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ANALYSIS, SYSTEMATIZATION AND PREDICTION OF THERMODYNAMIC CHARACTERISTICS OF ORGANIC COMPOUNDS AND THEIR SOLUTIONS BASED ON THE ADDITIVE-GROUP METHOD

D. V. Batov

Batov D.V., Doctor of Chemical Sciences
G.A. Krestov Institute of Solution Chemistry of Russian Academy of Sciences, Akademicheskaya st., 1, Ivanovo, Russia, 153045
E-mail: bat21dv@yandex.ru

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The article summarizes the literature data and the results of the description, systematization and prediction obtained by the authors within the framework of the additive-group approach of the physicochemical properties of organic substances of various classes and their solutions, as well as the parameters of the fire hazard of liquids.

Introduction

This article summarizes the literature data and the results obtained by the authors on the additive-group approach to describe and predict various physical and chemical properties and fire hazard parameters of organic solvents.

The study of the relationship between the structure of compounds and their properties remains an emergent chemical problem. Within the additive-group method, this problem can be solved both qualitatively and quantitatively. This approach makes it possible to predict the properties of many new objects with sufficient accuracy, using data for a relatively small number of groups. At the same time, deviations from additivity should be considered as a result of the mutual influence of atoms and groups in the molecule of an organic compound. Currently, additive schemes are widely used to calculate the properties of molecules in the gas phase. For condensed systems, including solutions, the additive-group method is underdeveloped. This problem is solved herein for enthalpy characteristics of solvation of organic compounds in individual and mixed solvents, as well as for fire hazard parameters of liquids.

1. Essence, classification and theoretical justification of additivity rules

The additive-group approach is indisputably important for the analysis and systematization of physicochemical and thermodynamic characteristics of individual substances and solutions. Before turning to the analysis of the literature within the additive-group method, it is necessary to briefly discuss its essence and theoretical justification. The essence of the method lies in the fact that the value of any property of a substance is calculated as the sum of the contributions of the groups of atoms that make up the molecule of the substance. This approach makes it possible to predict the properties of many new objects with sufficient accuracy, using data for a relatively small number of groups. At the same time, deviations from additivity should be considered as a result of the mutual influence of atoms and groups in the molecule of an organic compound.

It has long been known to chemists and physicists that most of the properties of relatively complex molecules can be represented as the sum of the corresponding contributions of atoms or bonds. One of the founders of the additivity rules S. Benson gives a classification of additive schemes in his book "Thermochemical Kinetics" [1].

This property of a molecule (in the zero-order approximation) is the sum of the corresponding properties of all atoms. Each atom in a molecule can be ascribed a certain partial value of the property in question. There is only one case in which this rule is absolutely true: when it comes to molecular weight. Benson [1] concluded that physically, such patterns are based on the fact that the forces acting between atoms within a molecule or between atoms of different molecules are very close. They operate at distances of 1-3 angstroms. Because of this, the individual atoms in any molecule give almost constant contributions to properties such as refractive index, UV and IR absorption spectra, magnetic susceptibility, as well as entropy, molar heat capacity, and even the heat of formation of substances in the gas phase. The accuracy of calculations of entropy, heat capacity and heat of formation values according to the atomic-additive scheme is far from the experimental values.

The first order approximation is the additivity of the bonding properties. The paper [1] summarizes bond contribution values for calculation of some thermochemical characteristics of substances. It is shown that the bond additivity approximation makes it possible to calculate the heat capacity and entropy of substances with an error of the order of 4 J/(mol deg) and the enthalpy of gas formation with an average error of 8 kJ/mol. The indicated approximation gives the same values of properties of isomers and therefore cannot be used to compare their properties. Isomeric differences that result from significant steric effects cannot be characterized by simple additivity rules. In this case, it is necessary to compare properties of individual compounds.

In the next approximation (second order approximation), the properties of molecules are considered as the sum of additive contributions belonging to different groups included in the molecule. A group is defined as a multivalent atom together with its ligands, that is, the atoms to which it is bound [2]. Molecules containing one multivalent atom (H_2O, $CHCl_3$) and, therefore, one group cannot be considered based on the rules of additivity of group properties. As the number of substituents in the molecule increases, so does the number of groups. This constitutes a major limitation of this method. In the second order approximation, the calculation accuracy is significantly improved. Thus, the heat capacity and entropy of substances can be calculated with an error of the order of 1.2 J/(mol deg), and the enthalpy of gas formation with an average error of 2 kJ/mol.

All additive approaches can be considered as a practical application of the postulate of the classical theory of chemical structure: the properties of molecules and substances that have capacity factors can be represented as sums of properties by structural elements, pairs, triples, etc. of structural elements. This is expressed as

$$L = \sum_{k} L_k + \sum_{k,l} L_{k.l} + \sum_{k,l.m} L_{k,l,m} + \ldots, \tag{1.1}$$

where L is a property of a molecule or substance; L_k, $L_{k,l}$, $L_{k,l,m}$ are the partial values of the property L falling on a structural element, pair, triplet, etc. of structural elements.

The building blocks have to be classified to use this method. For example, V.M. Tatevsky describes the principles of classification of structural elements in his book [3]. According to the second postulate of the classical theory of chemical structure, which follows from the first postulate about connection of structure and properties of molecules and substances, separate structural elements (S_i) and groups of structural elements (S_i, S_j) included in different molecules or different substances (macrobodies) may be classified to some extent so that in any molecule (substance), a structural element of certain type (variety) has approximately the same partial value of the considered property which has a capacity factor and determines the molecule overall. The determining factor and basis for classification of structural elements is the same atomic composition and approximately the same equilibrium geometric configuration. It follows that such structural elements will have approximately the same electron density and two-particle probability density within the volumes of atoms comprising the structural element and, as a result, energy equivalence. Currently, to separate a molecule into fragments, the researchers use regularities established within the classical theory of chemical structure and properties of molecules [3, 4, 5]. According to these regularities, structural elements belonging to the same species, i.e., close in equilibrium configuration, have the same chemical structure formula and the same first environment.

Taking into account the approximate equivalence of structural elements, the equation (1.1), which only considers structural elements and their pairs, in which structural elements are located near or separated by one fragment, can be rewritten as

$$L = \sum_{I} K^I L^I + \sum_{I,J} \sum_{u} n_u^{I,J} L^{I,J}. \tag{1.2}$$

In this expression, the values of K^I and n_u, representing the quantities of structural elements and element pairs, are determined based on the molecular composition and structure. The partial property values could be calculated by regression method based on a small experimental data batch. However, expression (1.2) in this form cannot be used for regression analysis since the numbers of structural elements and pairs of structural elements turn out to be linearly dependent. Therefore, the expression [2] is used

$$P = \sum K^I p^I. \tag{1.3}$$

In equation (1.3) p^I is the effective partial value of the property which, besides the initial partial values used with the structural element S_I, includes the partial values used with the pairs of structural elements of the first environment of element I. These p^I values can already be almost fully determined by regression method from experimental data for a small number of molecules of the considered series.

2. Additive-group methods used to analyze and systematize the properties of organic compounds

2.1. Use of additive schemes to analyze the properties of individual substances

Analysis of available data has shown that this method is the most widely developed for calculations of thermodynamic parameters of molecule formation in the gas phase [1, 5], heats of phase transitions [6]. The works in this direction are still in progress. The authors [7] discussed and interpreted the enthalpies of formation of pyridines and their derivatives (methylpyridines, hydroxylpyridines, aminopyridines, cyanopyridines, etc.) in the gas phase based on contributions of atoms, bonds, groups and interactions between them in the molecule.

Over the years, the authors [6, 8, 9, 10, 11] have consistently applied the additive-group approach to the properties of substances of different classes in the condensed state. They have developed a scheme for dividing molecules into structural elements, taking into account their first environment [11], taking into account the recommendations [2, 3, 4, 5]. Atom groups that in some cases coincide with functional groups in organic chemistry (e.g., -CH_2-, -O-, -$C(NO_2)$, etc.) are used as fragments. In the paper [9], the additive group method is applied for molar volumes of liquids, in the paper [8] – for enthalpies of formation of substances in the condensed state. Work on the development of a numerical thermochemical database and methods for predicting the properties of organic radicals is in progress [10]. The author of [11] has analyzed the specific aspects of applying additive-group approach to some properties of substances.

2.2. Use of additive schemes for analysis and systematization of solution properties

When studying the properties of solutions, the additive-group methodology was used to describe the partial molar volumes of alkanes in individual aprotonic solvents [12]. In the partial molar volume decomposition, the coefficients of the equations were attempted to be justified theoretically. Thus, the authors of [13], based on the scale particle theory [14], showed that the free term in the equation for the expansion of the partial molar volumes should be equal to βRT.

$$\overline{V^0} = V^0 + nV^0(\mathrm{CH_2}) + 2\overline{V}^0(\mathrm{CH_3}). \tag{2.2.1}$$

This is observed for the partial molar volumes of alkanes and cycloalkanes in tetrachlormethane.

In the paper [15], the authors used the following dependence to describe $\overline{V^0}$:

$$\overline{V^0} = aV_w + b\,. \tag{2.2.2}$$

The justification for the expression used is, according to the authors [15], that the Van der Waals molar volume (V_w) represents an additive value relative to the structural fragments of the molecules. The expression (2.2.2) has been used to decompose $\overline{V^0}$ alkanes in water [15], aromatic compounds, and chloralkanes in tetrachloromethane, alkanes, alcohols, and cyclic compounds in benzene [16].

Considering deviations $\overline{V^0}$ from the simple additive scheme as a consequence of interaction of groups in the molecule, works [17, 18] use the equation

$$\overline{V^0} = V_c + \sum n_i I_i + \sum P_i \delta_i \,, \tag{2.2.3}$$

where V_c is a constant that does not depend on the size of molecules of the dissolved substance; n_i *is* the number of groups of a given species; I_i is the incremental volume per such group; P_i is the number of neighboring interacting groups; δ_i is the decrement of the volume due to the interaction of groups.

The additive-group method is used in the analysis of other thermodynamic properties of solutions as well. As a result of the analysis of thermodynamic data of hydration of alkanes and some of their mono- and polyfunctional derivatives, in works [19, 20], the contributions of hydrocarbon radicals and polar groups in enthalpy, entropy and Gibbs energy of hydration of molecules of organic compounds are calculated. The additive scheme used by the authors [19, 20] will be considered in more detail on the example of enthalpy characteristics of hydration.

The additive-group method is also used in applied research. Thus, to determine one of the main characteristics of surfactants - the hydrophilic-lipophilic balance (HLB) - group numbers reflecting the HLB of structural units of the surfactant molecule are used [21]. Davis [22] proposed the group numbers for the thermodynamic justification of the hydrophilic-lipophilic balance numbers of surfactants as well.

The authors of [10] note the combination of the necessary accuracy with a relatively simple and clear form of application in the additive-group method. This makes the above approach effective for mass calculations.

2.3. Application of additive-group methods for the analysis and systematization of enthalpy characteristics of organic compound solutions in individual solvents

A review of literature data shows that various schemes of additive-group approach are used in the study of enthalpy characteristics of dissolution and solvation of substances, but most often the analysis of the obtained data is limited to the determination of the contribution of the methylene group. For this work, it is reasonable to consider the issue of additivity of enthalpies of dissolution, solvation, and evaporation of organic compounds with respect to the contributions of nonpolar groups on the example of not only hydrocarbons but also their functional derivatives. The available experimental data do not allow us to draw sufficiently general conclusions concerning the additivity of the contributions of polar functional groups.

Fig. 2.3.1 presents the dependences of enthalpies of dissolution of homologs of different classes of organic compounds in water.

The enthalpies of dissolution of alcohols have been determined in works [23, 24, 25, 26, 27, 28], amines – [27, 29], alkyl acetates – [30], carboxylic acids – [27], diols – [31, 32], ketones – [33, 34], esters – [35], N-methylalkylamides [27] and N-alkylacetamides [27]. Similar dependences were obtained for sulfoxides - [31] and substances of other classes.

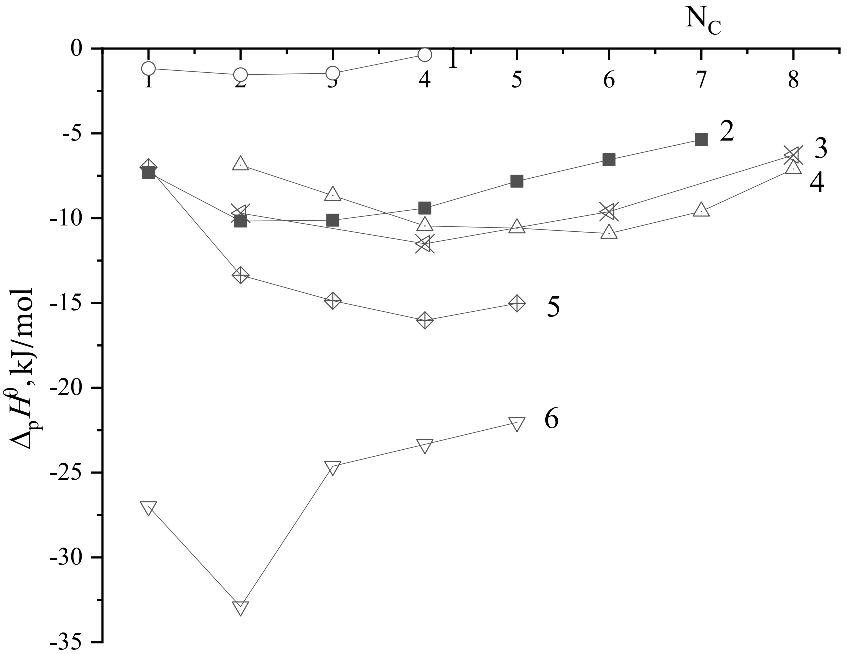


Fig. 2.3.1. Dependences of enthalpies of dissolution of organic compounds of some homologous series in water at 298.15 K on the number of carbon atoms in hydrocarbon radicals of their molecules:
1 – carboxylic acids; 2 – alkanols; 3 – ketones; 4 – diols; 5 – N-methylalkylamides; 6 – amines

It can be seen that the enthalpies of dissolution of substances in water do not change additively with respect to N_c within the whole homologous series. Increasing the size of the alkyl radical to N_c = 2-3 makes an exothermic contribution to the dissolution enthalpy. Further addition of methylene radicals leads to the opposite effect. Thus, the additivity with respect to the methylene group in the enthalpies of dissolution of monofunctional organic compounds in water is observed starting from the third member of the homologous series. The authors [36] explain the observed dependence by the competing action of hydrophobic hydration and the specific aspects of the dissolution mechanism of particles of different sizes in water. The predominance of hydrophobic hydration in the dissolution of the first members of the homologous series is because particles of small size can be placed in the voids present in the water structure. Such an explanation, according to the authors [36], is confirmed by the temperature dependence of the dissolution enthalpies. Fig. 2.3.1 presents the enthalpies of alcohols dissolution in water at 273.15 and 298.15 K. The contribution of hydrophobic hydration decreases as the solution temperature increases. As a result, the dependencies $\Delta_d H^o = f(N_c)$ become more monotone.

We have examined the patterns in change of enthalpies of substances dissolution in water above. The non-monotonicity of change of properties in a homologous series is most clearly shown on these thermochemical characteristics. However, it is known that the enthalpy of dissolution of a substance is the sum of enthalpies of its evaporation and solvation of molecules. Therefore, it is reasonable to analyze the additivity of these thermochemical characteristics and, thus, it is appropriate to consider the influence of interparticle solute-solvent and solvent-solvent interactions in a solution and intermolecular interactions in the condensed solute on the type of dependence $\Delta_d H^0 = f(N_C)$. Dependences of enthalpies of hydration of substances of several homologous series are shown in Fig. 2.3.2.

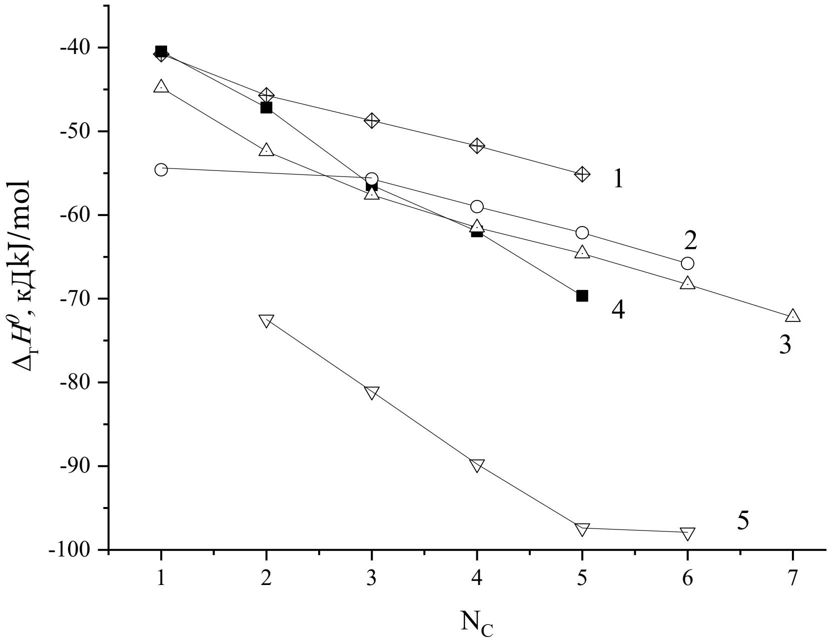


Fig. 2.3.2. Hydration enthalpy dependences: 2-ketones (1), 1-amines (2) 1-alkanols (3), monocarboxylic acids (4), diols (5) at 298.15 K on the number of carbon atoms in hydrocarbon radicals of their molecules

It can be seen that the additive decrease in the enthalpy of hydration of substances relative to the methylene group occurs at $N_c \geq 3$. That is, patterns in changes of dissolution enthalpies are caused by changes of hydration enthalpies. The above conclusions are confirmed by the results obtained by the authors [23, 35, 36]. The paper [36] notes that in spite of rather high correlation coefficient of dependences $\Delta_h H^o = f(N_c)$ for alcohols and amines the contribution of methylene group to $\Delta_h H^o$ is different. For example, for alcohols, it varies from 7.6 kJ/mol for C_1–C_2 to 3.9 kJ/mol for C_5–C_6. However, the additivity with respect to the CH_2-group will be observed if we consider the difference between the enthalpy of hydration of the molecule and $\Delta_s H^o$ "complex" polar group of -CH_2ON or -CH_2NH_2 type.

Table 2.3.1 shows the coefficients and regression parameters of equations (2.3.1) approximating enthalpy of hydration of alkanes, ketones, and alkanols for homologs with a number of carbon atoms in radicals greater than three, calculated earlier [37] from experimental data for alkanes from work [38], for ketones - [34], for alkanols - [28].

Table 2.3.1. Equation coefficients $\Delta_r H^0 = a_N + b_N N_C$ of approximate enthalpy of hydration of organic compound homologs at 298.15 K

Compounds	a_N	b_N	s	R	N_C
n-Alcanes	-15.51	-2.58	0.12	0.9996	3-6
2-Ketones^a	-38.57	-3.00	0.41	0.9988	4, 6, 8
1-Alkanols	-47.68	-3.44	0.30	0.9988	3-7

$$\Delta_S H^o = a_N + b_N N_c, \qquad (2.3.1)$$

where N_c is the number of carbon atoms.

A better additive scheme (equation (2.3.2)) was used by the authors [39] to decompose the enthalpies of hydration of cytosine derivatives with different number and arrangement of CH_2-groups in the molecule

$$\Delta_s H^o = A_0 + \Sigma n_i Z_i, \tag{2.3.2}$$

where n_i and Z_i are the number and type of allocated groups.

For hydroxy-, methoxy-, and methylates of cytosine with the same number of CH_2-groups, the $\Delta_s H^o$ differed. The differences were related to which atom was used to replace hydrogen in the methyl group. The following structural elements are highlighted: $CH_2(C)$, $CH_2(N)$, $CH_2(O)$ and O. The enthalpies of their hydration were: -5.9 ± 1.5, -8.6 ± 1.3, -14.3 ± 2.1, -14.9 ± 1.8 kJ/mol respectively. A_0 = -131.2 kJ/mol was considered as enthalpy of hydration of unsubstituted cytosine (experimental value – 128.9 kJ/mol).

The additivity of thermochemical characteristics of non-aqueous solutions of non-electrolytes has been studied substantially less than aqueous solutions. The vast majority of the data relate to alkane solutions. As mentioned above, the enthalpies of dissolution of alkane homologs are determined in about 40 organic solvents of different chemical nature [40, 41, 42, 43]. Polar hydrocarbon derivatives have been investigated in a less extensive set of solvents. Data are known for a number of alkylbenzenes [40], alcohols [40, 44, 45], amines [44], esters [35], ketones [46], amides [47].

Fig. 2.3.3 presents dependences of enthalpies of dissolution of 1-alkanol homologs in organic solvents on N_C.

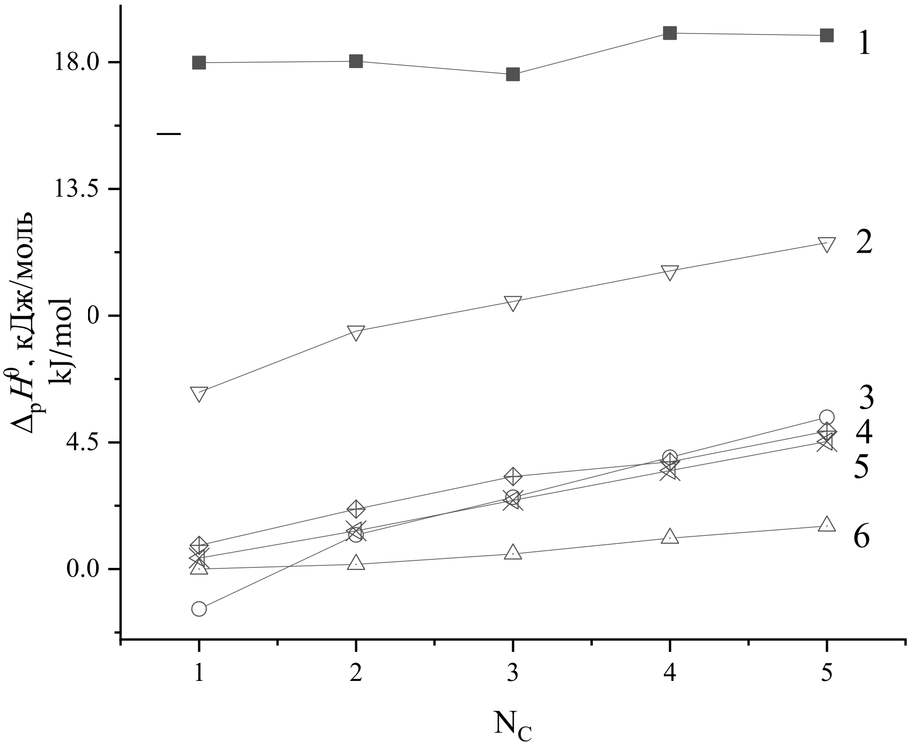


Fig. 2.3.3. Dependences of the enthalpies of dissolution: 1-alkanols in cyclohexane (1), propylene carbonate (2), dimethylsulfoxide (3), formamide (4), ethylene glycol (5), and methanol (6) at 298.15 K from the number of atoms of carbon in hydrocarbon radicals of their molecules

Similar dependencies are observed for substances of other homologous series. It can be noticed that the isotherms in Fig. 2.3.3 differ sharply from the shapes of similar dependences for aqueous solutions (see Fig. 2.3.1). The change in enthalpies of homolog dissolution in non-aqueous solvents is less spectacular than in water. The N_C-related additive increase of the enthalpies of dissolution starts already from the second term of the homologous series. And even the deviations of $\Delta_d H^0$ of the first term from the additive change are insignificant.

Similar patterns are observed in the changes in the enthalpy of solvation of homologs in non-aqueous solvents (Fig. 2.3.4).

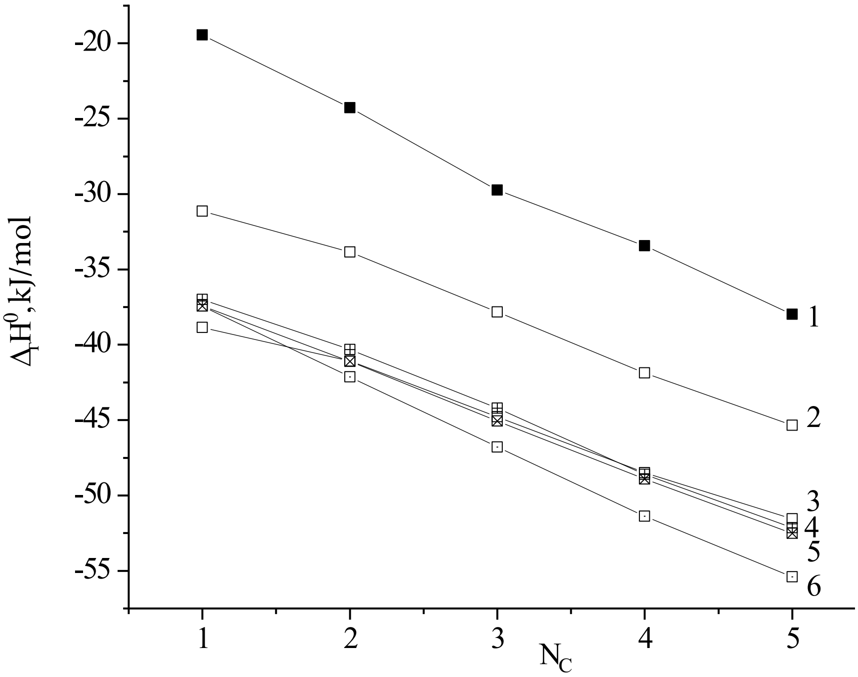


Fig. 2.3.4. Dependences of enthalpies of solvation of 1-alkanols in cyclohexane (1), propylene carbonate (2), dimethylsulfoxide (3), formamide (4), ethylene glycol (5), and methanol (6) at 298.15 K from the number of atoms of carbon in hydrocarbon radicals of their molecules

Table 2.3.2 presents the coefficients of equations of (2.3.1). Experimental data for alkanes from [41], for alkylbenzenes – [40], for ketones – [46], for alkanols – [40, 45] were used for calculation.

Comparison of the values given in Tables 2.3.1 and 2.3.2 shows that the coefficients a_N and b_N of the regression equations for aqueous solutions are generally more negative compared to non-aqueous solutions. It should also be noted that in aqueous solution the contributions of the methylene group (coefficient b_N) to the hydration enthalpies of the substances of the studied homologous series are strongly differentiated. In non-aqueous solutions, the b_N coefficients of the homologs have close values. This means that in non-aqueous media CH_2 groups are energetically equivalent not only for molecules of the same homologous series, but also for molecules of different chemical nature.

The authors [48] made similar conclusions on the additive contribution of the alkyl radical to the enthalpy of solvation of organic compounds of different homologous series in non-aqueous solvents. In their opinion, an essential argument in favor of this is the equality of the angular coefficients of the dependencies between the enthalpy of solvation and the molecular refraction found for alkanes, ketones, and aliphatic alcohols.

Variation of enthalpies of solvation of compounds belonging to the homologous series shows that interparticle interactions in solution are the main cause of non-monotonicity of dissolution enthalpies variation. This is particularly evident in aqueous solutions due to the specifics of water structure associated with the presence of a hydrogen bonding network.

Tablle 2.3.2. Coefficients of equations $\Delta_S H^0 = a_N + b_N N_C$ of solvation enthalpy approximation of homologs of organic compounds in non-aqueous solvents at 298.15 K

Solvent	**Alkanes**		**Alkylbenzenes**		**Ketones**		**Alkanols**	
	b_N	a_N	b_N	a_N	b_N	a_N	b_N	a_N
$MeNO_2$	-2.96	-0.06	-3.07	-28.31	-	-	-3.14	-24.40
Me_2SO	-3.18	1.17	-3.21	-29.79	-2.89	-21.03	-3.27	-35.09
MeCN	-3.39	-1.39	-3.50	-29.90	-	-	-3.56	-27.48
$C_4H_6O_3$	-3.62	0.66	-3.42	-30.92	-	-	-3.64	-27.07
Me_2NCOH	-3.70	-1.04	-3.58	-32.29	-3.56	-20.37	-3.86	-33.77
Me_2NCOMe	-3.94	-0.66	-3.60	-32.69	-	-	-3.92	-35.38
H_2NCOH	-3.83	-3.42	-3.61	-27.90	-	-	-3.86	-32.88
MeOH	-4.09	-1.96	-3.84	-31.04	-3.72	-17.17	-4.33	-33.65
EtOH	-4.33	-3.14	-4.09	-30.90	-	-	-4.36	-33.88
Bu^nOH	-4.60	-2.65	-4.36	-30.04	-	-	-	-
$(CH_2OH)_2$	-	-	-		-	-	-3.80	-33.62
CCl_4	-4.66	-1.77	-	-	-4.53	-14.78	-4.89	-14.44

Please note. The correlation coefficient for all cases is at least 0.999, the standard deviation does not exceed 0.6 kJ·mol^{-1}.

Table 2.3.3. Equation coefficients $\Delta_v H = a_N + b_N N_c$

Compounds	a_N	b_N	***se***	***R***	N_C
Nitriles	29.9	2.78	0.4	0.9999	1-5
Simple esters	12.1	3.62	0.9	0.9904	4,6,8,10
Alkyl acetates	27.4	3.73	0.4	0.9949	1-4
Ketones (MeCOR)	27.1	3.83	0.3	0.999,	1-5
Alkylformates	20.6	4.07	0.9	0.9809	1-4
Methylalkanoates	27.5	4.20	0.1	0.9999	1-4
Ethylalkanoates	29.8	4.26	0.5	0.9939	0-2
Diols	58.2	4.78	0.6	0.9932	2-5
Alkanols	32.5	4.91	0.2	0.9999	1-8
Alkanes	1.8	4.96	0.1	0.9999	5-16
Alkylbenzenes	30.9	5.05	0.6	0.9999	1-6
Acids	25.8	7.96	0.7	0.9999	0-4

Please note. N_C is the number of carbon atoms in the radical of the substance molecule.

Analysis of data on the enthalpies of evaporation of organic substances shows [6, 35, 41, 46, 49, 50] their additive change relative to the contribution of the methylene group within each homologous series. This is illustrated by the data obtained from the regression analysis of dependences $\Delta_v H = f(N_c)$ for alkanes and their monofunctional derivatives given in Table 2.3.3. It should be noted that the additivity of the enthalpies of evaporation relative to the contribution of CH_2-group is the same within the accuracy of determining the enthalpies of evaporation of substances (0.5-2 kJ/mol), which is considerably lower than the accuracy of calorimetric $\Delta_d H^o$ measurements.

In [51], the additive approach to the description of the enthalpies of evaporation of organic compounds is applied in the bond and group additivity approximation. The equation used for the calculations is

$$\Delta_v H = \Delta_v H(\mathrm{Y}) + n\Delta_v H(\mathrm{CH}). \qquad (2.3.3)$$

In expression (2.3.3), $\Delta_v H(\mathrm{Y})$ is the enthalpy of vaporization of the functional group; n and $\Delta_v H(\mathrm{CH})$ are the number and contribution of C-H bonds to the enthalpy of evaporation of the molecule. The methylene radical has two C-H bonds, the methyl radical has three. The results of calculations of $\Delta_v H(\mathrm{Y})$ and $\Delta_v H(\mathrm{CH})$ are given in [51, 52]. The authors [53] note the limitations of the values obtained in [51, 52] for two reasons. Firstly, for approximation, $\Delta_v H$ calculated by the Clapeyron-Clausius equation were used rather than the experimental standard $\Delta_v H$ at $P = 1$ atm and $T = 298.15$ K. Secondly, $\Delta_v H$ was used only for non-branched alkanes and their derivatives. However, it is known that the branched hydrocarbon chain strongly affects the enthalpies of evaporation of compounds, reducing their value. According to the authors [53], the branching of molecules increases the probability of intramolecular contacts. Since at a fixed molecular size (V_w equality of branched and non-branched chain compounds) the total number of intermolecular and intramolecular contacts remains constant, the increase of intramolecular interaction when the molecules branch weakens the intermolecular interaction. This leads to a decrease in the enthalpy of evaporation. Considering the above, the unification of hydrocarbon fragments by a set of C-H bonds [51] seems inappropriate. In the paper [53], it was proposed to use atomic group components CH_3, CH_2, CH, C, and Y as structural fragments, and to approximate the enthalpy of molecule evaporation by the expression

$$\Delta_v H = p\Delta_v H(\mathrm{Y}) + n\Delta_v H(\mathrm{CH_3}) + m\Delta_v H(\mathrm{CH_2}) + k\Delta_v H(\mathrm{CH}) + l\Delta_v H(\mathrm{C}), \qquad (2.3.4)$$

where p, n, m, k, l are numbers of corresponding groups in molecule $\Delta_v H(\mathrm{Y})$, $\Delta_v H(\mathrm{CH_3})$, $\Delta_v H(\mathrm{CH_2})$, $\Delta_v H(\mathrm{CH})$, and $\Delta_v H(\mathrm{C})$ respectively, are contributions of functional group and hydrocarbon fragments CH_3, CH_2, CH, and C to enthalpy of vaporization.

The solution of a system of equations (2.3.4) for 56 alkanes of different structures has established the contributions to the enthalpy of vaporization of radicals CH_3, CH_2, CH, and C, which are 5.74±0.30, 4.96±0.06, 2.63±0.50, and 0.41±0.50 kJ/mol respectively. In [53], it is also pointed out that the contribution of $\Delta_v H$ is small and can be skipped in the decomposition of $\Delta_v H$. The expression for the decomposition of the enthalpy of evaporation is as follows:

$$\Delta_v H = p\,\Delta_v H(\mathrm{Y}) + n\Delta_v H(\mathrm{CH_3}) + m\Delta_v H(\mathrm{CH_2}) + k\Delta_v H(\mathrm{CH}), \qquad (2.3.5)$$

where p, n, m, k are numbers of corresponding groups in molecule $\Delta_v H(\mathrm{Y})$, $\Delta_v H(\mathrm{CH_3})$, $\Delta_v H(\mathrm{CH_2})$, and $\Delta_v H(\mathrm{CH})$ respectively, are contributions of functional group and hydrocarbon fragments CH_3, CH_2, and CH to enthalpy of vaporization.

By solving systems of equations (2.3.5) the authors [53] determined group increments for 15 classes of organic monofunctional compounds. The data they obtained are shown in Table 2.3.4. Standard enthalpies of evaporation from [6, 54] were used for calculation. The presented values support the conclusion that the equivalence of C-H bonds in methylene, methylene, and methyl radical compounds is not observed. Moreover, for some homologous series, the contribution of the CH_2 group to the enthalpy of evaporation exceeds that of the CH_3 group.

Table 2.3.4. Contributions of hydrocarbon radicals and functional groups to the enthalpies of vaporization of organic compounds at 298.15 K

Range	**CH**	**CH_2**	**CH_3**	**Y**	***n***
>C=C<	2.75±0.14	4.96±0.02	8.20±0.11	0.09±0.40	12
COOH	2.40±0.19	4.95±0.40	4.85±1.70	45.90±2.20	9
Alkanes	3.24±0.43	4.94±0.03	5.87±0.07		56
OH	2.77±0.27	4.94±0.07	4.18±0.40	33.02±0.80	25
Cl	3.07±0.19	4.83±0.03	5.13±0.20	13.60±0.40	13
SH	1.86±0.39	4.83±0.03	4.41±0.06	17.65±0.09	15
O	2.79±0.31	4.80±0.06	5.56±0.30	6.76±0.90	26
Br	3.08±1.62	4.77±0.02	4.64±0.20	17.89±0.40	14
COO	2.76±0.12	4.74±0.09	4.52±0.80	20.68±2.00	16
I	2.47±0.47	4.47±0.05	4.03±0.10	23.31±0.20	9
NH_2	2.47±0.21	4.45±0.11	3.45±0.40	19.29±0.70	10
CHO	2.38±0.59	4.45±0.10	6.55±0.20	18.87±0.30	4
CN	-	4.42±0.10	3.31±0.70	27.87±1.30	14
S	-	4.38±0.06	4.16±0.06	19.22±0.30	7
CO	-	4.23±0.13	3.37±0.20	24.20±1.00	26

Please note: *n* is the number of connections.

Differences in the contribution of the methylene group to $\Delta_v H$ obtained by different authors (see Tables 2.3.3 and 2.3.4) are mainly due to the different sets of experimental data used for the regression analysis. In the general case, the constancy of the $\Delta_v H$ of structural elements is observed within a particular homologous series of compounds. However, based on the group contributions of methylene radicals which were determined with maximum accuracy, there are several groups of homologous series with similar $\Delta_v H^o$ of the radical CH_2. For example, one group includes alkanes, alkenes, alkanols, carboxylic acids, another group includes chlorine and bromine derivatives of alkanes, simple and complex ethers, the third group includes amines, nitriles, aldehydes, ketones. If we accept the experimental values of $\Delta_v H$ used for the analysis, the indicated proximity of group contributions may testify to the same geometrical configuration and energy equivalence of structural fragments (CH_2) in the selected groups of compounds.

To study the additivity of group contributions to the enthalpies of hydration of molecules of organic compounds, the authors [19, 20] used the equation

$$\Delta_h H = \Delta_{cav} H + \Delta_h H(\mathrm{H}) + \Sigma \Delta_h H(\mathrm{Y}) + \delta_h H(\mathrm{Y}_1,\mathrm{Y}_2,r_{\mathrm{Y1-Y2}}). \qquad (2.3.6)$$

Similar expressions were used for other thermodynamic hydration functions ($\Delta_h H^o$, $H = G, S, C_p$).

$\Delta_{cav} H$ is the contribution of cavity formation in solvent, $\Delta_g H(\mathrm{H})$ is the contribution of interaction of nonpolar part of molecule with water, $\Delta_g H(\mathrm{Y})$ - contribution of interaction of polar group with water, $\delta_g H(\mathrm{Y}_1,\mathrm{Y}_2,r_{\mathrm{Y1-Y2}})$ is the correction allowing for mutual influence of polar groups in polyfunctional molecule. $[\Delta_{cav} H + \Delta_g H(\mathrm{H})]$ was equated to the enthalpy of hydrocarbon hydration $\Delta_g H^*(\mathrm{RH})$, which were approximated by the linear equation (2.3.7).

$\Delta_h H$ reflect the isothermal transfer of the dissolved substance, represented by the scheme:

Hypothetical ideal gas with concentration 1 mol/dm^3	→	Hypothetical ideal aqueous solution with concentration 1 mol/dm^3

The $\Delta_g H$ values were calculated from the existing data on $\Delta_g H^o$ characterizing the transfer according to the scheme corrected for the change in the initial standard state of the dissolved substance:

Ideal gas in standard state (at $P = 1$ atm) → Hypothetical ideal aqueous solution in standard state (with a concentration of 1 mol/dm^3)

$$\Delta_h H = a_S + b_S S_w(\mathrm{RH}), \qquad (2.3.7)$$

where S_w(RH) is the surface area of N_A molecules of the hydrocarbon determined from the group contributions by the Bondi method [55]. In this case, the contribution of hydrocarbon radicals was determined according to the expression

$$\Delta_h H = b_S S_w(\mathrm{R}). \qquad (2.3.8)$$

In Equation (2.3.8), S_w(R) is the surface area of hydrocarbon radicals. For CH_3, CH_2, CH, and C the values of S_w(R) are equal: 2.12, 1.35, 0.57, and 0 cm^3/mol, respectively, and $\Delta_g H$(R) values: -4.81, -3.06, -1.29 and 0 kJ/mol. The authors [19, 20] took into account the influence of the polar group on the hydration of the hydrocarbon radical. If methyl radical was directly connected with functional group, its hydration enthalpy increased by $\delta_h H[CH_3(Y)] = 1.8$ kJ/mol. It should be noted that hydrocarbon radicals make equal contributions to the values of enthalpies of hydration $\Delta_r H$ and $\Delta_h H^o$. Comparison of expressions (2.3.8) and (2.3.1) shows that $b_N = b_S S_w(CH_2)$. Correction for the change in the initial standard state of the hydrocarbon affects the value of a_S. The contributions of polar groups in [19] were calculated from the enthalpies of hydration of monofunctional compounds:

$$\Delta_h H(\mathrm{Y}) = \Delta_h H(\mathrm{RY}) - \Delta_{cav} H + \Delta_H H(\mathrm{H}) = \Delta_h H(\mathrm{RY}) - [a_S + b_S S_w(\mathrm{R})]. \qquad (2.3.9)$$

Corrections, taking into account mutual influence of polar groups in bifunctional molecules, were determined by the equation

$$\delta_h H(\mathrm{Y}_1,\mathrm{Y}_2,r_{\mathrm{Y1-Y2}}) = \Delta_h H(\mathrm{RY}_1\mathrm{Y}_2) - [a_S + b_S S_w(\mathrm{R})] - \Sigma\Delta_h H(\mathrm{Y}) - \delta_h H(CH_3). \qquad (2.3.10)$$

In expression (2.3.10) m is the number of methyl groups directly bound to heteroatom Y; $\delta_g H(CH_3)$ is equal to $\Delta_g H[CH_3(Y)] - \Delta_g H(CH_3)$.

Group contributions to the thermodynamic functions of hydration calculated by the authors [19, 20] are given in Table 2.3.5.

The conclusions of the authors [19, 20] are consistent with the results presented above. The hydration energy of substances increases with increasing hydrocarbon radical length of molecules. The contributions of polar groups constitute a significant part of the hydration enthalpy due to the formation of hydrogen bonds of non-electrolyte — water. It can be seen from the above data that, as a rule, the additivity with respect to the contributions of polar groups is not observed. Thus, the doubled contribution of the hydroxyl group of alkanols to $\Delta_s H^o$ is greater compared with the enthalpy of hydration of the two OH-groups of diols.

The study of non-specific solvation of aromatic compounds in non-aqueous solvents conducted by the authors [42, 56, 57, 58] has shown that the enthalpies of their non-specific solvation are additive with respect to the group composition of molecules. The contribution that the aldehyde group in various aromatic compounds (benzaldehyde, p-chlorobenzaldehyde, 9-anthraldehyde) makes to $\Delta_c H^o$, for example, is the same. The contribution of an aromatic radical to the enthalpy of solvation depends on its size, but does not depend on whether the aromatic radical is bound to an aldehyde group, a nitro group, or a halogen group. Earlier in [59], based on the study of a large number of solutions of aromatic compounds in methanol and dimethylformamide, it was also shown that in most cases, the additivity in the enthalpy of transfer of aromatic compounds is observed in the case when there is no specific interaction.

Table 2.3.5. Group contributions to the thermodynamic functions of hydration of compounds

Group	$\Delta_h G^o$ kJ/mol	$\Delta_h S^o$ J/mol K	$-\Delta_h H^o$ kJ/mol
CH_3	6.17	-1.36	4.81
CH_2	3.93	-0.86	3.06
CH	1.67	-0.36	1.29
C	0	0	0
OH (primary alcohols)	8.61±0.45	29.0±0.2	37.6±0.5
OH (secondary and tertiary alcohols)	12.72	30.0	42.8
NH_2 (primary amines)	9.15±0.40	27.4±0.3	36.5±0.2
NH (secondary amines)	12.61	29.4	42.0
N (tertiary amines)	11.56±0.63	26.9±0.2	38.5±0.4
O (simple ethers)	4.92	21.7	26.6
CO (carboxylic acids)	-	-	38.4±2.5
COO (complex esters)	5.27	22.1	27.5
CO (ketones)	-0.77	24.7	23.8
CONH (secondary amides)	-	-	60.2
$CONH_2$ (primary amides)	-	47.6	-

Much attention has been paid to the study of the additivity of the aromatic cycle contribution to the enthalpy of solvation of organic compounds in non-aqueous media [60, 61, 62]. The authors of papers mentioned above on example of enthalpy of solvation of benzene, naphthalene, anthracene, biphenyl, phenanthrene, and azobenzene found that solvation of unsubstituted aromatic polycyclic compounds weakly depends on the nature of organic solvents. This allowed them to find out the common aspect of solvation in the studied systems. Increasing the number of benzene nuclei to two in naphthalene and to three in anthracene and phenanthrene increases the solvation of these compounds compared to benzene by 60% and 220% respectively. The reason for this is the universal solvation of additional benzene rings. Assuming that the molecules in the systems studied interact, apparently, by π-π-type, it was concluded that the enthalpy of solvation is determined by the number of delocalized π-electrons in the coupled bonding system. It turned out that the ratio of the enthalpy of solvation of the studied hydrocarbons to the number of π-electrons of their conjugated systems (n) has a constant value. This allowed the authors [60, 61, 62] to obtain a correlation equation to calculate $\Delta_c H^o$ of unsubstituted aromatic hydrocarbons in non-aqueous media

$$\Delta_s H^o = -(5.4 \pm 0.17)n. \qquad (2.3.11)$$

It should be noted, however, that the assumption of independence of enthalpies of solvation of unsubstituted polycyclic hydrocarbons from the nature of the solvent put forward by the authors [60, 61] seems to be unconvincing. The average value of $\Delta_s H^o$ of benzene, which is -32.5 kJ/mol according to formula (2.3.11), is too rough an approximation. Experimental data obtained by the authors [61, 62] show that differences in $\Delta_s H^o$ of benzene, naphthalene, and anthracene in different solvents reach 5-6 kJ/mol. In addition, the authors [42, 63] have shown that the solvation of benzene, in contrast to the solvation of alkanes, has a significant specific component and is largely determined by the polarity of the solvent. Therefore, it is reasonable to use equation (2.3.11) taking into account the influence of solvent on solvation of polycyclic compounds.

In works [60, 64], as a result of thermochemical study of non-aqueous solutions of benzene and its derivatives, the contributions of various substituents (OH, Cl, Br, CHO, CH_3, NO_2) in enthalpies of solvation of aromatic series compounds were isolated. For substituents not reacting with molecules of organic solvents in donor-acceptor interaction (Cl, Br, CH_3), it was proposed to use average value of group contributions for a number of solvents. The combination of the obtained thermochemical characteristics of substituents with the values of enthalpies of solvation of unsubstituted aromatic hydrocarbons calculated by the formula (2.3.11) formed the basis for the method proposed by the authors [60-62, 64] for calculation of enthalpies of solvation of aromatic compounds in non-aqueous media. This approach is valid for the majority of aromatic compounds (not only hydrocarbons but also heterocyclic compounds). It is stated that the position of the substituent in the molecule does not play a significant role, provided that the substituent does not form an intramolecular hydrogen bond with another substituent or heteroatom of the cycle. Obviously, the proposed methodology will be more valid for compounds the molecules of which have large aromatic cycles.

The additive-group method is widely used in interpretation of enthalpy coefficients of pairwise interactions [65, 66, 67, 68]. The values of enthalpy coefficients of heterotactic pairwise interactions of non-electrolytes (x and y) in aqueous solution were approximated by the equation depending on the number of equivalent methylene groups in a molecule

$$h_{xy} = mh(\mathrm{CH_2\text{-}X}) + h(\mathrm{Y\text{-}X}), \qquad (2.3.12)$$

where $h(\mathrm{CH_2\text{-}X})$ and $h(\mathrm{Y\text{-}X})$ are the contributions to h_{xy} of the paired interactions of the methylene and polar (Y) groups of the solute y with molecule x; m is the number of equivalent CH_2-groups in the molecule. According to [65] the methyl group is equivalent to half and the methyl group to one and a half CH_2-groups. This amounts to using the first approximation of the additive approach — additivity of bonds, in this case C-H bonds, as in [51]. It should be noted that the allocation of structural fragments in the above approach is not sufficiently justified. Obviously, the methyl groups of alkyl radicals associated with different functional groups are not equivalent. Thus, during the analysis of amide coefficients h_{xy} with urea in aqueous solution [67], the authors found that $H(\mathrm{CH_2\text{-}X})$ are different for tertiary and secondary (primary) amides. As a consequence, the use of the principle of equivalent methylene groups [65] meets certain difficulties and is limited to a small set of substances.

Everything mentioned above shows that the additivity of solution properties is intensively studied and applied to the interpretation of enthalpy characteristics of solutions of organic compounds. However, the applied separation of the methylene group as the main structural fragment of the molecule and the analysis of compliance with its contribution to the thermodynamic characteristics is a rather limited scheme, it does not allow making reasonable conclusions about the relationship between the properties of solutions and the composition and structure of the molecules of the dissolved substance. Therefore, it becomes important to apply new, more developed schemes for decomposition of molecules into structural fragments and use them to analyze experimental data.

3. A new scheme for separation of structural fragments in the molecules of organic compounds. Determination of contributions to the thermochemical characteristics of organic compounds and their solutions in water and non-aqueous solvents

3.1. Thermochemical characteristics of dissolution and hydration of organic compounds of normal structure.

Now, let us return to the dependences of the enthalpies of dissolution and hydration of organic compounds on the number of carbon atoms in the radical of their molecules. As already indicated, non-monotonic changes in these characteristics may be caused by a change in the hydration mechanism of molecules with an increase in their size and hydrophobic hydration. However, if for monofunctional compounds the above explanation seems logical, then for polyfunctional, including heterofunctional, compounds it does not seem quite convincing. For example, experimental evidence shows (see Fig. 2.3.1), that the increase in enthalpies of dissolution of α,ω-diols begins with 1,6-hexanediol. The addition of methylene groups in the series of alkoxyethanols causes a decrease in enthalpy of dissolution during the transition from methoxyethanol to ethoxyethanol [69], despite the fact that the methoxyethanol molecule already contains methyl and two methylene radicals. A similar example is the increase of the hydrocarbon radical in the N-alkylacetamide and N-methylalkylamide series (see Fig. 2.3.1). Thus, the above data allow us to state that in any homologous series, regardless of the size of the functional group, a decrease in enthalpy of dissolution of organic compounds in water is observed from the first to the second term of the series due to a strong increase in the exothermicity of hydration. The reason for this is probably not the change in the total size of the molecules and the associated change in the mechanism of hydration of molecules, but the specific aspects of hydration of hydrocarbon radicals containing not more than two carbon atoms.

Based on the structure of alkane molecules and in accordance with the recommendations [2, 3], four structural fragments are usually distinguished (taking into account the first environment): $(C)CN_3$, $(C)_2CN_2$, $(C)_3CH$, $(C)_4C$ [6, 8]. Here, the number and type of atoms in the first environment of the selected structural element is given in parentheses. In the molecules of monofunctional derivatives of aliphatic hydrocarbons, besides the groups indicated for alkanes, the structural elements are: $(Y)CH_3$, $(Y)CH_2(C)$, $(Y)CH(C)_2$, $(Y)C(C)_3$, and $Y(C)$. The symbol Y indicates a functional group, e.g: -OH, -Cl, $-NO_2$, -COOH, etc. The sizes of hydrocarbon radicals increase as groups appear in the molecules of compounds in the following sequence: $(Y)CH_3$, $(Y)CH_2(C)$, $(C)CH_3$, and $(C)_2CH_2$. Selected structural elements have a different first environment and, therefore, different equilibrium geometric configuration and are energetically non-equivalent. Therefore, it is logical to assume that the contributions to the enthalpies of hydration and dissolution of these groups will be different. And only starting from the third member of the homologous series, the hydrocarbon radical lengthens due to the addition of only the $(C)_2CH_2$ group. Exactly from this point one should expect a monotonic change in the enthalpy of dissolution in the homologous series of hydrocarbons and their monofunctional derivatives. Considering the above-mentioned points concerning the separation of structural elements in the molecule, we note that the observed course of the dependencies in Fig. 2.3.1 and 2.3.2 is expected. It is easy to see that the approach of the authors [36] is equivalent to the conclusions made above, based on the change in the structure of molecules in the homologous series. Indeed, if the (Y)(CH_2) fragment is singled out as a polar group, then the homolog molecules increase further due to the addition of the $(C)_2(CH_2)$ group. A similar effect is shown in the enthalpies of solvation of ketones and esters in cyclohexane [35]. According to the classification of structural fragments [2], CH_3 radicals are called end fragments, CH_2 radicals are called chain fragments. The enthalpies of methane and ethane hydration deviate from the linear relationship in Fig. 2.3.2 because their molecules consist only of terminal fragments.

Now, let us move on to quantitative description of enthalpy characteristics of dissolution and hydration of organic substances. V.M. Tatevsky [2] distinguishes two fundamentally different approaches to the partitioning of molecules into structural elements. The first assumes such a division of the molecule in which each nucleus belongs to only one structural element, i.e., the boundaries between structural elements do not pass through the nuclei. In the second method, the division of the molecule into structural elements occurs in such a way that individual nuclei may belong to two or more structural fragments, that is, the boundaries between structural elements pass through some nuclei. In this paper, the second approach was used. The CH bond was chosen as the main fragment of hydrocarbon radicals in the present work. This is done for several reasons: firstly, greater detailing allows one to consider more substances without changing the number of structural elements. When CH bonds are selected as a structural element, methane, for example, is included in the consideration, and when a larger particle is selected as a structural fragment, its addition to the data matrix is required. Secondly, to avoid using fractional values for radical contributions, for example, in formic acid and formamide molecules. It should be noted that the chosen scheme for dividing molecules into structural fragments should be classified as an additive-group scheme rather than an additivity bonding scheme. This stems from the fact that, firstly, functional groups are highlighted in it; and, secondly, the separated CH bonds in different hydrocarbon radicals are not equivalent. By summing the bond contributions, the contributions of the corresponding hydrocarbon radicals can be obtained.

From formula (1.3) for enthalpies of dissolution, solvation, transfer, and evaporation of aliphatic hydrocarbons we can form the expression

$$\Delta H^{o} = p\Delta H^{o}(\mathrm{CH})_{\mathrm{p}} + s\Delta H^{o}(\mathrm{CH})_{\mathrm{s}} + t\Delta H^{o}(\mathrm{CH})_{t} + h\Delta H^{o}(\mathrm{C}) + d\Delta H^{o}(\mathrm{CH})_{=} + e\Delta H^{o}(\mathrm{CH}), \quad (3.1.1)$$

where $\Delta H^{o}(\mathrm{CH})_{p}$, $\Delta H^{o}(\mathrm{CH})_{s}$, $\Delta G^{o}(\mathrm{CH})_{t}$, $\Delta H^{o}(\mathrm{CH})_{=}$, $\Delta H^{o}(\mathrm{CH})_{\equiv}$ are contributions to the enthalpy characteristic of the CH bond of primary, secondary and tertiary carbon atoms, CH bonds at multiple (double and triple) carbon-carbon bonds, respectively; ΔH^{o} is the contribution of the quaternary carbon atom, which can be considered as a correction to the CH-bond contributions; *p*, *s*, *t*, *h*, *d*, and *e*are the numbers of the corresponding fragments in the molecules, which are determined on the basis of their structure.

For aliphatic hydrocarbons, the hydration enthalpies of which are given in Table 3.1.1, a matrix of *p, s, t, h, d* and *e* values is presented in Table 3.1.2. The contributions of the extracted relationships are found by multiple linear regression. The calculation results are shown in Table 3.1.3.

The small errors in the description indicate the adequacy of the chosen model. The unaccounted C-C bonds are probably shielded and do not contribute significantly to the intermolecular interaction. There is no functional group in alkanes, so the free term is 0 within the margin of error of the data.

Table 3.1.1. Hydration enthalpies of non-polar substances at 298.15 K, number of water molecules in the solvate shell of a non-polar particle (N) and Van der Waals volume of a non-polar particle $v_w = V_w/N_A$ (nm^3)

Solved compound	$-\Delta_h H^o$	N	$v_w \cdot 10^2$	**Solved compound**	$-\Delta_h H^o$	N	$v_w \cdot 10^2$
He	0.59	11.7	0.94	n-C_5H_{12}	28.3	31.9	9.64
Ne	3.8	12.9	1.13	n-C_6H_{14}	31.1	35.4	11.34
Ar	11.98	16	2.25	n-C_7H_{16}	33.9		
Kr	15.29	17.3	2.44	C_2H_2	14.62	18.1	3.84
Xe	18.99	18.3	3.61	C_2H_4	16.46	18.8	3.97
O_2	10.66	15.1	2.16	c-C_3H_6	23.26	22.8	5.1
N_2	11.45	15.8	2.65	$CH_2{=}C_2H_4$	21.6	23	5.66
CH_4	13.18	16.9	2.84	$CH_2{=}C_3H_6$	24.88	26.7	7.36
C_2H_6	19.52	21.3	4.53	i-C_4H_{10}	24.19	27.7	7.94
C_3H_8	23.27	24.8	6.24	$C(CH_3)_4$	23.26	30	9.64
n-C_4H_{10}	25.92	28.4	7.94				

Please note. We have used data obtained by Dec and Gill in [70, 71]. V_w from the paper [55], a - [72].

Table 3.1.2. Number of extracted structural elements in hydrocarbon molecules

Carbon	$(CH)_p$	$(CH)_s$	$(CH)_t$	(C)	$(CH)_=$	$(CH)_\equiv$
C_2H_2	0	0	0	0	0	2
C_2H_4	0	0	0	0	4	0
$CH_2{=}C_2H_4$	3	0	0	0	3	0
$CH_2{=}C_3H_6$	3	2	0	0	3	0
CH_4	4	0	0	0	0	0
C_2H_6	6	0	0	0	0	0
C_3H_8	6	2	0	0	0	0
n-C_4H_{10}	6	4	0	0	0	0
n-C_5H_{12}	6	6	0	0	0	0
n-C_6H_{14}	6	8	0	0	0	0
n-C_7H_{16}	6	10	0	0	0	0
i-C_4H_{10}	9	0	1	0	0	0
$C(CH_3)_4$	12	0	0	1	0	0

Analysis of the data in Table 3.1.3 shows that the end structural groups (CH bonds of primary carbon atoms and, correspondingly, methyl radicals) are hydrated significantly more exothermally than the chain ones. The ratio of enthalpies of hydration of methylene and methyl radicals is approximately 1 : 3, not 1 : 1.5 as one would expect based on the number of CH bonds. The results suggest that the effect of hydrophobic hydration is associated specifically with the hydration of the end structural groups in the molecules. The data in Table 3.1.3 also show that the hydration enthalpies of the CH bond at the tertiary carbon atom and the quaternary carbon atom have positive values. $\Delta_s H^o$ of structural fragments are partial values.

The partial values of the properties can have different signs. Physically, the endothermicity of the hydration of $(CH)_t$ and (C) fragments can be explained by steric hindrances arising due to the branching of the hydrocarbon radical.

Table 3.1.3. Contributions of structural fragments to the enthalpies of hydration, evaporation and dissolution of hydrocarbons in water at 298.15 K

Property	$(CH)_s$	$(CH)_p$	$(CH)_t$	(C)	$(CH)_=$	$(CH)_\equiv$	*se*
$\Delta_h H^0$	-1.41	-3.31	5.64	16.51	-4.04	-7.51	0.3
$\Delta_v H^0$	2.48	1.95	2.76				
$\Delta_d H^0$	1.07	-1.36	8.40				

Turning to the enthalpies of dissolution and hydration of derivatives of hydrocarbons, one important, in our opinion, pattern should be noted. The dependences in Fig. 2.3.1 and 2.3.2 show that in any homologous series (including the series of alkanes) irrespective of the size of a functional group, there is an observable decrease in enthalpy of dissolution of organic compounds in water from the first to the second term of the series, due to strong increase in exothermicity of hydration. Apparently, the features of methane and ethane hydration, due to energy equivalence in the hydration of their CH-bonds, are preserved in the hydration of methyl, ethyl, ethylene, etc. radicals linked to the functional group and containing not more than two carbon atoms. This leads to the equivalence of all CH-bonds for each of such radicals. In Tables 3.1.4-3.1.7, such bonds are designated $(CH)_Y$, i.e., they are CH fragments located in the first environment of the functional group. *It should be emphasized that the allocation of such fragments is a priority.*

Table 3.1.4. Quantity of extracted structural elements in alkanol molecules, enthalpies of their evaporation and dissolution in water at 298.15 K

Compound	$(CH)_Y$	$(CH)_s$	$(CH)_p$	$(CH)_t$	Y_s	Y_t	$\Delta_d H^o$		$\Delta_v H^o$	
							exp	Δ	exp	Δ
MeOH	3						-7.32		37.48	
EtOH	5	0	0	0	0	0	-10.17		42.23	
Pr^nOH	4	0	3	0	0	0	-10.12		47.48	
Bu^nOH	4	2	3	0	0	0	-9.41		52.09	
Pe^nOH	4	4	3	0	0	0	-7.82		56.78	
Hex^nOH	4	6	3	0	0	0	-6.56		61.74	
Hep^nOH	4	8	3	0	0	0	-5.37		66.83	
Oc^nOH	4	10	3	0	0	0	-3.40		71.00	
Pr^iOH	7	0	0	0	1	0	-13.05	-0.18	45.35	0.41
Bu^2OH	6	0	3	0	1	0	-13.18	-0.02	49.72	-0.40
Bu^iOH	3	0	6	1	0	0	-9.33	0.00	50.77	0
Bu^tOH	9	0	0	0	0	1	-17.20	0.55	46.80	0.00
Pe^2OH	5	0	6	0	1	0	-12.80	0.66	53.30	-2.00
Pe^tOH	8		3	0			-18.60	-0.55		
Hex^3OH	5	2	6	0	1	0	-12.59	-0.47	56.81	-3.25
Hep^4OH	5	4	6	0	1	0	-12.68	-1.90	62.62	-2.21

Please note. Here and in Tables 3.1.4–3.1.7$\Delta = \Delta H^o_{(exp)} - \Delta H^o_{(calc)}$.

Table 3.1.5. Quantity of extracted structural elements in diol molecules, enthalpies of their evaporation and dissolution in water at 298.15 K

Compound	**$(CH)_Y$**	**$(CH)_s$**	**Y_s**	**$\Delta_d H^o$**		**$\Delta_v H^o$**	
				experimental	Δ	experimental	Δ
$HO(CH_2)_2OH$				-6.87	-0.08	65.60	0.02
$HO(CH_2)_3OH$	6	0	0	-8.67	0.22	72.40	-0.03
$HO(CH_2)_4OH$	8	0	0	-10.46	0.53	79.30	0.02
$HO(CH_2)_5OH$	8	2	0	-10.59	-0.64	86.80	0.00
$HO(CH_2)_6H$	8	4	0	-10.90	-1.99	87.00	-7.32
$HO(CH_2)_8OH$	8	8	0	-7.10	-0.27		
$HO(CH_2)_9OH$	8	10	0	-5.40	0.39		
$MeCHOHCH_2OH$	6	0	1	-10.48	0.18	71.20	0.00
$Me(CHOH)_2Me$	8	0	2	-14.72	-0.18		

Table 3.1.6. Quantity of extracted structural elements in ketone molecules, enthalpies of their evaporation and dissolution in water at 298.15 K

Compound	**$(CH)_Y$**	**$(CH)_s$**	**$(CH)_p$**	**Y_s**	**Y_t**	**$\Delta_d H^o$**		**$\Delta_v H^o$**	
						experimental	Δ	experimental	Δ
MeCOMe						-10.17		30.50	
EtCOMe	8	0	0	0	0	-10.72		34.95	
Pr^{n}COMe	7	0	3	0	0	-10.21		38.50	
Bu^{n}COMe	7	2	3	0	0	-9.46		42.33	
Pen^{n}COMe	7	4	3	0	0	-8.95		46.10	
EtCOEt	10	0	0	0	0	-10.90	0.06	38.60	-0.13
Pr^{i}COMe	10	0	0	1	0	-10.63	-0.48	36.80	-0.14
Pr^{i}COPr^i	14	0	0	2	0	-9.60	0.47	40.44	0.15
Bu^{t}COMe	12	0	0	0	1	-9.50	0.00	43.40	0.00

Table 3.1.7. Quantity of extracted structural elements in methylalkanoate molecules, enthalpies of their evaporation and dissolution in water at 298.15 K

Compound	**$(CH)_Y$**	**$(CH)_s$**	**$(CH)_p$**	**Y_s**	**Y_t**	**$\Delta_d H^o$**	**$\Delta_v H^o$**
MeCOOMe						-7.81	31.69
EtCOOMe	5	0	0	0	0	-8.65	36.02
Pr^{n}COOMe	4	0	3	0	0	-8.04	40.10
Bu^{n}COOMe	4	2	3	0	0	-7.28	44.32
Pr^{i}COOMe	7	0	0	1	0	-8.62	38.90
Bu^{t}COOMe	9	0	0	0	1	-7.32	42.30

If this is logical for the methyl radical, then, for example, for the ethyl radical containing a methyl group in addition to the methylene group, this idea is new. Returning to the reasons for the non-monotonicity of the change in $\Delta_d H^o$ from N_C and the nonlinearity of the change in $\Delta_g H^o$ from N_C, it can be noted that it can be caused by the specifics of hydration of hydrocarbon radicals containing not more than two carbon atoms, associated with the fact that all their CH bonds are energetically equivalent. The $(CH)_p$ and $(CH)_s$ bonds in functional hydrocarbon derivatives are bonds separated from the functional group by more than two carbon atoms. Tables

3.1.4 and 3.1.5 present, for example, matrices of initial data for 1-alkanols and α,ω-diols.

It is seen that in 1-alkanols the maximum number of $(CH)_Y$ fragments is 5 and belongs to the ethyl radical. In α,ω-diols, the maximum number of $(CH)_Y$ fragments is 8 and belongs to four methylene groups. That is why the exothermic solvation amplification in the series of 1-alkanols ends with ethanol, and in the series of α,ω-diols – with 1,4-butanediol.

According to formula (1.3), the enthalpies of dissolution, solvation, transfer, and evaporation of monofunctional alkane derivatives can be expressed by the relation

$$\Delta H^o = \Delta H^o(Y_p) + \delta H^o(Y_s) + \delta H^o(Y_t) + y\Delta H^o(CH)_Y + p\Delta H^o(CH)_p + s\Delta H^o(CH)_s + \\ + t\Delta H^o(CH)_t + h\Delta H^o(C), \qquad (3.1.2)$$

where $\Delta H^o(CH)_Y$ are the increments of CH bonds in hydrocarbon radicals included in the first environment of the functional group; $\Delta H^o(CH)_p$, $\Delta H^o(CH)_s$, $\Delta H^o(CH)_t$, and $\Delta H^o(C)$ are contributions of structural fragments of hydrocarbon radicals that are more than two carbon atoms distant from the functional group; y, p, s, t, and h are number of selected fragments; $\Delta H^o(Y_p)$ is the contribution of the functional group bound to the primary carbon atom; $\delta H^o(Y_s)$ and $\delta H^o(Y_t)$ are corrections to account for differences in the enthalpies of solvation of functional groups bound to secondary and tertiary carbon atoms with respect to the functional group bound to the primary carbon atom. The contribution of the functional group bound to the secondary carbon atom $[\Delta H^o(Y_s)]$, can be determined by summing the values of $\Delta H^o(Y_p)$ and the corresponding correction $\delta H^o(Y_s)$ according to the formula

$$\Delta H^o(Y_s) = \Delta H^o(Y_p) + \delta H^o(Y_s). \qquad (3.1.3)$$

A similar expression is used to calculate the contribution of the functional group associated with the tertiary carbon atom $[\Delta H^o(Y_t)]$:

$$\Delta H^o(Y_t) = \Delta H^o(Y_p) + \delta H^o(Y_t). \qquad (3.1.4)$$

The coefficients of equation (3.1.2) at $\Delta H^o(Y_p)$, $\Delta H^o(Y_s)$, and $\delta H^o(Y_t)$ for monofunctional compounds are equal to one.

Tables 3.1.4-3.1.7 present the amounts of selected structural fragments in the molecules of monofunctional compounds of some homologous series and literature data on the enthalpies of their dissolution in water and evaporation at 298.15 K. The following sources were used: [23, 73, 24, 25] for alkanols, [31, 32, 74, 75] for diols, [27, 29] for amines, [35] for ketones and methylalkanoates, [27] for carboxylic acids, [30] for alkyl acetates.

Calculated contributions of the isolated structural fragments to the enthalpies of dissolution in water and evaporation of monofunctional organic compounds of some homologous series are given in Tables 3.1.8 and 3.1.9. The functional group increment is calculated as a free term in the regression equation.

The small errors of description indicate that the proposed model adequately reflects the experimental data. The specified regression parameters are given for the description of enthalpy characteristics of substances of normal structure. Table 3.1.10 presents the increments of structural fragments in the hydration enthalpies, which are calculated by formula (3.1.5) using the corresponding data of fragment contributions to the dissolution and evaporation enthalpies from Tables 3.1.8 and 3.1.9.

The relationship between these enthalpies is expressed as follows

$$\Delta_s H^o = \Delta_d H^o - \Delta_v H^o. \tag{3.1.5}$$

In formula (3.1.5) $\Delta_s H^o$, $\Delta_d H^o$, and $\Delta_v H^o$ are the enthalpies of solvation (hydration), dissolution, and evaporation of the dissolved substance, respectively.

Table 3.1.8. Contributions of structural fragments of molecules to the enthalpies of dissolution of monofunctional compounds in water at 298.15 K

Compounds	Formula	Y	Y_p	$(CH)_Y$	$(CH)_s$	$(CH)_p$	$(CH)_t$	Y_s	Y_t	*se*
Diols (for compounds from Table 3.1.5)	$R(OH)_2$	OH	-1.30	-1.05	0.52			-1.78 (0.18)		0.53
Alkanols (for compounds from Table 3.1.4)	ROH	OH	-3.04	-1.43	0.67	-0.57	1.44 (0.00)	0.16 (0.26)	-1.88 (0.55)	0.32
Amines $N_C = 1 - 8$	$R^{n}NH_2$	NH_2	-18.1	-2.95	0.66	1.77				0.03
Ketones (for compounds from Table 3.1.6)	R_1COR_2	C=O	-9.14	-0.18	0.32	0.08		0.81 (0.48)	1.83	0.10
Sulfoxides $N_C = 1 - 4$, 6 – 8	$R^{n}SOMe$	S=O	-9.80	-1.50	0.67	-1.33				0.83
Acids $N_C = 1 – 5$	$R^{n}COOH$	COOH	-0.48	-0.22	0.55	-0.04				0.05
Methylalkanoates (for compounds from Table 3.1.7)	$R^{n}COOMe$	COOMe	-6.55	-0.42	0.38	0.06		0.87	3.01	0.00
Alkyl acetates $N_C = 1 – 5$	$R^{n}OOCMe$	OOCMe	-4.68	-0.81	0.07	-0.02				0.00

Please note. Here and in Table 3.1.9, correlation coefficient for compounds of normal structure does not go lower than 0.99. The standard error (*se*) is given to describe the $\Delta_d H^o$ of substances of normal structure. The parentheses contain the errors in the description of $\Delta_d H^o$ isomers when using the values of the contributions from this table. N_C is the number of carbon atoms in the compound radical, excluding the functional group.

Analysis of the calculation results shows that the contributions of structural fragments in the enthalpies of dissolution, evaporation, and hydration are quite different for different homologous series. The differences are particularly large for $(CH)_Y$ fragments. This shows the effect of the functional group on the hydrocarbon radical. However, there is no clearly pronounced dependence between the values of contributions of the nonpolar fragment $(CH)_Y$ and the functional group in the enthalpies of evaporation and dissolution in water.

At the same time, such relationship can be noted for enthalpies of hydration of substances. The data presented in Table 3.1.10 show that there is a tendency for symbiotic changes in the increments of $(CH)_Y$ and $(CH)_p$ bonds on the one hand and the polar group on the other hand. Contributions to the enthalpy characteristics of the end fragments also differ greatly. The smallest differences are observed for CH bonds of secondary carbon atoms. Let us consider in more detail the contributions of hydrocarbon fragments to the hydration enthalpies of organic compounds. We found a directly proportional relationship between the contributions of $(CH)_p$ and $(CH)_Y$ fragments to $\Delta_g H^o$ molecules shown in Fig. 3.1.1.

This dependence is described by the correlation equation

$$\Delta_h H^o[(CH)_Y] = 1.22\ \Delta_h H^o[(CH)_p], \quad se = 0.08, \quad R = 0.9948. \qquad (3.1.6)$$

Fig. 3.1.1 also demonstrates a linear correlation between the contributions of $(CH)_p$ and $(CH)_Y$ fragments to the enthalpies of vaporization of substances.

Table 3.1.9. Contributions of structural fragments of molecules to the enthalpies of vaporization of monofunctional compounds at 298.15 K

Compounds	Formula	Y	Y_p	$(CH)_Y$	$(CH)_s$	$(CH)_p$	$(CH)_t$	Y_s	Y_t	*se*
Diols (for compounds from Table 3.1.6)	$R(OH)_2$	OH	25.90	3.43	3.76			-1.23		0.04
Alkylbenzenes $N_C = 1 - 8$	R^nPh	Ph	32.27	1.67	3.01	1.89				0.79
Alkanols (for compounds from Table 3.1.5)	ROH	OH	30.35	2.38	2.38	2.52	-1.81 (0.0)	-2.04 (0.40)	-4.93	0.23
Amines $N_C = 1 - 8$	R^nNH_2	NH_2	39.16	-3.85	2.33	2.42				0.29
Ethers $N_C = 2 - 5$, Pr^iOPr^i	ROR	O	21.00	0.60	1.93	1.22		1.07		0.00
Ketones (for compounds from Table 3.1.7)	R_1COR_2	C=O	18.48	2.03	1.90	1.95		-1.79 (0.15)	-2.34	0.23
Nitriles $N_C = 1 - 4$	R^nCN	CN	29.92	1.03	1.56	1.24				0.00
Acids $N_C = 1 - 6$	R^nCOOH	COOH	35.58	3.78	4.58	3.24				0.80
Methylalkanoates (for compounds from Table 3.1.8)	RCOOMe	COOMe	25.19	2.17	2.11	2.08		-1.45	-2.38	0.00
Alkyl acetates $N_C = 1 - 5$	R^nOOCMe	OOCMe	26.91	1.51	1.42	1.96				1.09
Alkylformates $N_C = 1 - 4$	R^nOOCH	OOCH	15.42	2.84	1.67	2.09				0.00

Table 3.1.10. Contributions of structural fragments of molecules to the enthalpies of hydration of monofunctional compounds at 298.15 K

Compound	Formula	Y	Y_p	$(CH)_Y$	$(CH)_s$	$(CH)_p$	$(CH)_t$	Y_s	Y_t
Alkyl acetates	R^nOOCMe	OOCMe	-31.59	-2.32	-1.35	-1.98			
Ketones	R_1COR_2	C=O	-27.62	-2.21	-1.59	-1.87		2.60	4.17
Amines	R^nNH_2	NH_2	-57.31	0.90	-1.67	-0.65			
Alkanols	ROH	OH	-33.40	-3.80	-1.71	-3.09	0.89	2.09	3.60
Methylalkanoates	R^nCOOMe	COOMe	-31.74	-2.59	-1.73	-2.02		2.32	5.39
Diols	$R(OH)_2$	OH	-27.34	-4.47	-3.24			-0.55	
Acids	R^nCOOH	COOH	-36.06	-3.99	-4.03	-3.27			

It is described by the correlation equation

$$\Delta_v H^o[(CH)_Y] = -0.99 + 1.43\Delta_v H^o[(CH)_p], \quad se = 0.23, \quad R = 0.9738. \qquad (3.1.7)$$

It was shown above that the same hydrocarbon fragments contribute differently in magnitude to the enthalpies of hydration of compounds of different homologous series. The data obtained indicate that, in general, the modeling of hydrocarbon radicals of functional organic compounds by hydrocarbon radicals has significant limitations.

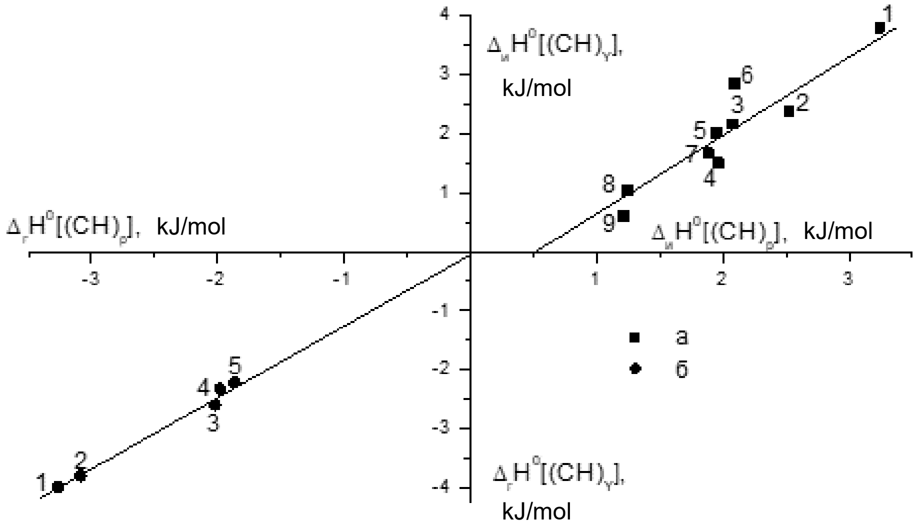


Fig. 3.1.1. Correlations between the increments of structural fragments $(CH)_p$ and $(CH)_Y$ in enthalpy of evaporation (a) and hydration (b) of compounds of some homologous series at 298.15 K: 1 - monocarboxylic acids, 2 - alkanols, 3 - methylalkanoates, 4 - alkyl acetates, 5 - ketones, 6 - alkyl formates, 7 - alkyl benzenes, 8 - ethers, 9 - alkyl nitriles

Based on the contribution values of hydrocarbon fragments, the compounds of the studied homologous series can be divided into two groups. The first group includes compounds without a hydrocarbon atom in their functional group (e.g., alkanols, esters, sulfoxides). The contributions of the fragments $(CH)_Y$ and $(CH)_p$ to the dissolution and hydration enthalpies of these compounds have large negative values. Another group includes compounds that have a carbon atom in their functional group (e.g., complex esters, ketones). For these compounds, the contributions of structural hydrocarbon fragments $(CH)_Y$ and $(CH)_p$ in $\Delta_h H^o$ and $\Delta_d H^o$ are on average 1.3 kJ/mol less negative than those of the first group compounds and hydrocarbons.

3.2. Thermochemical characteristics of dissolution and solvation of compounds of normal structure in non-aqueous media.

It is interesting to consider the following question: Are the laws of influence of the composition and structure of the dissolved substances molecules on their hydration during solvation of organic compounds molecules by non-aqueous solvents observed? Fig. 2.3.2 presents dependences of enthalpies of dissolution of alkanols in some non-aqueous solvents of different chemical nature and polarity. As it was mentioned above, in non-aqueous media, non-monotonicity of dissolution enthalpy changes in the homologous series of substances is also observed. However, a comparison with aqueous solutions (see Fig. 2.3.1) allows us to note that in organic solvents the deviations of the $\Delta_d H^o$ of the first members of the homologous series from the line formed by the $\Delta_d H^o$ of the following homologues are significantly smaller. The processing of $\Delta_d H^o$ values according to the proposed methodology led to the results presented in Tables 3.2.1 and 3.2.2.

Literature experimental data on dissolution enthalpies of compounds from works [35, 40, 45, 76] were used for calculation.

Table 3.2.1. Contributions of structural fragments of molecules to the dissolution and solvation enthalpies of alkanols in non-aqueous solvents at 298.15 K

Solvent		$(OH)_p$	$(CH)_Y$	$(CH)_s$	$(CH)_p$	*R*	*se*	Y_s	Y_t
$c\text{-}C_6H_{12}$	$\Delta_d H^o$	17.91	0.02	0.34	-0.06	0.8731	0.63		
	$\Delta_s H^o$	-12.45	-2.35	-2.04	-2.58				
$MeCHCH_2CO_3$	$\Delta_d H^o$	3.02	1.09	0.52	0.72	0.9999	0.04		-2.91 (0.60)
	$\Delta_s H^o$	-27.33	-1.29	-1.86	-1.80				2.02
Me_2SO	$\Delta_d H^o$	-5.36	1.32	0.71	0.89	1.0000	0.00		-2.23 (0.70)
	$\Delta_s H^o$	-35.72	-1.06	-1.67	-1.63				2.70
Me_2NCOH	$\Delta_d H^o$	-3.35	0.92	0.40	0.62	1.0000	0.00	-0.28 (0.13)	-1.47
	$\Delta_s H^o$	-33.71	-1.45	-1.98	-1.90			1.76	3.46
MeOH	$\Delta_d H^o$	-0.26	0.09	0.25	0.16	0.9991	0.05		
	$\Delta_s H^o$	-30.61	-2.29	-2.14	-2.36				
H_2NCOH	$\Delta_d H^o$	-1.10	0.64	0.40	0.57	0.9972	0.23		
	$\Delta_s H^o$	-31.45	-1.73	-1.98	-1.95				
$(CH_2OH)_2$	$\Delta_d H^o$	-1.07	0.49	0.52	0.52	0.9999	0.01		
	$\Delta_s H^o$	-31.42	-1.89	-1.86	-1.99				

Table 3.2.2. Contributions of structural fragments of molecules to the dissolution and solvation enthalpies of monofunctional compounds in cyclohexane at 298. K

Group	1-Alkanols $n = 1 - 5$		Ketones		Methylalkanoates	
	$\Delta_d H^o$	$\Delta_s H^o$	$\Delta_d H^o$	$\Delta_s H^o$	$\Delta_d H^o$	$\Delta_s H^o$
Y_p	17.91	-12.45	12.96	-5.52	10.1	-15.06
$(CH)_Y$	0.02	-2.35	-0.56	-2.59	-0.5	-2.67
$(CH)_s$	0.34	-2.04	-0.08	-1.98	-0.13	-2.24
$(CH)_p$	-0.06	-2.58	-0.67	-2.62	-0.57	-2.65
Y_s			1.08(0.90)	2.87	-0.13	1.32
Y_t			1.41	3.75	0.91	3.29
se	0.63		0.26		0	
R	0.8731		0.9889		1	

Evidently, in non-aqueous solvents, the differences in the solvation energetics of the isolated structural fragments of molecules of the given homologous series (see Tables 3.2.1, 3.2.2) and, consequently, the hydrocarbon radicals formed by them are less significant compared with aqueous solutions (see, e.g., Table 3.1.10). The nature of the solvent affects the ratio of contributions of non-polar fragments differently. In hydrogen-bonded solvents (methanol, formamide, ethylene glycol), all separated structural fragments make approximately equal contributions to the solvation enthalpies of 1-alkanols. In non-polar cyclohexane the bond increments $(CH)_Y$ and $(CH)_p$ of 1-alkanols, ketones, and methylalkanoates (see Table 3.2.2) in $\Delta_s H^o$ approximately 0.5 kJ/mol more exothermic than the contributions of $(CH)_s$ groups. Interestingly, a similar, only more pronounced, pattern is characteristic of aqueous solutions. In aprotonic dipolar solvents (propylene carbonate, dimethylsulfoxide, dimethylformamide), on the contrary, the $(CH)_Y$ bond contributions of 1-alkanols are approximately 0.5 kJ/mol more endothermic compared to the $(CH)_s$ and $(CH)_p$ bond contributions. The same conclusions can be made concerning the enthalpies of evaporation of organic compounds, which can be considered as enthalpies of their self-solvation.

Comparison of the contributions of hydrocarbon bonds of the same species to $\Delta_s H^o$ of compounds of different homologous series (1-alkanols, ketones, and methylalkanoates) (see Table 3.2.2) shows their energy equivalence.

Table 3.2.3 shows the contributions of structural fragments of n-alkane molecules to the enthalpies of their solvation in different solvents.

Table 3.2.3. Contributions of structural fragments of molecules to the enthalpies of solvation of n-alkanes in some solvents at 298.15 K

Solvent	p, kJ/cm^3	$(CH)_s$	$(CH)_p$
H_2O	2.298	-1.41	-3.29
H_2NCOH	1.446	-1.91	-1.85
$(CH_2OH)_2$	1.048	-2.03	-1.81
MeOH	0.859	-2.05	-1.69
c-C_6H_{12}	0.281	-2.35	-1.91
$MeCHCH_2CO_3$	0.474	-1.81	-1.10
Me_2SO	0.570	-1.59	-0.87
Me_2NCOH	0.574	-1.85	-1.41

These values are calculated using previously established regularities between enthalpies of solvation and Van der Waals molar volumes of alkanes by the following equations:

$$\Delta_s H^o(CH)_s = [b_v V_w(CH_2)]/2 = (10.23 b_v)/2, \tag{3.2.1}$$

$$\Delta_s H^o(CH)_p = [b_v V_w(CH_3) + a_v/2]/3 = (13.67 b_v + a_v/2)/3, \tag{3.2.2}$$

where the parameters $V_w(CH_2)$ = 10.23 cm^3/mol and $V_w(CH_3)$ = 13.67 cm^3/mol represent the Van der Waals molar volumes of the methylene group and methyl radical, respectively, according to Bondi [55]. The values of b_v and a_v are coefficients of the equation, the values of which for some solvents are given in Table 3.2.4 [77]:

$$\Delta_s H^o = a_v + b_v V_w. \tag{3.2.3}$$

Earlier [77] we showed that the coefficient a_v is a parameter that does not depend on the size of the alkane molecules and is determined by its structure and the properties of the solvent.

Comparison of Equations (3.2.1) and (3.2.2) proves that a_v defines the difference in enthalpies of solvation of end and chain fragments of the hydrocarbon radical. In aqueous solutions, the a_v coefficient has a maximum value (-12.2 kJ/mol), and, consequently, the end radicals (CH_3) contribute significantly more to $\Delta_s H^o$ than the chain fragments (CH_2). In non-aqueous solutions, the coefficient a_v is small, and differences in the energetics of solvation of end and chain fragments are insignificant. By transforming equation (3.2.3), it is possible to obtain the expressions for calculating the CH-bonding contributions of the tertiary carbon atom (3.2.4) and the quaternary carbon atom (3.2.5).

$$\Delta_s H^o(CH)_t = 6.78 \cdot b_v + 1.3 - a_v/2, \qquad (3.2.4)$$

$$\Delta_s H^o(C) = 3.33 \cdot b_v + 4.6 - a_v. \qquad (3.2.5)$$

Comparison of the data in Tables 3.2.2 and 3.2.3 shows that $(CH)_s$ group contributes very close in magnitude to the enthalpies of solvation of hydrocarbons and their monofunctional derivatives in non-aqueous solvents. At the same time, the CH bond contributions of primary carbon atoms of monofunctional compounds are more exothermic compared to the corresponding values of alkanes. However, the solvent properties have qualitatively the same effect on the increments of the $(CH)_s$ and $(CH)_p$ 1-alkanol groups. Both of these values increase with increasing solvent cohesion energy density in the separated groups of associated and non-associated H-bonded solvents [77].

Table 3.2.4. Molar masses (M, g/mol), Van der Waals and molar volumes (V_w and V, cm^3/mol), enthalpies of vaporization ($\Delta_v H^o$, kJ/mol), solvent cohesion energy densities (kJ/cm^3) and coefficients of equation (3.2.3) for approximation of solvation enthalpies of n-alkanes (a_v, kJ/mol, b_v, kJ/cm^3) at 298.15 K

N	Solvent	*M*	V_w	*V*	$\Delta_v H^o$	*p*	*av*	*bv*
1	Triethylamine	101.19	76.03	139.86	30.03	0.197	1.25	-0.476
2	Heptane	100.21	78.49	147.48	36.57	0.231	1.38	-0.483
3	Cyclohexane	84.16	61.38	108.78	33.03	0.281	1.07	-0.459
4	Chlorobutane	92.57	55.98	105.35	34.31	0.302	1.68	-0.458
5	Tetrachloromethane	153.82	52.29	97.09	32.43	0.308	1.37	-0.456
6	Chloroform	119.38	43.50	80.66	28.45	0.322	0.76	-0.425
7	Mesitylene	120.20		140.46			2.19	-0.477
8	Ethylacetate	88.11	54.47	98.50	35.14	0.332	1.94	-0.402
9	Toluene	92.14	59.51	106.85	37.99	0.332	1.80	-0.451
10	Hexamethylphosphotriamide	179.20	113.91	175.67	61.10	0.334	0.48	-0.412
11	Benzene	78.11	48.36	89.41	33.85	0.351	2.32	-0.424
12	Acetone	58.08	39.04	74.04	31.30	0.389	1.73	-0.380
13	Dichloroethane-1.2	98.96	44.30	79.45	34.38	0.401	3.17	-0.380
14	Dioxane-1.4	88.11	49.62	85.70	36.95	0.402	1.74	-0.387
15	Propylene carbonate	102.09	49.78	85.09	42.80	0.474	3.10	-0.354
16	Dimethylacetamide	87.12	57.04	93.02	50.23	0.513	1.99	-0.385
17	Dimethylformamide	73.10	46.77	77.41	46.89	0.562	1.45	-0.362
18	DMSO	78.13	44.71	71.30	43.09	0.570	3.31	-0.311
19	Acetonitrile	41.05	28.37	52.85	32.90	0.576	0.89	-0.331
20	Nitromethane	61.04	30.47	53.96	38.36	0.665	1.93	-0.289
21	1-Octanol	130.23	92.28	158.41	72.90	0.445	1.48	-0.468
22	1-Butanol	74.12	51.36	91.96	52.47	0.544	0.45	-0.450

N	Solvent	M	V_w	V	$\Delta_v H^o$	p	av	bv
23	1-Propanol	60.10	41.13	75.17	47.48	0.599	-0.35	-0.436
24	Ethanol	46.07	30.90	58.69	42.23	0.677	-0.23	-0.423
25	Methanol	32.04	20.67	40.74	37.48	0.859	0.79	-0.400
26	2-Propanol	60.10	41.12	76.95	45.35	0.557	-0.28	-0.427
27	t-Butanol	74.12	51.34	94.88	46.82	0.467	1.40	-0.426
28	Ethylene glycol	62.07	36.54	55.92	61.10	1.048		-0.397
29	Formamide	45.04	26.23	39.88	60.13	1.446	-0.85	-0.374
30	Water	18.02	10.43	18.07	44.01	2.298	-12.22	-0.275
31	Diethylformamide	101.13	67.23	111.4	50.32	0.429		
32	Diethylacetamide	115.18	77.50	127.3	54.11	0.406		

Summarizing the obtained results on non-aqueous solutions of organic compounds of normal structure, we can conclude that at the stage of formulating their enthalpy characteristics, it is possible to be limited to the isolation of only two structural fragments: CH-bonds in the radicals located in the first environment of the functional group and CH-bonds in the remaining radical.

3.3. Application of additive-group method to study the influence of isomerism on thermochemical solvation characteristics of organic non-electrolytes

Let us consider the problem of the influence of isomerism on the enthalpy characteristics of dissolution, solvation, and evaporation of organic substances. It should be noted that the amount of data for isomers is substantially inferior to that for substances of normal structure. In this regard, the development of additive-group method for predicting the properties of isomers is an urgent task. To solve it, we also need to study how the bond additivity scheme can be essentially used in this case. It was noted earlier that the bond additivity approximation gives the same properties for isomers [1].

One specific aspect of the proposed scheme for the separation of structural fragments of molecules is that the same CH bonds, which are included in different radicals, are energetically not equivalent. In addition, the functional groups of the same composition are also energetically not equivalent given their first environment. Thus, differences in enthalpy characteristics of isomers are accounted for, firstly, by isolating the CH bond of the tertiary carbon atom, the quaternary carbon atom in hydrocarbon radicals of molecules, secondly, by introducing corrections characterizing the difference between the contributions of the functional group bound to the primary carbon atom, and those of the functional groups bound to the secondary and tertiary carbon atoms. The above statements are reflected in equations (3.1.1) and (3.1.2). The contributions of the above structural fragments were calculated by substituting in expressions (3.1.1) and (3.1.2) the enthalpy characteristics of isomers and contributions of $(CH)_Y$, $(CH)_s$ and $(CH)_p$ bonds to $\Delta_s H^o$ of molecules of normal structure. The calculated data are given in Tables 3.1.8-3.1.10, 3.2.1 and 3.2.2. The errors of $(CH)_t$, (C), $(Y)_s$, $(Y)_t$ given in the above tables are arithmetic average errors for isomeric molecules from Tables 3.1.4 to 3.1.7, 3.2.1, and 3.2.2.

The analysis of calculation results shows that the proposed scheme of molecule division into structural fragments allows satisfactory description of enthalpy characteristics of compounds not only of normal structure, but also of their isomers.

The given data show that enthalpies of evaporation of secondary and tertiary alkanols, ketones, and methylalkanoates are less than corresponding values of primary compounds. The authors [53] explain this by steric reasons of weakening of intermolecular interactions. The obtained data lead to a conclusion that the presence of a functional group connected with a secondary carbon atom makes a constant contribution to the enthalpies of alkanols and ketones evaporation. This is evidenced by the small (< 0.5 kJ/mol) errors of the $(Y)_s$ values (see Table 3.1.9). For compounds of other homologous series, it is not possible to estimate the constancy of $(Y)_s$ and $(Y)_t$ contributions, since data are available only for one representative of the series. It should be noted that for enthalpies of evaporation of liquids, the negative correction to the group contribution corresponds to the sign of the difference of enthalpies of evaporation of secondary and primary compounds. The correction value is also close to the difference of enthalpies of evaporation. This is due to the fact that the contributions of hydrocarbon fragments in the enthalpies of evaporation have close values. Therefore, despite the strong differences in the group composition of isomers (see Tables 3.1.4-3.1.7), the total contributions of hydrocarbon radicals of a compound of normal structure and its isomer containing a secondary carbon atom will be approximately equal. Similar relations are observed for difference of enthalpies of evaporation of tertiary and primary compounds and correction $(Y)_t$. Thus, a decrease in enthalpy of evaporation of isomers containing secondary and tertiary functional groups can be caused not only by steric hindrances to intermolecular interaction, but also by a significant change in the affinity (ability) of secondary and tertiary functional groups to specific interactions. The decrease of the ability of OH-groups to specific intermolecular interaction is confirmed, in particular, by the sharp decrease of electron acceptor properties (E_T^N) in the series 1-butanol (0.60) – 2-butanol (0.50) – tert-butanol (0.41) [50]. The presence of a tertiary carbon atom in molecules also leads to a decrease in the enthalpy of vaporization of substances. This is illustrated, for example, by the data for alkanols (see Table 3.1.4) and alkanes (see Table 3.1.3). The contribution of the $(CH)_t$ group has a negative value (see Table 3.1.9).

The enthalpies of solvation of molecules containing secondary and tertiary functional groups in non-aqueous solvents are less exothermic compared to molecules of primary functional hydrocarbon derivatives. This pattern is reflected, for example, in the solvation of alkanol molecules by N,N-dimethylformamide (see Table 3.2.3). By analogy with the enthalpy of evaporation, the weakening of solvation energy can probably be explained by the steric factor and the smaller electron acceptor properties of secondary and tertiary hydroxyl groups. The latter reason is important considering that Me_2NCOH has a high electron-donating capacity. Fig. 3.3.1 presents correlations between enthalpies of solvation, contributions of functional groups in $\Delta_s H^o$, and electron acceptor properties of butanol isomers.

The hydration enthalpies of isomers change differently. Fig. 3.3.1 shows that the hydration enthalpies become more exothermic from Bu^nOH to Bu^2OH and Bu^tOH. However, the change in the contributions of hydroxyl groups to the hydration enthalpies is similar to the change in the contributions of these groups to the enthalpies of evaporation and solvation in N,N-dimethylformamide. That is, the contribution of specific solvation due to the donor-acceptor interaction of the polar group with the solvent contributes to weaker hydration of Bu^2OH and Bu^tOH compared to Bu^nOH. It follows that the observed increase in exothermicity of hydration of Bu^2OH and Bu^tOH molecules is due to the contribution of non-specific hydration or hydration of hydrocarbon radicals. The data presented in Table 3.1.4 show that at transition from normal butyl alcohol to secondary and tertiary alcohols, group composition of molecules strongly changes towards increase of $(CH)_Y$ fragments. The contributions of these groups to the $\Delta_h H^o$ of the molecules have the maximum exothermic values among the isolated hydrocarbon fragments.

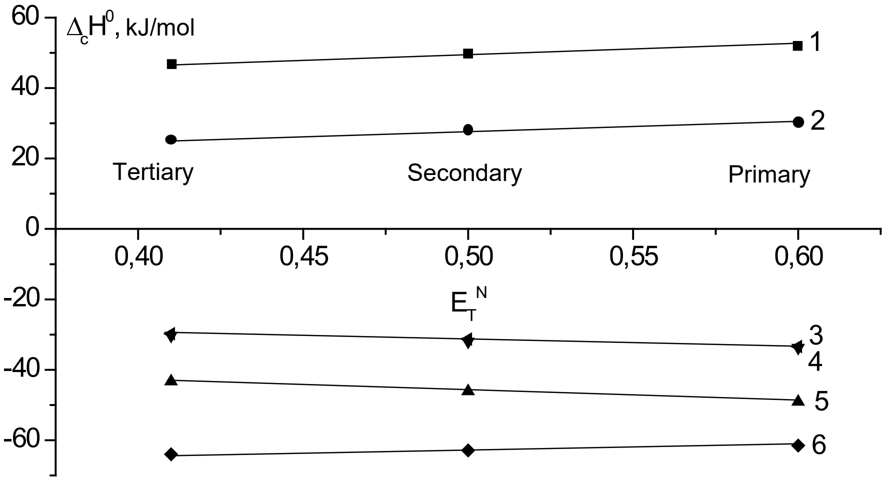


Fig. 3.3.1. Dependence of enthalpies of evaporation, hydration and solvation in N,N-dimethylformamide of primary, secondary and tertiary butanols and contributions of their functional groups on electron acceptivity of alcohols: 1, 5, 6 - molecular enthalpy characteristics; 2, 3, 4 - group contributions to the enthalpy characteristics; 1,2 - $\Delta_v H^o$, 3, 6 - $\Delta_h H^o$, 4, 5 - $\Delta_s H^o$ in Me_2NCOH

Corrections to the enthalpies of hydration by a secondary functional group (see Table 3.1.10) have close values for substances of different homologous series (ketones, methylalkanoates, alkanols). However, it can be noted that the isomerism of molecules due to the content of functional groups associated with secondary and tertiary carbon atoms is less reflected in the hydration enthalpy of alkanols. Corrections to the hydration contribution of $(OH)_P$ for them are minimal compared to methylalkanoates and ketones.

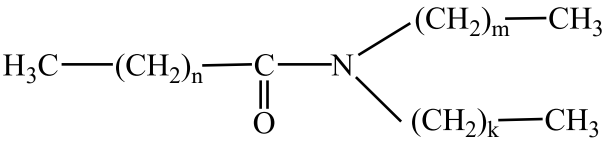
The net effect of the influence of isomerism on the enthalpies of evaporation and hydration is reflected in the values of corrections to the contribution of primary functional groups to the enthalpies of dissolution of monofunctional compounds in water. According to Table 3.1.8, these corrections can have different signs.

The obtained values of contributions of structural fragments can be used for prediction of enthalpies of dissolution and solvation isomers of alkanols, diols, ketones, and methylalkanoates in water and non-aqueous solvents.

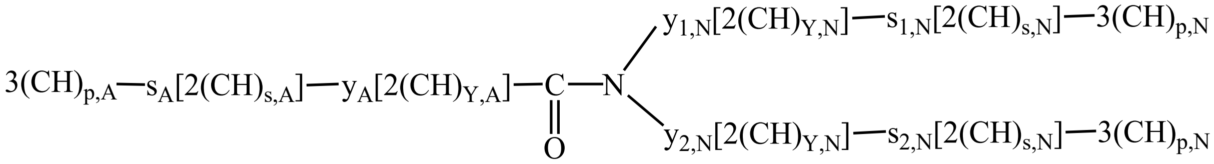
3.4. Enthalpic characteristics of dissolution and hydration of amides

Now let us consider the enthalpic characteristics of dissolution, solvation, and evaporation of compounds formed from fragments of molecules of different homologous series. Such compounds are sometimes called heterofunctional because of the noted peculiarity of their structure. In this section we discuss some properties of aqueous amide solutions. The interest in the study of amide solutions in water and mixed solvents is mainly because they can be used for modeling fragments of biomolecules.

From the dependence of the contributions of structural fragments on the nature of organic compounds it follows that in the molecules of organic compounds formed from fragments of molecules of different homologous series, the corresponding structural elements should be distinguished. Let us illustrate this with the example of aqueous amide solutions. The general formula of tertiary amides of monocarboxylic acids containing hydrocarbon radicals of normal structure is given in the following scheme:



Below is the same formula with highlighted structural fragments in monocarboxylic acid amide molecules.



They are the CH bonds of primary and secondary carbon atoms and the CH bonds in the radicals located in the first environment of the functional group. The O=C-N fragment has been identified as such a group. It should be emphasized that the separated CH bonds located in acyl [$(CH)_{p,A}$, $(CH)_{s,A}$, $(CH)_A$] and in N-substituents [$(CH)_{p,N}$, $(CH)_{s,N}$, $(CH)_N$] are not equivalent, as it is considered in the works of Wood and Savage [65] and other authors [66].

Data available in literature on enthalpic characteristics of dissolution of liquid amides of methane, ethane, propane, butane, and pentanoic acids of various degrees of N-substitution [27, 78] are given in Table 3.4.1. In accordance with the above formulas, data are presented only for primary, secondary, and tertiary amides in which the substituents at the nitrogen atoms are hydrocarbon radicals of n-alkanes.

Based on the proposed scheme, eight structural fragments have been identified for the given set of amides: six hydrocarbon bonds, NH bond, and functional amide group N-C=O. The type and number of structural fragments are given in Table 3.4.1. The peculiarity of distinguishing structural fragments in amide molecules is that the carbon atom refers to both the amide group and the hydrocarbon radical of the acid residue. Therefore, in formamide molecules, one CH bond in the first surroundings of the functional group belonging to the acyl is prominent. For amides of acetic, propionic, etc. of acids, the carbon atom of the carboxylic group is also included in the acyl radical, although this atom does not give CH structural fragments. As a result of this approach, the maximum number of $(CH)_A$ fragments for a given series of compounds is three and belongs to the acidic residue of acetic acid. The structural fragments in N-substituents were separated similarly to monofunctional compounds. It should also be noted that the isolation of CH bonds belonging to the first environment of the functional group has priority.

Table 3.4.1. Standard enthalpies of dissolution of monocarboxylic acid amides in water at 298.15 K, type and amount of separated structural fragments in the amide molecules and their contributions to the dissolution enthalpies. Regression parameters *se* = 0.41 kJ/mol, R = 0.9994

Amide	$\Delta_d H^o$	$\Delta_h H^o$	$(CH)_{p,N}$	$(CH)_{s,N}$	$(CH)_N$	$(CH)_{p,A}$	$(CH)_{s,A}$	$(CH)_A$	**(NH)**
H_2NCOH	1.97	-58.2	0	0	0	0	0	1	2
MeHNCOH	-7.00		0	0	3	0	0	1	1
Me_2NCOH	-15.22	-62.1	0	0	6	0	0	1	0
Et_2NCOH	-17.97	-68.3	0	0	10	0	0	1	0
MeHNCOMe	-13.36		0	0	3	0	0	3	1
$Pr^nHNCOMe$	-15.76		3	0	4	0	0	3	1
$Bu^nHNCOMe$	-14.72		3	2	4	0	0	3	1
Me_2NCOMe	-21.42	-71.7	0	0	6	0	0	3	0
Et_2NCOMe	-24.08	-78.2	0	0	10	0	0	3	0
MeHNCOEt	-14.87		0	0	3	3	0	2	1
Me_2NCOEt	-22.34		0	0	6	3	0	2	0
$MeHNCOPr^n$	-16.02		0	0	3	3	2	2	1
$MeHNCOBu^n$	-15.02		0	0	3	3	4	2	1
EtHNCOH			0	0	5	0	0	1	1
EtHNCOMe			0	0	5	0	0	3	1
EtMeNCOH			0	0	8	0	0	1	1
EtMeNCOMe			0	0	8	0	0	3	1
Groups contributions	$\Delta_d H^o(Y) = 7.88$		-0.64	0.52	-0.68	-1.49	-0.15	-3.18	6.31

Based on formula (1.3), the enthalpies of amides dissolution in water can be expressed by the relation

$$\Delta H^o = \Delta H^o(Y) + h\Delta H^o(NH) + p\Delta H^o(CH)_{p,A} + s\Delta H^o(CH)_{s,A} + a\Delta H^o(CH)_A + \\ + p_N\Delta H^o(CH)_{p,N} + s_N\Delta H^o(CH)_{s,N} + n\Delta H^o(CH)_N, \qquad (3.4.1)$$

where parameters h, p, s, a, p_N, s_N, n represent the number of structural fragments of a particular type and are determined based on the composition and structure of the amide molecules. Their values are given in Table 3.4.1.

The results of regression calculation of structural fragment contributions to the enthalpies of amides dissolution in water are presented in Table 3.4.1. As before, the functional group increment is calculated as a free term in the regression equation. Small errors of description indicate that the proposed model adequately describes the experimental data for primary, secondary, and tertiary amides of various degrees of N-substitution, whereas the use of the concept of equivalent methylene groups [65] did not provide such an opportunity. In [67], when studying the influence of the composition and structure of amides on their enthalpy characteristics and coefficients of pairwise interactions in aqueous solutions, we had to distinguish a group of tertiary amides on the one hand, and a group of primary and secondary amides on the other hand. As can be seen, our proposed approach has greater generality and the results obtained allow us to calculate with high accuracy the enthalpy characteristics of dissolution in water of a number of unexplored amides of monocarboxylic acids with different degrees of N-substitution (for example, amides containing different nitrogen atom-bound radicals). The obtained results allow estimating enthalpies of dissolution in H_2O of some amide isomers from Table 3.4.1. Thus the calculation for N-methylisobutyramide ($h = 1, a = 1, p_N = 6, n = 3, p = s = s_N = 0$) gives $\Delta_d H^o$ = -15.7 kJ/mol which agrees well with the experimental value equal to -15.8 kJ/mol [27]. However, for N-isopropylacetamide ($h = 1$, $a = 3$, $n = 7$, $p = p_N = s = s_N = 0$) the calculated (-15.9 kJ/mol) and experimental (-17.2 kJ/mol) [27] values differ significantly.

Unfortunately, there is no reliable calorimetric data on the enthalpies of evaporation of propanoic, butane, and pentanoic acid amides shown in Table 3.4.1 in the literature. This makes it impossible to discuss their hydration characteristics. Therefore, further analysis will be performed for N-methyl- and N-ethyl-substituted amides of formic and acetic acids. One important feature of their molecular structure from the point of view of the scheme of separation of structural fragments used in this work is the presence of only hydrocarbon fragments included in the first environment of the functional group. Therefore, the enthalpic characteristics of dissolution, solvation, and evaporation can be expressed by the relation

$$\Delta H^o = \Delta H^o(Y) + h\Delta H^o(NH) + a\Delta H^o(CH)_A + n\Delta H^o(CH)_N. \qquad (3.4.2)$$

Table 3.4.2 presents the results of calculation of the contributions of the isolated groups to the enthalpy properties of dissolution, evaporation, and hydration of amides.

It can be seen that the experimental values of $\Delta_d H^o$ and $\Delta_v H^o$ are perfectly described within the framework of the used scheme of separation of structural fragments. The group contributions to the enthalpies of hydration of amides were calculated using Equation (3.1.5) from the corresponding contributions to the enthalpies of dissolution and evaporation from Table 3.4.2.

Analysis of the obtained values shows that changes in the composition and structure of the hydrocarbon radical of the acid residue have a significantly greater impact on the enthalpy properties of amides.

Table 3.4.2. Contributions of structural fragments to the enthalpies of dissolution in water and evaporation of primary and tertiary amides of formic and acetic acids and hexamethylphosphotriamide at 298.15 K

	$(CH)_N$		**$(CH)_A$**		**(NH)**		**(Y)**		**N_3PO**	***R***	***se***
	$\Delta_d H^o$	*se*	$\Delta_d H^o$	*se*	$\Delta_d H^o$	*se*	$\Delta_d H^o$	*se*			
$\Delta_d H^o$	-0.68	0.01	-3.08	0.02	6.58	0.05	-8.10	0.05	-37.28	0.9999	0.05
$\Delta_v H^o$	0.91	0.06	1.78	0.11	9.42	0.26	39.51	0.52	44.65	0.9998	0.23
$\Delta_h H^o$	-1.59		-4.86		-2.84		-47.61		-81.93		
DN	1.09	0.01	0.57	0.02	7.95	0.06	19.53	0.11	19.2	0.9999	0.05

The contribution of the $(CH)_A$ in $\Delta_h H^o$ is 200% larger than that of the $(CH)_N$ group. Comparison of the values for heterofunctional and monofunctional compounds given in Tables 3.4.2 and 3.1.10 shows that the magnitude of the contribution of the $(CH)_A$ bond in $\Delta_h H^o$ of amides does not correspond to that of the $(CH)_Y$ bond included in the immediate environment of the carboxylic group of carboxylic acids. There is also no quantitative correspondence between the contribution of the $(CH)_N$ bond in the $\Delta_h H^o$ of the amides with that of the bonds belonging to the nearest environment of the functional group of the primary amines. However, it may be noted that the contribution of $(CH)_Y$bonds to the $\Delta_g H^o$ of carboxylic acids is substantially more exothermal than the contribution of $(CH)_Y$ groups to the $\Delta_g H^o$ of primary amines.

The increments of the isolated hydrocarbon bonds in the enthalpies of amide evaporation differ much less than their contributions to the enthalpies of hydration. Since the enthalpy of dissolution is the sum of enthalpies of solvation and evaporation of the dissolved substance, the reason for the nonmonotonicity of enthalpy properties of dissolution in the amide homologous series lies in the solute-solvent interactions, rather than in the interparticle interactions in the condensed dissolved substance. Earlier it was shown that it is common for substances of most classes of organic compounds. It is also relevant that the largest differences in the contributions of non-polar groups occur in aqueous solution. This effect may be interpreted as follows. The change in the solvent-solvent interaction caused by the introduction of solute molecules contributes to the hydration enthalpies of the structural fragments. This contribution has a maximum value in aqueous solutions.

Let us consider the contributions of polar groups to the enthalpies of hydration of formic and acetic acid amides. It can be seen that the increment of the NH group in $\Delta_h H^o$ exceeds the contribution of this group to the intermolecular interaction in pure liquid amides ($\Delta_v H^o$). This is the main reason of endothermicity of primary amides dissolution in water. Positive $\Delta_d H^o$ values are also characteristic of primary aromatic amines. The $\Delta_d H^o$ of aniline in H_2O is 1.82 kJ/mol [79], 1.88 kJ/mol [80]. It can be assumed that the endothermicity of the dissolution of primary amines is due to the destructive effect of their electron acceptor groups on water. The nitro group probably has a similar effect. $\Delta_p H^o$ of nitromethane (CH_3NO_2) in water is 3.23 kJ/mol [81]. The conclusion about destabilization of aqueous environment around NH_2-groups of formamide and urea was made by the authors [82, 83] as a result of study of dielectric permittivity of their aqueous solutions and absorption of electromagnetic radiation of millimeter range of wavelengths.

The amide group makes a significant exothermic contribution to the enthalpies of hydration and dissolution of amides (see Table 3.4.2) due to the ability of donor-acceptor interaction with the solvent. Within the framework of the proposed model for the decomposition of enthalpy characteristics of solvation into contributions, the increment of the amide group is a constant value for all the studied amides. However, it is known that the donor numbers of the amides due to the presence of this group are different. The donor number (DN) represents the enthalpy of the interaction (kcal/mol) of the amide with $SbCl_5$ in 1,2-dichloroethane. DN for formamide, N,N-dimethylformamide, N,N-diethylformamide, N,N-dimethylacetamide, N,N-diethylacetamide, and hexamethylphosphotriamide are 36, 26.6, 31.0, 27.8, 32.1, and 38.8 kcal/mol [50]. It can be seen that the change in the donor numbers does not correspond to the change in the hydration enthalpies even for tertiary amides. Thus, changes in the composition and structure of the hydrocarbon radical have different effects on the thermodynamic characteristics of hydration and interaction of amides with $SbCl_5$. The interactions of amides with $SbCl_5$ are probably influenced by their solvation with 1,2-dichloroethane.

Formally, the donor numbers of amide molecules can also be described by equation (3.4.2). The contributions of the selected structural fragments and regression parameters are presented in Table 3.4.2. It can be seen that the used scheme for the separation of structural fragments allows adequate description of the donor numbers of the amides. As a result, it is possible to predict *DN*s for other compounds with high accuracy. Using the DN contribution values of the selected groups from Table 3.4.2 and the group composition of N-methylformamide, N-ethylformamide, N-methylacetamide, N-ethylacetamide N-methyl-N-ethylformamide and N-methyl-N-ethylacetamide molecules from Table 3.4.1, their donor numbers were calculated to be 31.3, 32.5, 33.5, 34.6, 36.8 and 37.9 kcal/mol respectively.

Assuming energy equivalence of $(CH)_N$ fragments in tertiary amides of formic and acetic acids and in hexamethylphosphotriamide, we calculated the contribution of the N_3PO group to the donor number of $[(CH_3)_2N]_3PO$. The value of this contribution was 19.2 kcal/mol. It can be seen that the obtained value is approximately equal to the corresponding contribution of the NCO amide group (19.5 kcal/mol). The obtained result seems to confirm the conclusions of the authors [84, 85] that the negative charge centers in amides of carboxylic acids and hexamethylphosphotriamide are oxygen atoms.

Important properties of interparticle interactions in solution include pairwise interaction coefficients (enthalpic - h_{xx}, entropic - s_{xx} and Gibbs coefficients - g_{xx}). They reflect the total effect of the overlapping of the solvation spheres of molecules and provide quantitative information on the interaction energy of dissolved non-electrolytes. Based on the signs and ratios of pairing factor values in aqueous solution (g_{xx}, h_{xx}, s_{xx}), all non-electrolytes are classified into hydrophobic ($g_{xx}< 0$, $Ts_{xx}>h_{xx}> 0$), hydrophilic urea-like ($g_{xx}< 0$, $h_{xx}<Ts_{xx}< 0$), and hydrophilic sucrose-like substances ($g_{xx}> 0$, $h_{xx}>Ts_{xx}> 0$) [36, 86]. Secondary and tertiary amides of monocarboxylic acids are classified as hydrophobic non-electrolytes, formamide - as hydrophilic substances [86]. The enthalpy coefficients of pairwise interactions of amides in water were determined by the authors [65, 67, 87, 88, 89] and for H_2NCOH, MeHNCOH, EtHNCOH, Me_2NCOH, Et_2NCOH, H_2NCOMe, MeHNCOMe, Me_2NCOMe, Et_2NCOMe, Me_2NCOEt were -115.0, -272.0, -350.0, -737.0, -1767.0, 12.0, -286.0, -1081.0, -2355.0, -1797.0 J kg/mol^2 respectively. The h_{xx} values of N-mono- and disubstituted amides are positive and increase with the size of the hydrocarbon radical of the molecules. Positive values of h_{xx} are caused by the endothermic interaction of hydrated hydrocarbon radicals and polar groups. According to the authors [67, 86], the endothermicity of this process is due to the dehydration of hydrocarbon radicals at the convergence of different-type solvate shells of interacting molecules in the aqueous medium.

Using regression analysis of the data in Table 3.4.1 and h_{xx} values based on Equation 3.4.1, we have determined the contributions of selected polar and non-polar groups to the enthalpy coefficients of pairwise amide-amide interactions in aqueous solution at 298.15 K. The parameters for acetamide, N-methylacetamide and N-ethylformamide, which fall out of most of the dependencies, were excluded from the available data set [78]. The values of group contributions and regression parameters are presented in Table 3.4.3.

Table 3.4.3. Contributions of structural fragments to the enthalpy coefficients of amide-amide pair interactions in water at 298.15 K

$(CH)_N$	**$(CH)_A$**	**$(CH)_{Ap}$**	**(NH)**	**(Y)**	***se***	***R***
288.4	233.7	296.5	469.2	-1290	86	0.9985

The results confirm the conclusions drawn in [67, 86] about the positive contribution of hydrocarbon radicals to the h_{xx} values. It is also seen that the contribution values of the $(CH)_N$, $(CH)_A$, and $(CH)_{Ap}$ groups are close to each other. A consequence of this is the possibility of using the concept of equivalent methylene groups [65, 67] to analyze the effect of the composition and structure of amide molecules on their enthalpy coefficients of pairwise interactions

$$h_{xx} = n_{CH_2} H_{CH_2\text{-}Y} + H_{Y\text{-}Y} \tag{3.4.3}$$

In formula (3.4.3), n_{CH_2} is the number of equivalent methylene groups in the amide molecule (CH groups were considered equivalent to one-half methylene group, radical CH_3 to one-half methylene groups); $H_{CH_2\text{-}Y}$ is the contribution from the interaction of the methylene group with the amide molecule; $H_{Y\text{-}Y}$ is the average contribution from the interaction of a polar group with an amide molecule in aqueous solution.

Comparison of expressions (3.4.1) and (3.4.3) shows that the latter does not take into account the contribution of the NH group. A consequence of this is the necessity to divide the amides into groups depending on the degree of N-substitution, namely, to single out a group of tertiary amides in which the NH group is absent. The NH group makes a significant positive contribution to the h_{xx} values. The positive value of the contribution of this group may be due to destabilization of its aquatic environment.

The contributions of non-polar groups to the enthalpies of dissolution of amides in water (see Table 3.4.1), in contrast to their contributions to the enthalpy coefficients, are significantly different. This seems to be due to the fact that the enthalpy coefficients of pairwise interactions are calculated from the concentration dependences of enthalpy transfer of substances. That is, changes in the composition and structure of the hydrocarbon radicals of the acid residue and N-substituents have a close effect on the enthalpies of amide transfer. A similar effect is observed for the enthalpy of transfer of amides from water to mixed solvents and, consequently, for the enthalpy coefficients of paired heterotactic amide-non-electrolyte interactions [78].

In conclusion, we would like to note the main results.

We propose the additive-group scheme of enthalpy characteristics decomposition of organic non-electrolyte solutions into contributions. Functional groups and CH bonds in hydrocarbon radicals are distinguished as structural fragments of molecules, and the distinguished CH bonds in hydrocarbon radicals are not equivalent. The paper presents a three-type classification of hydrocarbon bonds: end and chain CH bonds, as well as CH bonds included in the first environment of the functional group. The first environment of a functional group includes structural fragments directly related to the functional group and separated from it by one carbon atom. In the molecules of organic compounds formed from fragments of molecules of different homologous series the corresponding structural elements are highlighted. The proposed additive scheme allowed us to take into account the specific aspects of the structure of the first members of the homologous series, compounds of normal structure and their isomers.

The terminal structural groups (CH bonds of primary carbon atoms and, correspondingly, methyl radicals) are hydrated much more exothermally than the chain ones. The ratio of enthalpies of hydration of methylene and methyl radicals in alkanes is approximately 1 : 3, not 1 : 1.5, as one would expect based on the number of CH bonds.

The contributions of hydrocarbon bonds to the solvation energetics of compounds belonging to different homologous series differ significantly. The largest differences are characteristic of CH-bonds of the first environment of the functional group, the smallest differences are characteristic of CH-bonds of chain methylene groups.

The paper contains the results of the research into contributions of the isolated amide structural fragments to the hydration enthalpies, enthalpy coefficients of pair interactions, and donor numbers of the amides. It was shown that an increase in the size of the acyl hydrocarbon radical makes a significantly greater contribution to the enhancement of amide solvation as compared to the change in radicals in N-substituents. Notably, it is possible to use the additive method to describe the thermodynamic properties of primary, secondary, and tertiary amide solutions from a unified position.

The contributions of the isolated hydrocarbon elements to the enthalpy characteristics of solutions of organic compounds in non-aqueous media differ significantly less in comparison with aqueous solutions. It is possible to limit the decomposition of enthalpy characteristics of non-aqueous solutions of organic non-electrolytes to isolation of only two structural fragments: CH-bonds in the radicals located in the first environment of the functional group and CH-bonds in the remaining radical.

4. Application of a new additive scheme for the analysis and systematization of thermodynamic characteristics of aqueous solutions

In this section we will consider the applicability of the proposed approach [77] for the analysis and systematization of other thermodynamic characteristics of aqueous solutions. Let us consider thermodynamic characteristics of single-atom alcohols, as it has been made in [90, 91]. For this class of organic compounds, one of the largest databases is available in the literature.

Table 4.1 shows the type and number of structural fragments singled out according to the scheme used in molecules of a number of one-atom alcohols for which volumetric properties, heat capacity, and entropic characteristics of their extremely dilute aqueous solutions are known.

The mentioned thermodynamic characteristics of aqueous solutions of alkanols were described by the equation similar to formula (3.1.2):

$$\Delta P^{o} = \Delta P^{o}(\mathrm{Y}_{p}) + \delta P^{o}(\mathrm{Y}_{s}) + \delta P^{o}(\mathrm{Y}_{t}) + y\Delta P^{o}(\mathrm{CH})_{\mathrm{Y}} + p\Delta P^{o}(\mathrm{CH})_{p} + s\Delta P^{o}(\mathrm{CH})_{s} + t\Delta P^{o}(\mathrm{CH})_{t} + h\Delta P^{o}(\mathrm{C}), \tag{4.1}$$

where ΔP^{o} is a physicochemical or thermodynamic property; $\Delta P^{o}(\mathrm{CH})_{\mathrm{Y}}$ are increments of CH bonds in hydrocarbon radicals included in the first environment of the functional group; $\Delta P^{o}(\mathrm{CH})_{p}$, $\Delta P^{o}(\mathrm{CH})_{s}$, $\Delta P^{o}(\mathrm{CH})_{t}$, and $\Delta P^{o}(\mathrm{C})$ are contributions of structural fragments of hydrocarbon radicals separated from the functional group by more than two carbon atoms; *y, p, s, t*, and *h* - number of selected fragments; $\Delta P^{o}(\mathrm{Y}_{p})$ is the contribution of the functional group bound to the primary carbon atom; $\delta P^{o}(\mathrm{Y}_{s})$ and $\delta P^{o}(\mathrm{Y}_{t})$ are corrections to account for differences in the enthalpies of solvation of functional groups bound to secondary and tertiary carbon atoms with respect to the functional group bound to the primary carbon atom.

Table 4.1 (last row) presents the calculated group contributions to the limiting partial molar volumes ($\overline{V}_2^{\infty}$) of alkanols and regression parameters. The literature data on $\overline{V}_2^{\infty}$ from the papers [92, 93, 94, 95, 96] were used for the calculation.

Table 4.1. The limiting partial molar volumes of alkanols in aqueous solution at 298.15 K, the type and number of structural fragments isolated in their molecules and the group contributions to the bulk properties

No.	**Alcohol**	$\overline{V}_2^{\infty}$		**$(\mathrm{CH})_{\mathrm{Y}}$**	**$(\mathrm{CH})_{s}$**	**$(\mathrm{CH})_{p}$**	**$(\mathrm{CH})_{t}$**	**$(\mathrm{OH})_{s}$**	**$(\mathrm{OH})_{t}$**	**$(\mathrm{OH})_{p}$**
		Experimental	Calculation							
1	MeOH	38.17		3	0	0	0	0	0	
2	EtOH	55.2		5	0	0	0	0	0	
3	$\mathrm{Pe}^{n}\mathrm{OH}$	102.6		4	4	3	0	0	0	
4	$\mathrm{Bu}^{i}\mathrm{OH}$	86.72		2	0	6	1	0	0	
5	$\mathrm{Bu}^{t}\mathrm{OH}$	87.8		9	0	0	0	0	1	
6	$\mathrm{Pe}^{2}\mathrm{OH}$	102.6		6	2	3	0	1	0	
7	$\mathrm{Pe}^{3}\mathrm{OH}$	101.2		5	0	6	0	1	0	
8	$\mathrm{Pr}^{n}\mathrm{OH}$	70.74	70.06	4	0	3	0	0	0	
9	$\mathrm{Bu}^{n}\mathrm{OH}$	86.67	86.30	4	2	3	0	0	0	
10	$\mathrm{Hex}^{n}\mathrm{OH}$	118.7	118.80	4	6	3	0	0	0	
11	$\mathrm{Pr}^{2}\mathrm{OH}$	71.93	71.45	7	0	0	0	1	0	
12	$\mathrm{Bu}^{2}\mathrm{OH}$	86.57	86.30	6	0	3	0	1	0	
13	$\mathrm{Pe}^{t}\mathrm{OH}$	101.9	102.66	8	0	3	0	0	1	
14	$\mathrm{Hex}^{2}\mathrm{OH}$	118.5	118.80	6	4	3	0	1	0	
15	$\mathrm{Hex}^{3}\mathrm{OH}$	117.1	117.41	5	2	6	0	1	0	
16	$\mathrm{Hep}^{2}\mathrm{OH}$	134.4	135.04	6	6	3	0	1	0	
17	$\mathrm{Hep}^{3}\mathrm{OH}$	133.3	133.65	5	4	6	0	1	0	
18	$\mathrm{Hep}^{4}\mathrm{OH}$	133.2	133.65	5	4	6	0	1	0	
Contributions (base set)				8.51	8.12	7.79	10.3	-0.78	-1.46	12.6
Contributions (*se* = 0.25, *R* = 0.9999)				8.8	8.01	7.84	10.3	-1.59	-3.46	11.8

It can be seen that the experimental data are well described within the proposed approach. It is possible to differentiate compounds rather finely in the composition and structure of their molecules by singling out hydrocarbon bonds in radicals directly connected with functional group and separated from it through one carbon atom as structural fragments included in the first environment of functional group. As it was already noted in the discussion of enthalpy characteristics, such separation of structural fragments is especially effective in the decomposition of the properties of aqueous solutions and is related to its properties and structural peculiarities. The specific mechanism of the observed phenomenon is not yet clear. The equality of group contributions reflects their energy equivalence, which in turn indicates approximately the same geometric configuration. Since the decomposition of solution properties essentially analyzes intermolecular interactions between the dissolved substance and the solvent, as well as the solvent-solvent interactions caused by them, the energy equivalence and close geometric configuration of groups is likely to let us conclude that the solvate environment is approximately the same.

The approach used makes it possible to take into account the specific aspects of the structure of the first two members of the homologous series, the point of which is that all of their hydrocarbon bonds are energetically equivalent. As a result, the properties of the first members of the homologous series deviate from the line of subsequent homologs. This effect is also evident in the discussed bulk properties (see Table 4.1).

The data presented in Table 4.1 show that the used scheme of separation of structural elements allows to distinguish the structure of isomers rather finely. The latter is fully consistent with a change in their properties. Thus, Table 4.1 shows that group composition of 2-pentanol (2-hexanol) essentially differs from composition of 3-pentanol (3-hexanol). And, as one would expect, the limiting partial molar volumes of 2-alkanols and 3-alkanols differ markedly. On the other hand, the group composition of 3-heptanol does not differ from that of 4-heptanol according to the applied scheme. Accordingly, the experimental and calculated bulk properties of the above isomers are practically equal (see Table 4.1).

The data on volumetric properties help to illustrate the high predictive power of the additive-group method used. Let us restrict the basic data set for determining the contributions of selected fragments to the properties of the first seven compounds from Table 3.5.1 and calculate the contributions of structural fragments from them. The results are shown in the second to last row of Table 4.1. Now, using these results, let us calculate the values $\overline{V}_2^{\infty}$ for the remaining eleven compounds. It can be seen that there is good agreement between the calculated and experimental values. The arithmetic mean error of the calculation is 0.43 cm^3/mol.

Using equation (4.1), data on the type and number of structural fragments of alkanol molecules from Table 4.1, and experimental data on molar volumes [50], we have determined limiting partial heat capacities of alkanols in aqueous solution [24, 97, 98], dissolution entropies [24, 73], limiting activity coefficients [24, 73, 99], group contributions to the specified characteristics. The calculation results are presented in Table 4.2.

It is seen that these thermodynamic properties of pure liquids and solutions are successfully decomposed within the proposed additivity scheme as well. The errors of description are comparable with experimental errors, which are for $\overline{V}_2^{\infty}$ - 0.1 cm^3/mol, $\overline{C}_{p_2}^{\infty}$ - 3–6 J/(mol·K), $\Delta_p S^{o}$ - 1 J/(mol·K).

Table 4.2. Group contributions to molar volumes (V_m), marginal partial molar heat capacities ($\overline{C}^{\infty}_{p_2}$), marginal activity coefficients (γ_2^{∞}) in aqueous solution, and dissolution entropies ($\Delta_p S^o$) in water of alkanols at 298.15 K

Property	**(OH)**$_p$	**(CH)**$_Y$	**(CH)**$_s$	**(CH)**$_p$	**(CH)**$_t$	**(OH)**$_s$	**(OH)**$_t$	***se***	**Compounds**
V_m	13.61	9.03	8.28	8.60	7.89	-0.59	0.03	0.55	1-5, 8-10, Pe^{i}OH, Oc^{n}OH
$\overline{C}^{\infty}_{p_2}$	-6.70	54.10	51.84	45.27	71.25	-2.72	-9.20	12.00	1-5, 7-9, 11, 12, Pe^{i}OH, Pe^{neo}OH
$\Delta_p S^o$	-9.87	-6.88	-5.06	-5.66		-2.51	-5.24	1.51	1,2,5,7-9,11 12, 15, 18
γ_2^{∞}	1.40	0.09	12.33	4.70	17.34	8.21	10.12	4.15	1-5, 7-9, 11, 12, 15, 18

Please note. Units of measure of $\overline{C}^{\infty}_{p_2}$ v$\Delta_p S^o$ is J/(mol·K). The last column contains numbers of compounds from Table 4.1, the properties of which were used in the regression analysis. The correlation coefficient of approximation for all is always higher than 0.996.

Thus, the applicability of the used additive scheme for the analysis and interpretation of various thermodynamic characteristics of solutions of monatomic alcohols is shown on the example of volumetric properties, heat capacity, and entropic characteristics of aqueous solutions. We also note the high predictive ability of the used additive-group method.

5. Use of additive-group method for analysis, systematization, and prediction of flash point of liquids

There is a wide range of fluids used in domestic and industrial applications. The vast majority of them are combustible. The most important indicators of the fire hazard of organic solvents are those that determine the conditions of formation of a combustible medium and the rate of the combustion process. For liquids, these include the flash point temperature (t_{fp}), ignition temperature, and flame propagation temperature limits. The main sources of fire hazard indicators for simple substances and chemical compounds are reference books [100, 101, 102, 103].

However, for many compounds, experimental data on fire hazard indicators are not available. In this case, it is advisable to use calculation methods to determine the fire and explosion hazard of substances. It should be noted that even in the specified reference books [100-103], there are calculated values of fire hazard indicators for some substances.

GOST [104] and Manual [105] outline a number of calculation methods based on correlations of flash point with physico-chemical properties (e.g. boiling point) as well as simple additive-group methods.

A large analytical study was carried out by the authors of a series of works [106, 107, 108, 109, 110, 111, 112, 113], devoted to the investigation of the relationship between the fire hazard characteristics of compounds with the chemical structure of their molecules. The authors have proposed equations to calculate flash, ignition, autoignition temperatures, temperature and concentration limits of flame propagation for alkanols, ketones, simple and complex ethers, aldehydes, carboxylic acids, and nitroalkanes. The approach used in the mentioned works consisted in description of fire hazard characteristics by polynomials of 1-2 degree, logarithmic equations, or power functions from the number of carbon atoms in a compound molecule. The mutual influence of atoms in a molecule is accounted for using the "carbon chain" rule. Correlations of flash point temperature with stoichiometric coefficient before oxygen in reaction of complete combustion of substance (β), stoichiometric concentration (C_{stc}) of combustible mixture, or molar mass of combustible substance were obtained for some series of compounds in works [106-113].

Table 5.1 shows the equations for calculating the flash point of the substances studied by the authors of papers [106-113].

Table 5.1. Equations for the description and prediction of the flash point of organic substances

Compounds	Equation	N_C	R^2
Alkanols	$t_{fp} = 11.42 \cdot N_C - 8.2198$	$1 \leq N_C \leq 14^*$	0.9980
Aldehydes	$T_{fp} = 14.799 \cdot N_C + 203.7$ $T_{fp} = 199.2 + 12.569 \cdot \beta - 0.139\beta^2$ $T_{fp} = \dfrac{1038.75 + 602 \cdot C_{stc}}{1 - 0.106 \cdot C_{stc}}$ $T_{fp} = 1.055 \cdot M + 186.8$	$2 \leq N_C \leq 13$ $1 \leq \beta \leq 19$ $1.1 \leq C_{stc} \leq 19$ $30.3 \leq M \leq 198.4$	0.9935 0.9951 0.9953 0.9916
Ketones	$t_{fp} = 13.73 \cdot N_C - 58.7$ $t_{fp} = 901.75 - \dfrac{53513}{N_C + 55}$ $t_{fp} = 9.1533 \cdot \beta - 54.12$ $T_{fp} = -3.2545 \cdot C_{stc}^3 + 40.16 \cdot C_{stc}^2 -$ $-174.48 \cdot C_{stc} + 255.9$	$3 \leq N_C \leq 18$	0.9884 0.9897 0.9884 0.9879
Simple esters	$T_{fp} = \dfrac{10^4 \sqrt{N_C}}{8.93\sqrt{N_C} + 67.82}$ $T_{fp} = -0.5466 \cdot N_C^2 + 23.44 \cdot N_C + 149.68$	$4 \leq N_C \leq 16$ $4 \leq N_C \leq 16$	0.9941 0.9952
Complex esters	$T_{fp} = -0.3107 \cdot N_C^2 + 17.475 \cdot N_C + 206.4$	$2 \leq N_C \leq 16$	0.9853
Carboxylic acids	$T_{fp} = -0.57 \cdot N_C^2 + 30.43 \cdot N_C + 273.0$ $T_{fp} = 69.10 \cdot \ln(N_C) + 23.56$ $T_{fp} = -0.09 \cdot N_C^2 + 7.18 \cdot N_C + 335.2$ $T_{fp} = 286.4 + 13.112 \cdot \beta - 0.253\beta^2$ $T_{fp} = -0.04\beta^2 + 4.70 \cdot \beta + 340.0$	$2 \leq N_C \leq 12$ $13 \leq N_C \leq 26$ $13 \leq N_C \leq 26$ $2 \leq N_C \leq 12$ $13 \leq N_C \leq 26$	0.9967 0.9997 0.9997 0.9967 0.9997

Please note. *Interval of the number of carbon atoms in the molecules of compounds whose properties are used for approximation. *R* - correlation factor.

Next, let us consider how the above-described scheme for the separation of structural fragments in an organic compound molecule [77] has been tested for the description and prediction of the flash point of the three classes of compounds: alcohols, ketones, and esters [114, 115, 116, 117].

A multi-parameter equation was used to describe and predict the flash point

$$\begin{gathered} t_{fp} = t_{fp}(\mathrm{Y}_p) + \delta t_{fp}(\mathrm{Y}_{pp}) + \delta t_{fp}(\mathrm{Y}_s) + \delta t_{fp}(\mathrm{Y}_t) + \\ + \sum_{i=1}^{n} [y_i t_{\mathrm{fp}}(\mathrm{CH}_{y,i}) + p_i t_{fp}(\mathrm{CH}_{p,i}) + s_i t_{fp}(\mathrm{CH}_{s,i}) + t_i t_{fp}(\mathrm{CH}_{t,i}) + h_i t_{fp}(\mathrm{CH}_{h,i})], \end{gathered} \tag{5.1}$$

where t_{fp} is the flash point of the substance in the closed crucible; $t_{fp}(\mathrm{Y}_p)$ is the contribution to the flash point of the polar group associated with the primary carbon atom (CH_2-group); $\delta t_{fp}(Y_s)$, and $\delta t_{fp}(\mathrm{Y}_t)$ are corrections taking into account the differences in the properties of the functional groups associated with the secondary and tertiary carbon atoms.

Literature data, including those on t_{fp} of complex esters [100-103], indicate that the properties of the first member of the homologous series significantly differ from the properties of subsequent compounds. Therefore, in the present work a correction $\delta t_{fp}(\mathrm{Y}_{pp})$ was introduced in equation (5.1) that takes into account differences in properties of functional group, the oxygen atom of which is connected with methyl radical, to better detail molecules of organic compounds and take into account the specific aspects of structure and properties of the first member of homologous series. The contribution of the functional group associated with a methyl radical, secondary or tertiary carbon atom can be determined by summing the values of $t_{fp}(\mathrm{Y}_p)$ and the corresponding correction $\delta t_{fp}(\mathrm{Y}_{pp})$, $\delta t_{fp}(\mathrm{Y}_s)$, or $\delta t_{fp}(\mathrm{Y}_t)$. $t_{fp}(\mathrm{CH}_{y,i})$ is the contribution to the flash point of C-H bonds of carbon atoms in the first environment of the polar group in the *i*-th hydrocarbon radical bound to it. The first environment of the functional group includes C-H bonds of the carbon atom bound to the functional group and following it; $t_{fp}(\mathrm{CH}_{p,i})$, $t_{fp}(\mathrm{CH}_{s,i})$, $t_{fp}(\mathrm{CH}_{t,i})$, $t_{fp}(\mathrm{CH}_{t,i})$, $t_{fp}(\mathrm{CH}_{h,i})$ are contributions to the flash point of C-H bonds in methyl, methylene and methylene radicals, respectively, as well as the quaternary carbon atom not included in the first polar group environment; y_i, p_i, s_i, t_i, and h_i are the numbers of extracted structural fragments in the *i*-th hydrocarbon radical. They are determined by the composition and structure of the molecules.

We have described the methodology of structural fragment extraction in detail in [90, 91, 114].

Table 5.2 shows the contributions of selected structural fragments to the flash point of alcohols, ketones, and complex esters obtained by regression analysis using equation (5.1) of experimental values of t_{fp}, species and number of structural elements.

It can be seen that the standard error of the additive model description of t_{fp} is less than 2 degrees for esters and alcohols, but increases to 3.5 degrees for ketones. However, it should be noted that for ketones other techniques also give worse results. The paper [114] indicates that such an error is higher than the calculation error based on the correlation of t_{fp} with the boiling point.

The predictive ability of our additive is illustrated in [114]. It is shown that reducing the sample size of the experimental data (columns 4 and 5 of Table 5.2), allows us to maintain high accuracy of the calculations. Calculated and experimental t_{fp} of alcohols not included in the sample are presented in Table 5.3.

Table 5.2. Group contributions to flash point and multiple correlation parameters by equation (5.1) for complex esters, alcohols, and ketones

Structural fragment	**Complex esters:** $Y = (-O-\overset{O}{\overset{\|}{C}}-)$	**Structural fragment**	**Aliphatic saturated monatomic alcohols, Y = -OH**		**Structural fragment**	**Aliphatic saturated ketones,** $Y = (-\overset{O}{\overset{\|}{C}}-)$
$CH_{p,A}$	5.11±0.31	CH_p	5.83±0.65	6.53±1.00	CH_p	5.57±0.29
$CH_{s,A}$	7.92±0.12	CH_s	6.07±0.11	5.86±0.18	CH_s	6.75±0.25
$CH_{t,A}$	8.37±1.37	CH_t	1.92±1.61	-1.32±3.13	CH_t	11.18±3.31
$CH_{Y,A}$	2.76±0.44	CH_Y	5.83±1.97	7.29±2.78	CH_Y	8.17±0.91
Y_p	-34.57±2.88	Y_p	-17.07±9.95	-23.29±14.05	Y_p	-65.98±7.46
Y_{pp}	-7.29±1.56	Y_{pp}	5.57±4.60	7.43±6.33	Y_{pp}	0.00±0.00
		Y_t	-22.12±7.76	-30.09±11.37	Y_t	-
Y_s	0.71±1.23	Y_s	-11.07±3.72	-16.01±6.04	Y_s	-14.72±4.25
$CH_{Y,Ac}$	6.59±0.24					
$CH_{s,Ac}$	6.66±0.29					
$CH_{p,Ac}$	6.61±0.23					
n	33		23	14		17
se	1.55		1.98	2.41		3.55
R	0.9990		0.9987	0.9988		0.9961

Please note: n is the number of approximated points, *sd* is the standard deviation, *R* is the correlation coefficient.

Table 5.3. Experimental and calculated by formula (5.1) t_{fp} for alcohols

Compound	**t_{add} (exp), °C**	**t_{add} (calc), °C**
Propanol	23	25
1-Butanol	35	37
2-Butanol	24	24
2-Pentanol	36	36
2-Methyl-2-butanol	24	25
2-Methyl-2-pentanol	39	36
4-Methyl-2-pentanol	46	40
1-Octanol	86	84
1-Decanol	110	108
2-Heptanol		61
3-Heptanol		60
5-Methyl-1-hexanol		67
5-Methyl-2-hexanol		56
2-Methyl-2-hexanol		49

It can be seen that there is good agreement between the calculated and experimental values. The average deviation is 2.0 °C. Based on this, it can be assumed that the additive-group approach we used will allow us to predict the flash point of many new (even non-synthesized) compounds with an error equal to the approximation error. For example, Table 5.3 shows the calculated flashpoints of some heptanol isomers.

Summarizing the above, we can conclude that our proposed version of the additive-group method, adapted to calculate the flash point of liquids, allows us to describe and predict the flash point of substances with high accuracy.

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