

Electronic supplementary information to the manuscript entitled “How does the entropy of ternary polymer-solvent-cosolvent mixtures depend on the molar solvent fraction?”

Evangelos Voyiatzis^{a,b} and Michael C. Böhm^a

^a Eduard-Zintl-Institut für Anorganische und Physikalische Chemie and Center of Smart Interfaces, Technische Universität Darmstadt, Alarich-Weiss-Strasse 4, 64287 Darmstadt, Germany.

^b Faculty of Physics, University of Vienna, Boltzmannngasse 5, 1090 Vienna, Austria.

All quantities in the present work are reported in Lennard-Jones units. The Lennard-Jones potential, V , is given by the expression $V(\bar{r}) = 4\epsilon[(\sigma/\bar{r})^{12} - (\sigma/\bar{r})^6]$ where \bar{r} is the distance between two interacting particles, ϵ is the depth of the potential and σ the finite distance at which the potential energy is equal to zero. The Lennard-Jones units can be derived by scaling the quantities of interest with an appropriate combination of the ϵ and σ parameters of the Lennard-Jones potential as well as the mass of a particle, which is denoted as m . A set of scalings for the most important quantities in the current study is presented in Table S.1, where k_B is the Boltzmann constant. A bar over a quantity denotes its unscaled value.

Table S.1: Lennard-Jones scalings of important quantities discussed in the present work

Quantity	Symbol	Scaling
Length	\bar{r}	$r = \bar{r}/\sigma$
Energy	\bar{E}	$E = \bar{E}/\epsilon$
Time	\bar{t}	$\tau = \bar{t}\sqrt{\epsilon/m\sigma^2}$
Temperature	\bar{T}	$T = k_B\bar{T}/\epsilon$
Number density	$\bar{\rho}$	$\rho = \bar{\rho}\sigma^3$

The system is studied under periodic boundary conditions in all three Cartesian coordinates. The simulation box is cubic and its axes have a length of approximately 24.565σ . The reduced number density, ρ , is equal to 0.85. All particles have the same mass. Bonded polymer particles interact via a finitely extensible nonlinear elastic potential

$$V_b(l) = -33.75 \ln[1 - (l/1.5)^2]$$

where l is the bond length. The dispersion interactions are described by shifted and truncated Lennard-Jones potentials. The explicit form of this potential is

$$V_{LJ}(r) = \begin{cases} 4[(r^{-12} - r^{-6}) - (r_c^{-12} - r_c^{-6})], & r \leq r_c \\ 0, & r > r_c \end{cases}$$

where r_c is the cut-off distance. In the present study, the ϵ parameter is equal to unity for all interactions. A complete listing of the employed σ and r_c values of all pairs for particle types is given in Table S.2. Additionally, the variation of the pair potential energy as a function of the distance between two particles is shown in Fig. S.1.

Table S.2: Lennard-Jones parameters for the dispersion interactions

Pair	σ	r_c
Polymer-Polymer	1.0	$2^{1/6}$
Solvent-Solvent	0.5	$2^{-5/6}$
Cosolvent-Cosolvent	0.5	$2^{-5/6}$
Polymer-Solvent	0.5	$2^{-5/6}$
Polymer-Cosolvent	0.75	2.5
Solvent-Cosolvent	0.5	$2^{-5/6}$

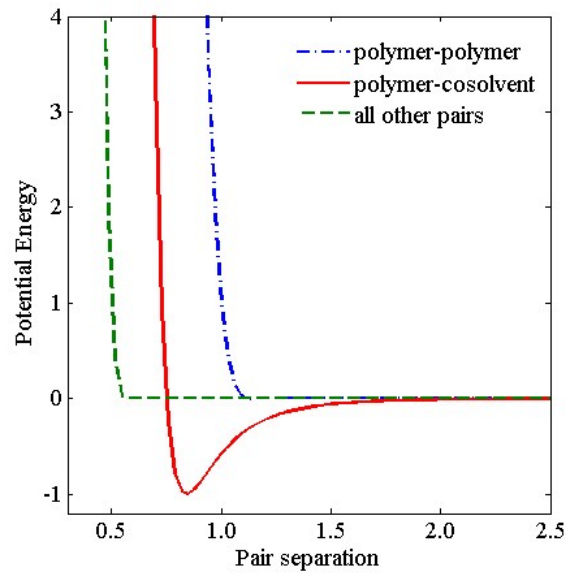


Figure S.1: Potential energy profiles employed in the present work

The molecular dynamics simulations are performed in the canonical statistical ensemble. The starting configurations were generated by creating a self-avoiding random walk chain in the center of the simulation box. The solvent and cosolvent beads were placed in a lattice around the chain to guarantee that they fill the space uniformly. The equations of motion are integrated using the velocity-Verlet algorithm with a timestep of 0.005τ . The temperature is controlled by the Nosé - Hoover thermostat. All systems are equilibrated for $5 \cdot 10^5 \tau$. Configurations are sampled every $10^3 \tau$.