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Volume and Surface Area of Alkane Molecules and Their Solvation Enthalpies

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Abstract—The solvation enthalpies of normal and isoalkanes in cyclohexane are correlated with directly calculated volumes and surface areas of the molecules. The account for the relative molecular sizes of alkane and solvent make it possible to embrace compounds with various degrees of branching of the hydrocarbon skeleton by a common dependence.

The volumes and surface areas of molecules are widely used in structure–property correlations. The objects for correlation may include various physicochemical properties of organic compounds that reflect any aspect of solute–solvent interactions (vaporization and solvation enthalpies, energies of solvent void formation, chromatographic retention parameters, etc.) [1–4]. Therewith, the volumes and surface areas are calculated by additive schemes [5], or certain experimental values proportional to the required molecular parameters are used. The most commonly used experimental values are the molar volume of a compound or its proportional molecular refraction [6]. However, calculations by additive schemes take no account both of the real molecular geometry and of the error produced by the application of averaged parameters to concrete objects [7]. The situation with experimental values is not easier, since required data are not always available. Experimental values not infrequently fail to adequately model a process studied, which necessitates introduction of certain indicator variables, thereby masking the physical sense of the correlations and reducing their prognostic power. Thus, Solomonov *et al.* in their study on the solvation enthalpies of cycloalkanes [8] found that molecular refraction MR_D fairly models the molecular volumes for unbranched cycloalkanes, whereas cycloalkanes with a side chain deviate from the correlation. The same was observed with compounds to other classes, having branched hydrocarbon radicals. This phenomenon was explained by the weak sensitivity of molecular refraction to isomeric variations of the hydrocarbon skeleton of the molecule.

In view of the above difficulties, direct calculation of the volume and surface area of organic compounds has received increasing researcher's attention. Here, a molecule is considered as a set of interpenetrating spheres whose centers are the centers of atoms constituting the molecule and the radii are equal to the van der Waals radii of the corresponding atoms. The vigorous recent development of computational techniques favored progress of numerical methods of such calculations. Most of these methods are based on dividing the volume occupied by a molecule with a continuous grid with a fairly small step (less than 0.1 Å) and calculating the number of elements falling inside the molecule [7]. However, this "geometric" approach takes no account of one important circumstance, namely, the relative size of solute and solvent molecules. For steric shielding reasons, a part of the surface of solute molecules is inaccessible for solvent. The same reason is responsible for the build-up of the "effective" molecular volume at the expense of the volume adjacent to the surface and inaccessible for other molecules.

We developed a method for calculation of the volume of the void occupied by a solute molecule in a solution, as well as of the size of the arising interface, which accounts for the above steric effects [9]. In the cited work we proposed a procedure for geometric smoothening of the shape of a molecule, which represents the molecular boundary as a smooth surface. For the rounding radius of the surface one can accept, for instance, the effective molecular radius of a certain compound interacting with the molecule in question. For solvation processes, for instance, this is the effective molecular radius of a solvent. Figuratively speaking, a molecule is represented by an area which is obtained from the initial van der Waals model by rolling the "smoothening step" over its surface. This approach allows the molecular boundary to be represented by a surface comprising spherical fragments or fragments of revolution surfaces even at multiple intersection of van der Waals spheres.

The aim of the present work is to employ the developed method for searching for correlations between the geometric characteristics and solvation enthalpies of molecules, which is necessary for constructing quantitative models of solute–solvent interactions.

To substantiate the expedience of introducing the volumes and surface areas of molecules, obtained by direct calculation, into the practice of correlation analysis, we should find out if molecular refraction is an adequate measure of molecular volume. As mentioned above, the parameter MR_D is presently widely used for correlation of the molecular structures of organic compounds with their physicochemical properties. However, the MR_D values first of all reflect the mobility of the electronic shell of a molecule on its interaction with photons. For chemically similar compounds, this parameter is primarily dependent on the number and nature of atoms constituting the molecule and is practically insensitive to isomerism of the hydrocarbon skeleton (Table 1) [8]. The data in Table 1 show that directly calculated molecular volumes adequately reflect the chemical notion of the tendencies in variation of the volumes of molecules with the degree of branching of their hydrocarbon skeletons, whereas MR_D values are almost insensitive to such variations. In view of the aforesaid, when modeling the geometric molecular volumes of organic compounds in constructing structure–property correlations one should operate by directly calculated values.

Table 1. Molecular refractions and molecular volumes (without smoothening) of unbranched and branched alkanes

n(C)	Alkane	MR_D	V, Å^3
5	2,2-Dimethylpropane	25.13	93.7
5	Pentane	25.25	94.5
6	3-Methylpentane	29.80	109.6
6	Hexane	29.89	111.0
7	2,2-Dimethylpentane	34.62	125.6
7	3-Ethylpentane	34.28	125.0
7	Heptane	34.56	127.4
8	2,2,4-Trimethylpentane	39.26	138.2
8	2,2-Dimethylhexane	39.24	142.1
8	Octane	39.18	143.9
9	2,2,4,4-Tetramethylpentane	43.89	150.8
9	3,3-Diethylpentane	43.14	155.9
9	Nonane	43.86	160.3

The problem of the effect of geometric characteristics of molecules on their physical properties is expedient to consider on the simple and illustrative example of solvation of alkanes in a standard hydrocarbon solvent, cyclohexane. On the one hand, this system involves dispersion intermolecular interactions only, but, on the other, already here one cannot construct a common solvation enthalpy–molecular volume correlation dependence for normal and isoalkanes. As known, the solvation enthalpy is related to the mixing and vaporization enthalpies by Eq. (1):

$$\Delta H_{\mathrm{solv}} = \Delta H_{\mathrm{mix}} + \Delta H_{\mathrm{vap}}. \quad (1)$$

As found by Solomonov and Konovalov [10], the vaporization enthalpy–molecular volume (modeled by MR_D) dependence for various alkanes falls into several linear correlations (with the same slopes) belonging to compounds with various degrees of branching of the hydrocarbon skeleton (cyclic, normal, and with one or two branchings in the chain). The referees gave no explanation for such a “segregation” for closely related compounds. The solution enthalpy of an alkane in an alkane is close to zero [11], and the same is true of the solvation enthalpies of alkanes in cyclohexane.

On the other hand, the solvation enthalpy of an alkane is a sum of the enthalpy of void formation and the enthalpy of nonspecific solute–solvent interaction.

$$\Delta H_{\mathrm{solv}} = \Delta H_{\mathrm{void}} + \Delta H_{\mathrm{int}}. \quad (2)$$

The enthalpy of nonspecific interaction is related to molecular polarizability. In view of the fact that the polarizabilities of alkanes depend almost exclusively on their molecular weights (Table 1), but a rough correlation of this term with the molecular volume can be expected for isoalkanes. The enthalpy of void formation depends on the energy expended for building a new interface, and, therefore, is will probably correlate with the surface areas of alkanes.

At the same time, it is quite obvious that the volumes and surface areas of molecules are closely interrelated. As shown in [9], calculated V and S values uniquely correlate only in very narrow homologous series (n-alkanes, isoalkanes). There is no common correlation both for the initial and smoothened volumes and surface areas of alkanes (Fig. 1). In their turn, the smoothened molecular volumes of unbranched and branched alkanes uniquely correlate with the initial volumes and fit a common dependence (the square of the multiple correlation coefficient r^2 is ~0.9991). No such pattern is observed for the surface areas: linear molecules and their isomers fit

Table 2. Initial (R_S 0 Å) and smoothened (R_S 2 Å) volumes and surface areas of unbranched and branched alkanes and their solvation enthalpies in cyclohexane [11, 12]

n(C)	Alkane	*V* (R_S 0 Å), Å^3	*S* (R_S 0 Å), Å^2	*V* (R_S 2 Å), Å^3	*S* (R_S 2 Å), Å^2	$-\Delta H_{solv}$, kcal/mol
	Unbranched alkanes					
5	Pentane	94.5	130.0	101.8	123.0	6.1
6	Hexane	111.0	150.3	120.2	141.3	7.3
7	Heptane	127.4	170.6	138.6	159.5	8.4
8	Octane	143.9	190.9	157.0	177.9	9.5
9	Nonane	160.3	211.3	175.3	196.2	10.6
10	Decane	176.4	231.0	193.2	214.2	11.7
12	Dodecane	209.3	271.8	230.0	250.7	14.0
14	Tetradecane	242.1	312.3	266.7	287.5	16.3
16	Hexadecane	275.0	353.0	303.4	324.0	18.3
	Branched alkanes					
5	2,2-Dimethylpropane	93.7	127.2	102.2	116.1	5.1
5	2-Methylbutane	93.6	125.6	100.7	117.6	5.8
6	2,2-Dimethylbutane	109.2	141.1	118.2	128.9	6.4
6	3-Methylpentane	109.6	142.8	118.1	132.8	6.9
7	2,2-Dimethylpentane	125.6	161.5	136.6	147.2	7.5
7	3-Ethylpentane	125.0	156.8	134.2	144.3	7.9
8	2,2,4-Trimethylpentane	138.2	173.0	150.8	155.5	8.2
8	2,2-Dimethylhexane	142.1	181.8	155.0	165.5	8.5
8	3-Methylheptane	142.4	183.4	154.9	169.4	9.0
9	2,2,4,4-Tetramethylpentane	150.8	183.7	164.8	162.9	9.0
9	2-Methyloctane	159.3	206.9	174.2	190.9	10.3
10	2,2,5,5-Tetramethylhexane	173.4	213.6	192.0	188.9	9.6

different dependences. In view of the aforesaid, one should not expect a common solvation enthalpy–molecular volume correlation for alkanes with various degrees of branching. With the surface areas, the prognosis is more favorable.

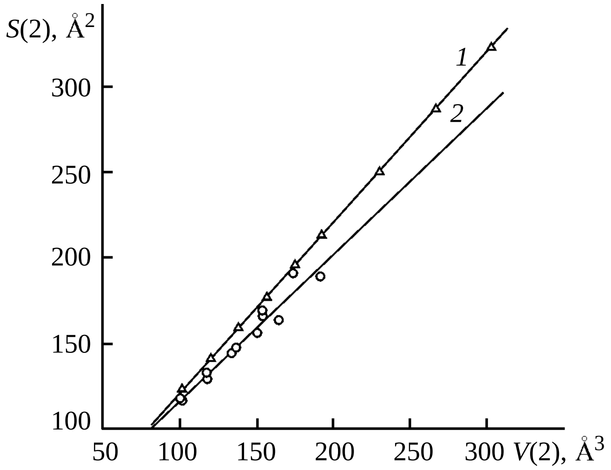

Fig. 1. Smoothened surface area (smoothening radius R_S 2 Å) vs. smoothened molecular volume for (*1*) unbranched and (*2*) branched alkanes. $S(2) = 0.9977\,V(2) + 21.34$, r^2 1 (*1*); $S(2) = 0.8593\,V(2) + 29.81$, r^2 0.9548 (*2*).

The results of the direct calculation of the molecular volumes and surface areas of alkanes (initial and smoothened), as well as their solvation enthalpies in cyclohexane [11, 12] are listed in Table 2. The smoothening was performed with the smoothening sphere radius R_S of 2 Å, since, as shown in [9], in the range 2–4 Å (this range includes the effective radii of most organic solvents) the molecular surface areas are almost invariable. As seen from Table 2, there is no single correlation dependence between the molecular volumes (both initial and smoothened) and solvation enthalpies of alkanes (Fig. 2). The same is also true of the initial surface areas of alkanes (Fig. 3*a*). A common correlation equation for branched and unbranched alkanes can only be obtained when the void formed is modeled by a smoothened surface area (Fig. 3b).

The above results should not be treated as if the solvation enthalpy depends on the surface area, i.e. on the area of the newly formed interface, rather than volume of the solute. We only state that there is no single correlation between the ΔH_{solv} values of alkanes and their molecular volumes (both initial and smoothened). In essence, this situation is similar to

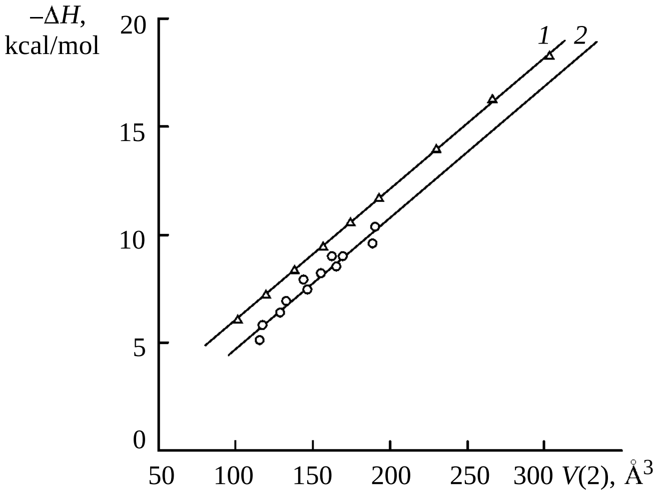

Fig. 2. Solvation enthalpies in cyclohexane vs. smoothened molecular volumes for (*1*) unbranched and (*2*) branched alkanes. (*1*) $-\Delta H = 0.0608\,V(2) - 0.0445$, r^2 0.9997; and (*2*) $-H = 0.0611\,V(2) - 1.4234$, r^2 0.9564.

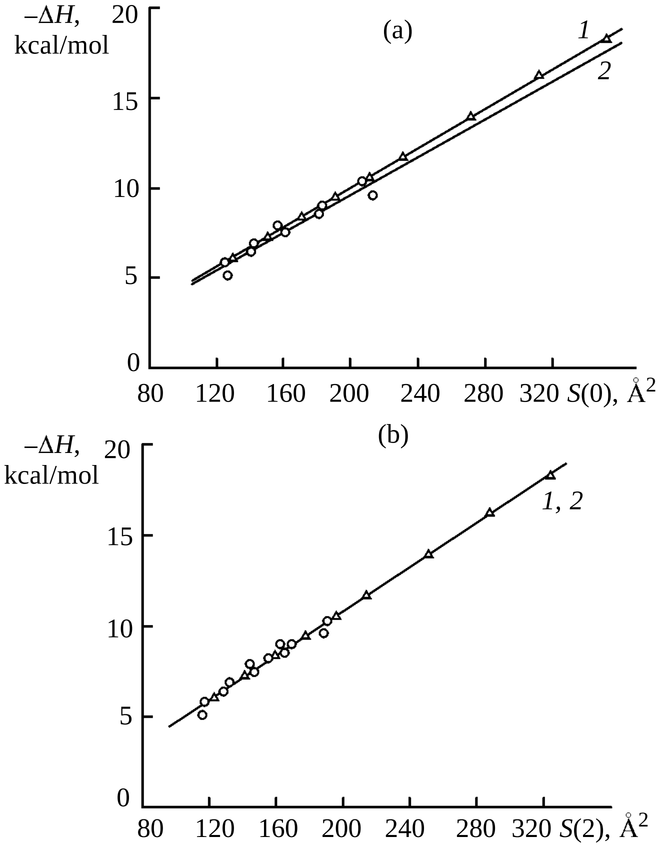

Fig. 3. Solvation enthalpies in cyclohexane vs. (a) initial and (b) smoothened surface areas for (*1*) unbranched and (*2*) branched alkanes. (a): (*1*) $-\Delta H = 0.055\,S(0) - 0.9957$, r^2 0.9997; and (*2*): $-\Delta H = 0.0525\,S(0) - 0.8825$, r^2 0.938. (b): (*1*) $-\Delta H = 0.061\,S(2) - 1.3458$, r^2 0.9998; and (*2*) $-\Delta H = 0.0611\,S(2) - 1.4234$, r^2 0.9564.

that with MR_D [10] (up to the same slopes for homologous series of unbranched and branched alkanes). This is probably explained by the fact that molecular volume is an “unsuitable” parameter for correlation with solvation energies. As noted above, it fails to reflect, to a full measure, both interaction and void formation enthalpies. At the same time, molecular surface area adequately reflects the energy expences for void formation and, indirectly, via its correlation with volume, reflects the solute–solvent interaction enthalpy. It can be said that surface area “takes up,” to a greater or lesser probability, both components of solvation enthalpy, which gives rise to a correlation including compounds with various degrees of branching of the hydrocarbon skeleton. Comparison of the plots in Fig. 3 shows, that the account for the real structure of a solute (via smoothened surface areas) allows one to appreciably better describe the solvation phenomenon and no longer use indicator variables in structural descriptions.

Thus, the molecular volumes and surface areas of solutes, obtained by direct calculation with account for the relative sizes of solute and solute molecules allow one to correctly represent solvation enthalpies for compounds with various degrees of branching of the hydrocarbon skeleton, which makes possible more adequate description of molecular interactions in solutions.

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