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High Frequency Relaxation in Fluid Mixtures, Protein Solubility and Entropy-Enthalpy Compensation JACK DOUGLAS, Polymers Division, NIST Gaithersburg, JACEK DUDOWICZ, James Franck Institute, U. Chicago, KARL FREED, James Franck Institute, U. Chicago — Additives to polymeric materials can lead to appreciable changes in the rates of relaxation and reaction in these mixtures that can greatly alter material properties and function. Correspondingly, the presence of polymers in solution can significantly affect self-assembly processes essential to living systems and manufacturing applications. This general class of problems is addressed in a specific practical context by developing a virial expansion to describe the influence of polymeric additives on the equilibrium constant governing protein self-assembly and solubility in solution. We find that the well known enhancement of protein self-assembly by polymer additives arising from a modification of the entropy of the assembly by repulsive polymer-protein excluded volume interactions is progressively compensated by attractive polymer-protein interactions that alter the enthalpy of assembly. Equilibrium constants and rate constants for diverse association, reaction, and relaxation processes in condensed state mixtures are amenable to the same type of statistical mechanical treatment so that this entropy-enthalpy compensation effect is predicted to be a rather generic phenomenon. Observations on the high frequency relaxation times of diverse mixtures confirm the generality of this relationship.

> Jack Douglas NIST

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