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The potential of a molecular surface in intermolecular interactions

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A calculation procedure for the potential of the smoothed surface of a solute molecule at the interaction with a solvent is proposed.

In the quantitative models of solution chemistry and crystal chemistry, the energy of the molecular interaction of organic substances with a surrounding condensed phase is the principal value. An approach under which a molecule is placed into a cavity formed in a solvent is widely used.[1,2] The necessary part of such models is the calculation of the potential of a smoothed molecular surface, which takes into account the space structure and commensurable sizes of interacting molecules.

The significant success in practical calculations of the energy of interaction was achieved by estimating molecular adsorption characteristics on a flat uniform carbon surface at the atom-atomic assumption.[3–5] The use of a similar approach for condensed phases (for example, the description of solvation) requires calculation of the potential of the curvilinear surface of a solute molecule, taking into account the shape and orientation of solvent molecules.

We consider the solvation process of normal alkanes and isoalkanes in cyclohexane. In such systems, dispersion forces are the main contribution to the energy of intermolecular interactions. The solute and solvent molecules are represented as a space combination of atoms with van der Waals radii. The *trans* conformations of molecules were considered. The values 1.75 and 1.17 Å were used as the radii of carbon and hydrogen atoms, respectively.[6] The effective boundary of separation is introduced as a smoothed surface covering the solute molecule and limiting volume inaccessible to solvent molecules.[7] The energy of the molecular interaction was calculated based on the atom-atomic assumption; interatomic potentials were used in the Buckingham–Corner form[3]

$$\varphi = C_1 r^{-6} + C_2 r^{-8} + B\exp(-qr),$$

where C_1 and C_2 are the parameters of attraction forces; B and q are the parameters of repulsion forces. The following values were used for different pairs of interacting atoms (C_1/J Å^6 mol^{-1}, C_2/J Å^8 mol^{-1}, B/J mol^{-1}): C–C (-1.75×10^6, -2.54×10^6, 1.55×10^8), C–H (-6.29×10^5, -1.16×10^6, 2.74×10^7) and H–H (-2.35×10^5, -5.10×10^5, 7.10×10^6). The parameter q for all pairs of atoms is the same and assumes the numerical value of 3.57 Å^{-1}; φ is evaluated in J mol^{-1}.

Table 1 Effective potential of the smoothed molecular surface of alkanes.

Molecule	*n*	*m*	*p*	*F*/J mol^{-1}
Hexane	6	0	0	–15100
Heptane	7	0	0	–15450
Octane	8	0	0	–15800
Nonane	9	0	0	–16050
Decane	10	0	0	–16400
2,2-Dimethylpropane	5	2	0	–15300
2-Methylbutane	5	1	0	–15200
2,2-Dimethylbutane	6	2	0	–16150
3-Methylpentane	6	1	0	–15850
2,2-Dimethylpentane	7	2	0	–16400
3-Ethylpentane	7	1	1	–16650
2,2,4-Trimethylpentane	8	3	0	–17350
2,2-Dimethylhexane	8	2	0	–16600
3-Methylheptane	8	1	0	–16350
3,3-Ethylmethylpentane	8	2	1	–18050
2,2,4,4-Tetramethylpentane	9	4	0	–18250
2-Methyloctane	9	1	0	–16350
3,3-Diethylpentane	9	2	2	–18100
2,2,5,5-Tetramethylhexane	10	4	0	–17650
3,3-Diethylhexane	10	2	2	–18850

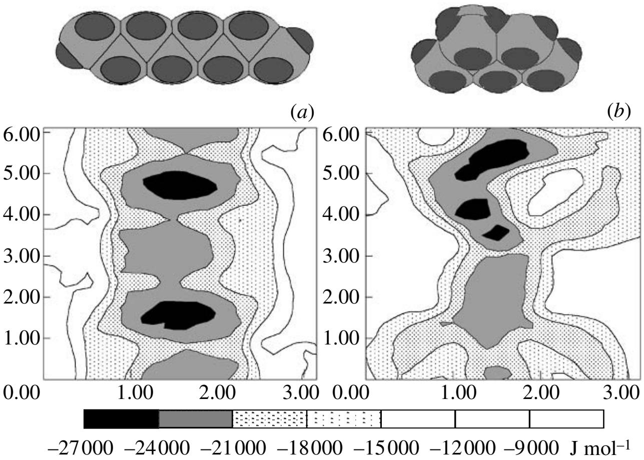

Figure 1 The map of the potential of interactions of (*a*) *n*-octane and (*b*) isooctane with the test cyclohexane molecule. Coordinates: azimuth and polar angles of the centre of the test molecule in the coordinate system associated with the main axes of a solute molecule. Equipotential curves are drawn at 3 kJ mol^{-1} intervals.

The dynamics of solvent molecules is simulated by calculating all configurations of the system, consisting of a stationary solute molecule and a test solvent molecule approaching it from different directions. These directions are fixed by the consequent choices of azimuth and polar angles, which defined the mutual position of the centres of molecules. Then, the rotation of a solvent molecule by three Euler angles is conducted for each approach direction. The energy of the most favourable orientation of the solvent molecule, which corresponds to the minimum of the potential energy of interaction, is taken as the local potential F_i of a small element of solute molecular surface. To calculate this element, the solute molecule is inserted into a sphere with a radius equal to the distance between the centre of the molecule and the most remote element of the molecular surface. For each solid angle, which is obtained as a projection of the solvent molecule on this sphere, we find the effective area of this surface element S_i, from its distance from the centre of molecule. The specified procedure makes it possible to obtain a map of the potential of the smoothed surface of the solute molecule; here, the comparable sizes of solute and solvent molecules are taken into account. The effective potential of the smoothed molecular surface is calculated by averaging the local values of the potential

$$F = \sum_i F_i S_i \Big/ \sum_i S_i,$$

it corresponds to the intensity of dispersion interaction of 1 Å^2 of the solute surface with one molecule of cyclohexane.

Typical maps of the potential distribution for the interaction of a cyclohexane molecule with the molecules of normal alkanes and isoalkanes are presented in Figure 1. The step for angles is 10°. The places with maximum of potentials (in absolute values) on the molecular surface correspond to the qualitative chemical hypotheses about the localization of places with the most powerful dispersion interaction.

The calculation of the averaged potential for normal alkanes and isoalkanes has shown that the intensity of solute dispersion interactions with a hydrocarbon solvent depends on the total number of carbon atoms in the solute molecule and on the carbon skeleton branching, such as the total amount of branchings and the length of lateral fragments of the chain. Quantitatively, this dependence can be approximated by the linear equation

$$F = -306(\pm 45)n - 452(\pm 55)m - 750(\pm 110)p - 13320(\pm 340),$$

where n is the total number of carbon atoms in the solute molecule; m is the total amount of branching of the carbon skeleton of the molecule; p is the number of carbon atoms in lateral fragments of the chain (longer than methyl). The square of the multiple correlation coefficient R^2 is 0.95. Some molecular potentials, which were used for deriving this correlation equation, are presented in Table 1. Under the accepted model, the absolute error in the computation of potentials was ±60 J mol^{-1}.

Considering the significant contribution of branching factors to the total energy of interaction, it is possible to conclude that compact isoalkane molecules exhibit more intense dispersion interactions with the solvent than the linear molecules of normal alkanes.

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