

Supporting Information for

## **Aqueous Solutions of Poly(ethylene oxide) - Crossover from Ordinary to Tricritical Behavior**

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### **Flory-Huggins Theory of the Associating Aqueous PEO Solution.**

The Flory-Huggins (FH) parameter of common polymer solutions is determined by van der Waals forces showing miscibility at high temperature and phase decomposition at low temperature, i.e. a so-called UCST behavior. The corresponding normalized free energy density of mixing  $\Delta F(T, V, \Phi)$  in mean field approximation and normalized by the product of the gas constant  $R$  and absolute temperature  $T$  is given in units of  $\text{mol}/\text{cm}^3$  as

$$\Delta F/RT = \frac{\Phi}{V_p} \ln \Phi + \frac{1-\Phi}{\Omega_w} \ln (1-\Phi) + \Phi(1-\Phi) \chi. \quad (\text{S1})$$

The first two terms represent the translational entropy and are determined by the polymer volume fraction ( $\Phi$ ) and the molar volumes of the polymer ( $V_p$ ) and the solvent ( $\Omega_w$ ), respectively. The third term stands for the FH-parameter ( $\chi$  in units of  $\text{mol}/\text{cm}^3$ ) describing a segmental free energy density of mixing between solute and solvent and is written as  $\chi = \chi_h/T - \chi_\sigma$  with the enthalpic ( $\chi_h$ ) and entropic ( $\chi_\sigma$ ) terms.

Aqueous PEO solutions belongs to the class of associating polymer solutions as hydrogen bonding between water and PEO as well as between water and water play a relevant role, with the result that PEO is soluble at low temperatures as the strength of hydrogen bonding (2-25 kJ/mol) is stronger than van der Waals interaction (0.4-0.5 kJ/mol). The occurrence of hydrogen

bonding needs an additional term in the free energy of mixing of eq S1. Such a term has been formulated within mean field approximation by Semenov and Rubinstein [1] for one type of association interaction and has been extended particularly for aqueous PEO solutions by Dormidontova [2] considering two types of hydrogen bonding, namely the binding between PEO/water and water/water. The outcome of the last approach together with the van der Waals interaction between water and the CH<sub>2</sub> backbone unit of PEO [3] delivers a Flory-Huggins parameter which we compared with the experimental Flory-Huggins parameter obtained from a low concentration ( $\Phi = 3.43\%$ ) PEO solution (Figure 7).

The contribution of hydrogen bonding of PEO/water and water/water to the free energy is formulated in ref 2 on basis of the partition function according to

$$Z_{\text{ass}} = P_{\text{comb}} W_p \exp\left(\frac{\Delta E_p}{kT} n_p\right) W_w \exp\left(\frac{\Delta E_w}{kT} n_w\right). \quad (\text{S2})$$

The combinatorial factor  $P_{\text{comb}}$  describes the number of possible ways of forming hydrogen bonds between PEO/water ( $n_p$ ) and water/water ( $n_w$ ) molecules (eq 2.7; ref 1 and eq 5; ref 2). The parameters  $\Delta E_p$  and  $\Delta E_w$  represent the gain of energy when forming PEO/water and water/water hydrogen bonds, whereas  $W_p$  and  $W_w$  represent the probability that the corresponding groups of PEO and water come enough close together to form bonds. Inserting  $P_{\text{comb}}$  (eq 10; ref 2) into eq S2 delivers the free energy  $F_{\text{ass}}$  ( $F_{\text{ass}} = -(RT/V) \ln Z_{\text{ass}}$ ;  $V$  volume of the sample) as a function of the average fractions of PEO/water ( $x_p$ ) and water/water ( $x_w$ ) bonds, respectively. Both parameters are defined as

$$x_p := \frac{n_p}{2 N_p N} \quad \text{and} \quad x_w := \frac{n_w}{2 N_w} \quad (\text{S3})$$

e.g. the number of hydrogen bonds ( $n_p$ ,  $n_w$ ) divided by twice the number of PEO monomers ( $N_p N$ ,  $N$  degree of polymerization) and water molecules ( $N_w$ ). After minimizing the total free energy with respect to the fractions of the hydrogen bonds  $x_p$  and  $x_w$  one obtains the effective FH-parameter taken in the limit of  $\Phi \rightarrow 0$  and in units of  $[\text{mol}/\text{cm}^3]$  as follows (eq 30; ref 2):

$$\chi_{\text{eff}} = \chi + \frac{-2}{(1+x_w)\Omega_w} \left[ x_p \left( \frac{\Omega_w}{\Omega_p} \right) - x_w + \frac{x_p^2}{2(1-x_w)} \left( \frac{\Omega_w}{\Omega_p} \right)^2 \right]. \quad (\text{S4})$$

The limit of  $\Phi \rightarrow 0$  should be a sufficiently good approximation as we discuss the FH-parameter of a  $\Phi = 3.43\%$  PEO solution in Figure 7. The first term corresponds to the hydrophobic interaction corresponding to the FH-parameter in eq S1 whereas the second term is due to the hydrophilic interactions of the hydrogen bonds. The hydrophilic terms are determined as a function of the average fractions of hydrogen bonding,  $x_p$  and  $x_w$ , and the molar volumes,  $\Omega_p$  and  $\Omega_w$ , of the PEO monomer ( $\Omega_p = 39 \text{ cm}^3/\text{mol}$ ) and water ( $\text{D}_2\text{O}$ ) ( $\Omega_w = 18 \text{ cm}^3/\text{mol}$ ), respectively.

The average bond fractions,  $x_p$  and  $x_w$ , are determined in eqs S5 and S6. The ratio between both parameters is determined as

$$\frac{x_p}{1-x_p} = \exp\left\{\left(\Delta F_p^* - \Delta F_w^*\right)/RT\right\} \frac{x_w}{1-x_w} \quad (\text{S5})$$

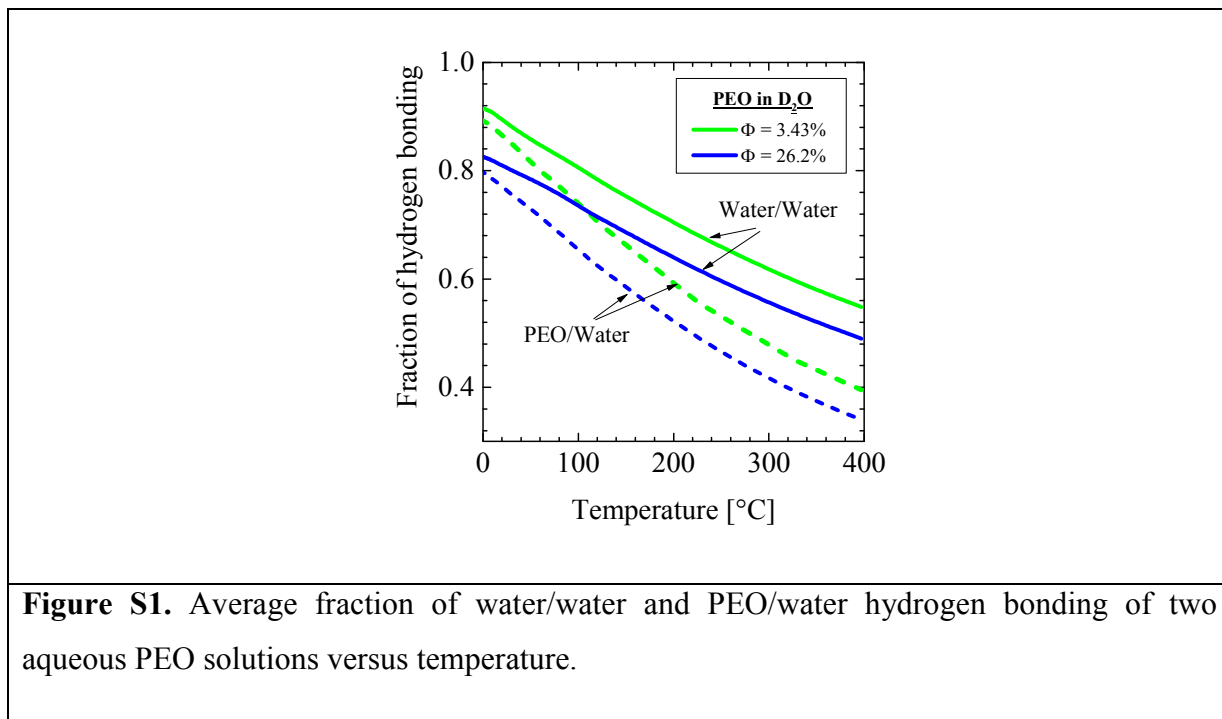
from which  $x_p \{x_w\}$  is determined via eq S6 (gas constant  $R = 8.31 \text{ J}/(\text{mol K})$ ). The normalized

$$x_p \{x_w\} = \exp(\Delta F_{p\{w\}}^*/RT) (1-x_p \{x_w\})^2 (1-\Phi) \left[ 1 - x_w - x_p \frac{\Phi \Omega_w}{(1-\Phi)\Omega_p} \right] \quad (\text{S6})$$

free energy of mixing per binding  $\Delta F^*/RT$  is a dimensionless quantity.

Numerical values of the average fractions of PEO/water ( $x_p$ ) and water/water hydrogen ( $x_w$ ) bonding are depicted in Figure S1 for two solutions of PEO volume fraction of 3.43% and 26.2% (Table 2) in a temperature interval between 0 and 400°C. The numerical values of the free energies of mixing  $\Delta F_w^*$  and  $\Delta F_p^*$  were taken from ref 2. The energy per association of water-water and PEO-water hydrogen bonding was chosen as  $\Delta E_w^*/R = 1800 \text{ K}$  (15 kJ/mol) and  $\Delta E_p^*/R = 2000 \text{ K}$  (16.7 kJ/mol), respectively. The corresponding entropic loss was assessed as  $\Delta S_w^*/R = 2.35$  and  $\Delta S_p^*/R = 3.27$  leading to the corresponding gain of free energies  $\Delta F_w^*/RT = 1800/T - 2.35$  and  $\Delta F_p^*/RT = 2000/T - 3.27$ . The change of free energy is determined as the difference of the free energy of the disordered (non-associated state) and ordered (PEO/water and water/water associated) state. According to  $\Delta F^* = \Delta E^* - T \Delta S^*$  the association through hydrogen bonding leads to a gain in energy  $\Delta E^*$  and a loss in entropy  $\Delta S^*$ . At high temperatures, i.e.  $T \Delta S^* > \Delta E^*$  the entropy will dominate the energy and will be the driving force for the

destruction of the PEO/water hydrogen bonds. This process becomes macroscopically visible from phase decomposition at high temperatures, i.e. beyond the LCST phase boundary.



The fraction of hydrogen bonds  $x_p$  and  $x_w$  in Figure S1 shows the expected decline of PEO/water and water/water hydrogen bonding at enhanced temperature and PEO concentration. A decline of PEO/water hydrogen bonding ( $x_p$ ) leads to a reduced hydrophilicity whereas a decline of water/water bonding ( $x_w$ ) to an enhanced solubility. The observed LCST characteristic of aqueous PEO shows a dominance of PEO/water hydrogen bonds with respect to water/water hydrogen bonds and van der Waals interaction. It should be mentioned that the average fraction of hydrogen bonds of the present model is independent from PEO molar mass.

## REFERENCES

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