RELATIONSHIPS BETWEEN ENTHALPY AND VOLUME CHANGES ON MELTING OF ORGANIC NON-ELECTROLYTES

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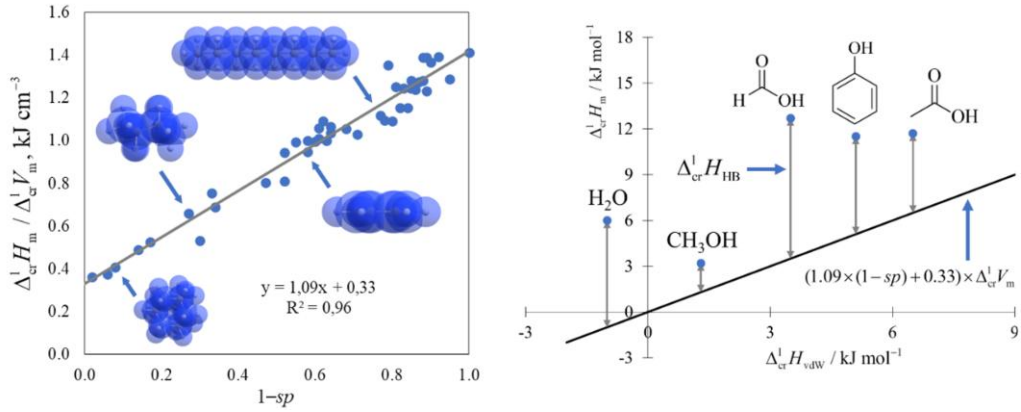
The search for the connection between thermochemical and structural parameters of matter has been a relevant direction of investigations in the field of thermodynamics of organic compounds for many decades. In this work, the relationship between the thermodynamic characteristics of melting and the molecular shape was analyzed. For non-associated compounds, a linear correlation was found (see Figure (left)) between the ratio of the fusion enthalpy to molar volume change during melting and the sphericity parameter (*sp*), defined as the ratio of the molecule's thickness to its length [1]:

$$\Delta H_m/\Delta V_m = 1.09 \cdot (1 - sp) + 0.33$$

This equation was used to investigate the influence of hydrogen bonding on the relationship between the thermochemical and volumetric characteristics of melting, and to identify the contributions of van der Waals interactions and hydrogen bonding to the fusion enthalpy of the associated compounds [2] (see Figure (right)). Correlations between enthalpy and volume changes accompanying phase transitions in liquid and plastic crystals were also found.



Left – correlation between the $\Delta H_m/\Delta V_m$ ratio and *sp* for non-associated organic compounds. Right – contributions of van der Waals forces (black line) and hydrogen bonding (grey arrows) to the fusion enthalpies of associated compounds.

1. Sokolov, A. A., Solomonov B. N., Yagofarov M. I. // J. Mol. Liq. 2025. V. 424. P. 127074. https://doi.org/10.1016/j.molliq.2025.127074

2. Sokolov, A. A., Solomonov B. N., Yagofarov M. I. // Phys. Chem. Chem. Phys. 2025. V. 27. № 41. P. 22196-22203. https://doi.org/10.1039/D5CP02393A

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