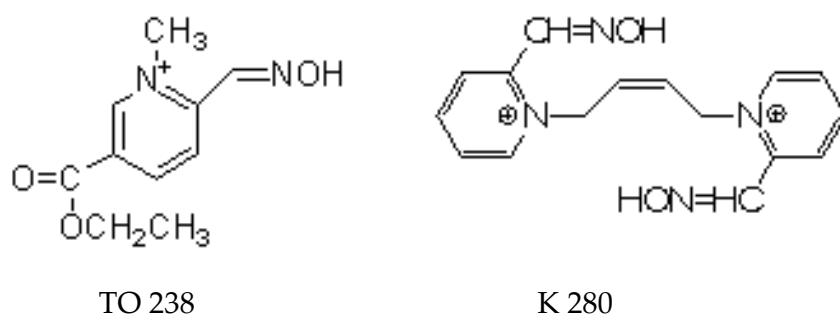


Figure 5. Chemical structure of two reactivators of acetylcholinesterase signed as TO 238 and K 280

Example of usage of the new model for reactivation ability prediction for TO 280 reactivator:

$$R_{p,calc}(\text{TO 238}) = P_1 + 2 \cdot P_6 + P_7 = 26.365 + 2 \cdot (-32.437) + 88.073 = 49.546 \%$$

$$R_{p,exp}(\text{TO 238}) = 48.00 \%$$

$$AE = R_{p,calc}(\text{TO 238}) - R_{p,exp}(\text{TO 238}) = 1.55 \%$$

Example of usage of the new model for reactivation ability prediction for K 280 reactivator:

$$R_{p,calc}(\text{K 280}) = P_9 + P_{17} = 26.580 + (-22.105) = 4.475 \%$$

$$R_{p,exp}(\text{K 280}) = 4.00 \%$$

$$AE = R_{p,calc}(\text{K 280}) - R_{p,exp}(\text{K 280}) = 0.48 \%$$

For model development for reactivators AChE inhibited by sarin the input database included data of reactivation ability R_p for 18 reactivators (K 127, K 128, K 141, K 276, K 311, K 277, K 077, K 142, K 131, K 100, K 233, K 194, K 191, K 067, K 119, K 053, Pralidoxime, HI-6) of concentration $c=1 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ were taken. Due to the smaller database in comparison with the chlorpyrifos-inhibited case it was not possible to apply the same structural fragments. Values for 11 new structural different groups with the AAE of 3.39 % of R_p have been calculated. Designed groups with their calculated values of R_{pi} are presented in Table 12. These calculated parameters were tested on the test set of 4 independent compounds (TO 055, TO 058, K 197, Obidoxime) of which experimental data were not applied to group contributions determination. The AAE of R_p prediction for this test-set was 2.18 %. Table 13 presents experimental data and predicted values for 4 independent compounds.

no.	Fragment description	R_{pi} / %	no.	Fragment description	R_{pi} / %
P ₁	Quarternary nitrogen atom N inclusive in aromatic ring	22.50	P ₇	Other member of ring between two quarternary nitrogen atoms N ⁺ or/and bonded at the last quarternary nitrogen atom N ⁺ of molecule	-6.41
P ₂	Presence of oxime group	-31.21	P ₈	Presence of oxygen atom O in molecule other than mentioned in the following group	2.16
P ₃	<i>ortho</i> - position of substituent on aromatic ring	46.03	P ₉	Presence of group >C=O in molecule	7.88
P ₄	<i>meta</i> - position of substituent on aromatic ring	14.49	P ₁₀	Presence of group -NH _x (x = 0, .., 2) in molecule	-12.20
P ₅	<i>para</i> - position of substituent on aromatic ring	40.01	P ₁₁	Presence of a double bond between two carbon atoms in a ring between two quarternary nitrogen atoms N ⁺ in molecule	1.66
P ₆	Presence of cycle in a molecule	-10.03			

Table 12. List of structural fragments and their values for estimation of reactivation ability of reactivators for acetylcholinesterase inhibited by sarin

As it is shown in Table 12, the highest and the positive values of group contributions are given for fragments P₁, P₃-P₅, P₈ and P₉. On the other hand the smallest contribution (the negative ones) to the total value of reactivation ability yield fragments P₆, P₇ and P₁₀. Also the value of fragment P₂ for oxime group seems to have a negative effect to the total value but it should be said, that the oxime group has to be summed up with some group for its position on aromatic ring. It results in a fact that the oxime group in *meta*- position has the negative influence to the total value of reactivation ability, on the other hand the total value of R_p increases with oxime group in positions of *ortho*- or *para*-. These values resulted in fact that reactivation ability of new reactivators for reactivation AChE inhibited by sarin should be increased by the presence of the following function groups in molecules: another quarternary nitrogen atom in aromatic ring, the oxime groups in *ortho*- or *para*- positions, presence of oxygen atom or group >C=O in molecule. It is clear that reactivation ability decreases with presence of cycle ring and also with presence of the group NH_x (x = 0, .., 2) in molecules. Also *meta*- position of oxime group, as same as the longer ring (CH_x)_n (x = 0, .., 2) bonded at quarternary nitrogen atoms, that means group P₇, do not contribute positively.

Reactivator	$R_{p,exp}$ / %	$R_{p,calc}$ / %	Deviation / %
TO 055	30.00	32.38	2.38
TO 058	25.00	27.63	2.63
K 197	4.00	4.08	0.08
Obidoxime	41.00	44.70	3.70

Table 13. Results for estimation of reactivation ability of the test dataset of 4 reactivators of acetylcholinesterase inhibited by sarin

Illustration of new method for reactivation ability prediction of two reactivators (TO 055 and TO 058) of which experimental data were not used for parameters calculation follows.

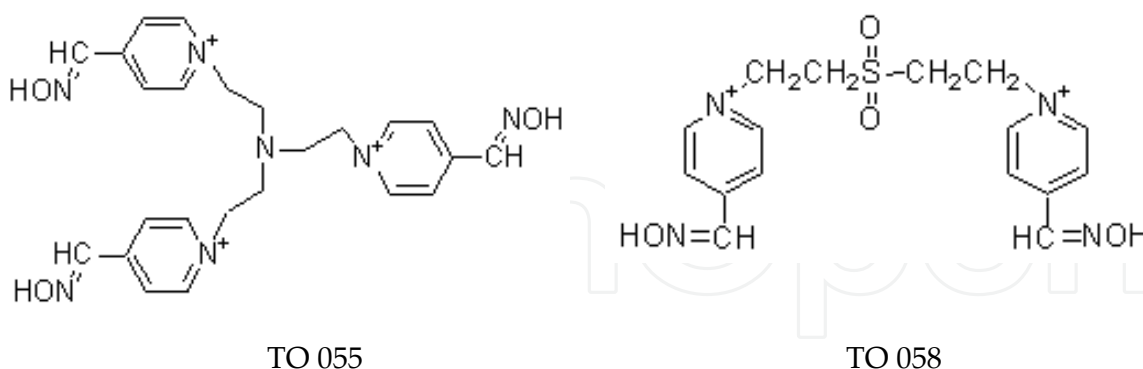


Figure 6. Chemical structure of two reactivators of acetylcholinesterase signed as TO 055 and TO 058

Example of usage of the new model for reactivation ability prediction for TO 055 reactivator:

$$R_{p,\text{calc}}(\text{TO 055}) = 3 \cdot P_1 + 3 \cdot P_2 + 3 \cdot P_5 + 3 \cdot P_6 + 3 \cdot P_7 + P_{10} = 3 \cdot (22.50) + 3 \cdot (-31.21) + 3 \cdot (40.01) + 3 \cdot (-10.03) + 3 \cdot (-6.41) + (-12.20) = 32.38 \text{ \%}; R_{p,\text{exp}}(\text{TO 055}) = 30.00 \text{ \%}$$

$$AE = R_{p,\text{calc}}(\text{TO 055}) - R_{p,\text{exp}}(\text{TO 055}) = 2.38 \text{ \%}.$$

Example of usage of the new model for reactivation ability prediction for TO 055 reactivator:

$$R_{p,\text{calc}}(\text{TO 058}) = 2 \cdot P_1 + 2 \cdot P_2 + 2 \cdot P_5 + 2 \cdot P_6 + 3 \cdot P_7 + 2 \cdot P_8 = 2 \cdot (22.50) + 2 \cdot (-31.21) + 2 \cdot (40.01) + 2 \cdot (-10.03) + 3 \cdot (-6.41) + 2 \cdot (2.16) = 27.63 \text{ \%}; R_{p,\text{exp}}(\text{TO 058}) = 25.00 \text{ \%}$$

$$AE = R_{p,\text{calc}}(\text{TO 058}) - R_{p,\text{exp}}(\text{TO 058}) = 2.63 \text{ \%}.$$

As it is clear, in comparison with the previous cases, these models are applicable only for the same inhibitors but for new reactivators of AChE inhibited by the same inhibitors (the first for chlorpyrifos, the second one for sarin). But on the other hand, it can be also used as a tool for easy prediction of reactivation potency of some newly synthesized reactivators without any other *in vitro* standard tests.

3. Conclusion

Most of the industrial applications and products contain a mixture of many components and for the production it is important to know the properties of individual substance and the properties of aggregates. The accomplishments of all of these experiments are too expensive and time-consuming, so the calculation or estimation methods are good way to solve this problem. The group contribution methods are the important and favourable estimation method, because they permit to determine value of property of extant or hypothetic compound. Group contribution methods are the suitable tool for estimation of many physico-chemical quantities of pure compounds and mixtures too as it was showed and confirmed above for some cases. It can be used for estimation of pure compounds, as well as mixtures, for one temperature estimation, as well as for temperature range, etc. The biggest advantage of these methods is they need knowledge only chemical structure of compounds

without any other input information. The presented models have been developed for estimation of many variable properties, enthalpy of vaporization, entropy of vaporization, liquid heat capacity, swelling of Nafion, flash temperature and reactivation ability of reactivators of acetylcholinesterase inhibited by organophosphate compounds. Proposed models and their structural fragments, accuracy and reliability depend mainly on frequency of input data and their accuracy, correctness and reliability. The most of presented models of group contribution methods, not only in the cases presented in this chapter, can be applied for the wide variety of organic compounds, when groups describing these molecules are presented. Some of models can be applied from only limited families of compounds due to their parameters were calculated only for limited database of compounds. Group contribution methods can be applied either for estimation or prediction of properties at one temperature or as a temperature function depending on their development. The accuracy of developed models is the higher, the input database is more reliable.

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