Thermodynamics of polymer solutions
in the entropy-fractal approach

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As a statistical theory of open systems, only entropy has a set of properties that allows it to be used in quantitative statistical uncertainty in microstates, natural polymers (hyperbranched structures, dendrimers, lignins, biological systems, dendrites, systems of internal organs, blood vessels, etc.). In the entropy-fractal approach, the Renyi entropy Rn [1] effectively "works" for equilibrium systems and the Tsallis entropy Ts [2] for open systems.

A functional relationship has been established between entropies S and the fractal dimension d − the most important characteristic of real objects, including natural polymers: $S \approx ln\varepsilon^{-d}$, where is the coating element of a fractal object (polymer). In this communication it is shown that the generalized non-ideality factor of systems (GNF) [3] can be introduced into the equations of informational entropy of Renyi and Tsallis and new expressions of informational and thermodynamic entropy can be obtained with a moment of order g_{th} . Equations in the Renyi

$$S_{g_{th}}^{M-Rn} = \frac{R}{g_{th}} ln\left(\sum_{i=1}^{N} p_i^{g_{th}-1}\right) \tag{1};$$

$$(S_{g_{th}}^{M-Ts}(p) = \frac{R(1- \sum_{i}^{N(\varepsilon)} p_i^{1-g_{th}})}{g_{th}} , \tag{2}$$

describing self-organized structures of equilibrium (1) substantially nonequilibrium (2) systems. These equations can be used to study the thermodynamic properties of solutions of high molecular weight compounds.

$$\text{GNF: } g = 1 + \langle - \beta_{ord} + \alpha_{nord} \rangle = 1 + \langle - p_i(\beta) + p_i(\alpha)\rangle, \tag{3}$$

where $\beta_{ord} \equiv 1/n\sum_{i}^{n} \beta_i$ and $\alpha_{nord} \equiv 1/n \sum_{i}^{n} \alpha_i$ − relative average characteristics (p_i is statistical probabilities) of opposite processes. The thermodynamic factor g_{th} varies in the range $0 \leq g_{th} \leq 2$ and depends on which of the competitive processes prevails. For example, dioxane lignin DL_{pin} of pine in the dioxane with fractal dimension d = 2,50 ± 0,08 and g_{th} = 0.83 at T = 298 K enthalpy of mixing ΔH_{mix} = −0.055 kJ/mol and ΔG_{mix} = −18.55 kJ/mol. For a polyelectrolyte in the system: dialyzed lignosulfonate DLS with d=2,44 ± 0 and g_{th} = 0.79 ΔH_{mix} practically equal to zero show that ΔG_{mix} = −17.35 kJ/mol. Thus, the conformational behavior of DL_{pin} in dioxane and DLS in a buffer solution determines the thermodynamic factor TΔS.

References
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