Superposition-additive approach in the description of thermodynamic parameters of formation and clusterisation of substituted alkanes at the air/water interface

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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 of formation and clusterisation at the water/air interface of alkanes, fatty alcohols, thioalcohols, amines, nitriles, fatty carbon acids ($C_nH_{2n+1}X$, X is the functional group) and *cis*-monoienic carbon acids ($C_nH_{2n-1}COOH$) is studied.

The thermodynamic quantities determined using the proposed approach agree well with the available data, either calculated using the semiempirical (PM3) quantum chemical method, or obtained in the experiments. In particular, for the enthalpy and Gibbs' energy of the formation of substituted alkane monomers from the elementary substances, and their absolute entropy, the standard deviations of the values calculated via the superposition-additive scheme with the mutual superimposition domain $C_{n-2}H_{2n-4}$ (n is the number of carbon atoms in the alkyl chain) from the results of PM3 calculations for the alkanes, alcohols, thioalcohols, amines, fatty carbon acids, nitriles and *cis*-monoienic carbon acids are respectively: 0.05, 0.004, 2.87, 0.02, 0.01, 0.77, and 0.01 kJ/mol for the enthalpy; 2.32, 5.26, 4.49, 0.53, 1.22, 1.02, 5.30 J/(mol·K) for the absolute entropy; 0.69, 1.56, 3.82, 0.15, 0.37, 0.69, 1.58 kJ/mol for the Gibbs' energy; while the deviations from the experimental data are: 0.52, 5.75, 1.40, 1.00, 4.86 kJ/mol; 0.52, 0.63, 1.40, 6.11, 2.21 J/(mol·K); 2.52, 5.76, 1.58, 1.78, 4.86 kJ/mol (for the nitriles and *cis*-monoienic carbon acids no experimental data are available). The proposed approach also provides for quite

accurate estimates of the enthalpy, entropy and Gibbs' energy of boiling and melting, critical temperatures and standard heat capacities for several classes of substituted alkanes.

For the calculation of thermodynamic functions of clusterisation of dimers, trimers and tetramers of fatty alcohols, thioalcohols, amines, carbon acids and *cis*-monoienic carbon acids two superposition-additive schemes are proposed which ensure the correct superimposition of the molecular graphs, including the intermolecular hydrogen-hydrogen interactions in the clusters. The calculations involve the thermodynamic parameters of clusterisation obtained earlier by PM3 method. It is shown that the proposed approach reproduces quite accurately the values calculated earlier and is applicable for the prediction of the thermodynamic parameters of formation of surfactant monolayers.