Concentration dependence of the Flory-Huggins interaction parameter in aqueous solutions of capped PEO chains

Lawrence R. Pratt

Department of Chemical & Biomolecular Engineering

Tulane University

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\[ \chi(\varphi) \text{ in Aqueous Solutions} \]
Abstract

1. For aqueous solutions, the FH interaction ‘constant’ $\chi(\varphi)$ is a strong function of composition $\varphi$, thus the FH theory is not naively correct.

2. A principal reason for this is that a vdW picture fails for typical aqueous conditions.

3. For aqueous solutions, a focus on the small molecule solvent (the water) can be effective, avoids direct polymer stat-mech, and connects to osmotic stress experiments.
Capped PEO (aq): classic hydrophobic bond

\[ -kT \log v_P(r) \text{ (kcal/mol)} \]

\[ r \text{ (nm)} \]

\[ T = 297 \text{ K} \]

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1 M. I. Chaudhari and L. R. Pratt, OIL SPILL REMEDIATION: COLLOID CHEMISTRY-BASED PRINCIPLES AND SOLUTIONS, pp. 247-257, editors P. Somasundaran, R. S. Farinato, P. Patra, and K. Papadopoulos (John Wiley & Sons, Hoboken New Jersey, 2014): “Microstructures of capped ethylene oxide oligomers in water and n-hexane.”

[See: http://arxiv.org/abs/1303.6597 and https://dx.doi.org/10.6084/m9.figshare.3123898.v1 ]
High concentrations (here $m=11$, $M = 27.6$)
Flory-Huggins $\chi_{wp}(\varphi)$

1. FH theory

$$\frac{\beta \Delta G_{\text{mix}}}{n_w + M n_p} = \varphi \ln \varphi + \frac{(1 - \varphi)}{M} \ln (1 - \varphi) + \varphi (1 - \varphi) \chi_{wp}$$

2. ‘$w$’ = solvent (water), ‘$p$’ = polymer (internally complicated)

3. $p$ = PEG, $\chi_{wp}(\varphi)$ dependence on $\varphi$.
   - strong for water
   - substantial for methanol (but different from water)
   - weak for ethanol. Of course, $\text{PEG} = H - (\text{CH}_2 - \text{CH}_2 - \text{O}-)_M H$
Solution: follow the water

- The water reports on the polymer as in osmotic stress approaches:

\[ \beta \Delta \mu_{w}^{(ex)} = -\ln \varphi - \beta \pi \bar{v}_w \]

- Retain the concentration dependence of \( \chi_{wp} (\varphi) \):

\[ \beta \Delta \mu_{w}^{(ex)} = \left(1 - \frac{1}{M}\right) (1 - \varphi) + \frac{\partial (\varphi \chi_{wp})}{\partial \varphi} (1 - \varphi)^2 \]

- In the low p-concentration limit (\( p_{\text{solution}} \) = constant)

\[ \frac{\beta \pi V}{n_p} \sim 1 + \left( \frac{n_p}{V} \right) \bar{v}_w M^2 \left( \frac{1}{2} - \frac{\partial (\varphi \chi_{wp})}{\partial \varphi} \right) \]
Liquid water is an easy case by now.

- P Ball, *LIFE’S MATRIX: A BIOGRAPHY OF WATER* (University of California Press, 2001)

Figure 6.5 *Water molecules*—with hands representing hydrogens and feet representing lone pairs of electrons—perform a dance that involves grabbing neighbors by the ankles. These clasps, due to hydrogen bonding, lead to a tetrahedral arrangement of neighbors around each molecule. This is the central motif of the structure of water, and the key to all its anomalous properties.
Results

\[ \beta \Delta \mu_w^{(ex)} - \left( 1 - \frac{1}{M} \right) (1 - \varphi) \]

\[ \chi_{wp} \]

1. MI Chaudhari, LR Pratt, and ME Paulaitis, “Concentration dependence of the Flory-Huggins interaction parameter in aqueous solutions of capped PEO chains,” *J. Chem. Phys.* **141**, 244908 (2014).
Predicted/confirmed water-PEO phase separation

\[ \frac{\beta \Delta G_{\text{mix}}}{n_W + M n_p} \]

\( \chi(\varphi) \) in Aqueous Solutions
Osmotic pressure \( (p_{\text{solution}} = \text{constant}) \)

\[
\beta \pi \bar{v}_w = -\ln \varphi - \beta \Delta \mu_w^{(ex)}
\]

\( p_{\text{solution}} = \text{constant} \)
Conclusions

1. For aqueous solutions, the FH interaction ‘constant’ $\chi (\varphi)$ is a strong function of composition $\varphi$, thus the FH theory is not naively correct.

2. A principal reason for this is that a vdW picture fails for typical aqueous conditions.

3. For aqueous solutions, a focus on the small molecule solvent (the water) can be effective, avoids direct polymer stat-mech, and connects to osmotic stress experiments.