The Effect of Molecular Weight on Liquid-Liquid Immiscibility in Aqueous Solutions of Polyethylene Glycol Polymers Using the SAFT-VR Approach with Transferable Parameters

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The phase equilibria of aqueous solutions of polyethylene glycol (PEG) of moderate molecular weight are characterized by the presence of so-called cloud curves, which represent the region of liquid-liquid immiscibility between a water-rich phase and a polymer-rich phase. The systems exhibit a lower critical solution temperature (LCST), which denotes the lower limit of immiscibility; in some cases, a complete closed-loop region with an upper critical solution temperature (UCST) is seen corresponding to re-entrant miscibility. The low molecular weight aqueous PEG systems are completely miscible in water. At intermediate molecular weights of approximately 2000 g/mol, the systems start exhibiting a closed-loop region of liquid-liquid immiscibility. The immiscibility is brought on by the large asymmetry between the sizes of the water and polymer molecule; this polymer type of cloud point behavior is the same as that observed with, for example, solutions of polyethylene in cyclohexane. The mechanism is, however, different from that responsible for liquid-liquid immiscibility in aqueous solutions of the related alkyl polyoxyethylene (CiEj) surfactants [1]; in this case, the LCST is a direct consequence of the hydrogen-bonding between H_2O and CiEj at the lower temperatures, which give rise to a favorable change in enthalpy < 0. We use the SAFT-VR [2] equation of state to develop transferable models for the H_2O + PEG system and examine the liquid-liquid equilibrium phase behavior. By computing the thermodynamic functions of mixing (change in Gibbs free energy, enthalpy, and entropy of mixing), we examine the mechanism of phase separation as a function of molecular weight. Finally, we explore a relationship between the structure of the PEG molecule and the value of the unlike intermolecular potential parameter, which enables one to predict the phase behavior of aqueous solutions for any member of the PEG homologous series.

[1] M.N. Garcia-Lisbona, A. Galindo, G. Jackson, and A.N. Burgess, *Journal of the American Chemical Society* **120**, 4191 (1998).
[2] A. Gil-Villegas, A. Galindo, P.J. Whitehead, S.J. Mills, G. Jackson, and A.N. Burgess, *Journal of Chemical Physics* **106**, 4168 (1997).