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Superposition-additive approach: Thermodynamic parameters of monosubstituted alkanes

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ABSTRACT

The superposition-additive approach developed earlier was shown to be applicable for the calculations of the thermodynamic parameters of formation and atomisation of conjugate systems, their dipole polarisability, molecular diamagnetic susceptibility, π-electronic ring currents etc. In this publication, the applicability of this approach for the calculation of the thermodynamic parameters (enthalpy and Gibbs' energy of formation from elementary substances, and absolute entropy) of alkanes, fatty alcohols, thioalcohols, amines, nitriles, fatty carboxylic acids and nitriles with the general composition $C_nH_{2n+1}X$ (X is the functional group) is studied. It is shown that the thermodynamic quantities determined using the proposed approach agree to within the satisfactory precision with the available calculated and experimental data.

The superposition-additive method was proposed earlier and verified in the calculations of the thermodynamic characteristics of conjugate systems [1], their dipole electric polarisabilities [2], molecular diamagnetic susceptibilities and π-electron ring currents [3–5]. The superposition-additive approach is theoretically based on the Bader's [6] postulate about the way in which atoms exist in molecules: each atom (or atomic group) in a molecule retains its individuality in various chemical combinations (i.e., in various molecules). It follows therefore that the properties of atoms in molecules are transferable; also, atomic-related values, being summed over all atoms of the molecule, yield the molecular average, i.e., the molecular average is the additive value. In this paper we use this approach to calculate thermodynamic parameters (enthalpy, entropy and Gibbs' energy) of substituted alkanes with long alkyl chains which can form monolayers at the air/water interface. This approach has been tested in the description of clusterisation processes [7].

The superposition-additive approach is based on the transferability of atomic properties and the additivity of molecular properties. The essence of the procedure is the assumption that when two molecular graphs are virtually superimposed, the properties of the constituent atoms remain unchanged. If the same superposition can be constructed in different ways (see Fig. 1), each one involving two entities, it becomes possible to calculate the structure and properties of one of these entities (ions, radicals, clusters etc.), provided the structure and properties of the other three entities being known, see e.g. [1–5].

This principle and corresponding procedure is graphically illustrated in Fig. 1. The molecules (1), (2), (4) and (5) are the structures which involve the hydrocarbon chain and the functional groups X and Y (X can be either the same as Y, or these groups can be different). The structure (3) is the result of the superposition of the structures (1) and (2), and also of the structures (4) and (5). As these two superpositions lead to the same result, the properties of any of the four molecules could be expressed as the algebraic sum of the corresponding properties of three other molecules. More specifically, to calculate any thermodynamic parameter of the molecule (4) one has to add the corresponding values for the molecules (1) and (2) and to subtract the value of the molecule (5).

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