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Comments

UNIFAC-FV Applied to Dendritic Macromolecules in Solution: Comment on “Vapor−Liquid Equilibria for Dendritic-Polymer Solutions” (Lieu, J. G.; Liu, M.; Fréchet, J. M. J.; Prausnitz, J. M. *J. Chem. Eng. Data* 1999, *44*, 613−620)

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Dendrimers have been proposed as rheology modifiers for use as processing aids,[1] as well as for other more specialized applications where predicting solubility in both small molecule solvents and polymer melts will be essential for tailoring the dendritic molecules for specific uses. The large number of end groups, core−shell structure, and constrained molecular conformations due to the high degree of branching make thermodynamic modeling of these macromolecules challenging.

In a recent article, Lieu et al.[2] report solvent activity coefficients measured in vapor−liquid equilibria experiments on dendritic polymer solutions. They further demonstrate that some but not all of their data can be correlated by a modified version of the Flory−Huggins lattice theory. The use of a model derived for linear polymer chains in semidilute solution to describe the more globular structure of dendrimers in solution is questionable, however, given the wealth of recent X-ray and small angle neutron scattering measurements as well as simulations[3] of dendrimer structures in solution.[4−10] Similarly, solution rheological properties strongly suggest a globular, unentangled structure for most dendrimers in solution and in the melt.[9−13] Given this recent wealth of structural data, we propose that the solvent activity of dendrimer solutions may be *predicted* by group-contribution methods that have been modified to account for the free volume contributions of the molecular architecture.

The free-volume modification[14] of the UNIFAC[15] model (UNIFAC-FV) is a predictive group-contribution method that accounts for the free volume of mixing of a structured macromolecule with a small molecule solvent. Flory’s polymer equation of state[16] provides a correction for the effects of polymer architecture (as characterized by the molecular free volume) on raising the free energy of the solution. This correction involves a “reduced volume” (ratio of specific volume to the hard-core specific volume) for the solvent and the mixture (which is presumed to be additive). In calculating this reduced volume, an empirical dimensionless parameter (b) is introduced as an adjustable fit parameter. Oishi and Prausnitz[14] successfully correlated VLE data for solutions of linear chains with the UNIFAC-FV theory with a single parameter value of $b = 1.28$. As this parameter reflects the determination of the hard-core specific volume of the molecules, we might anticipate that it will be affected by a high degree of branching in the macromolecule, as this would be expected to affect the ability of the solvent to penetrate into the dendrimers. Further, this would be expected to manifest itself as an increasing value of the excluded hard-core volume as the solvent’s molecular size is increased for a fixed macro-

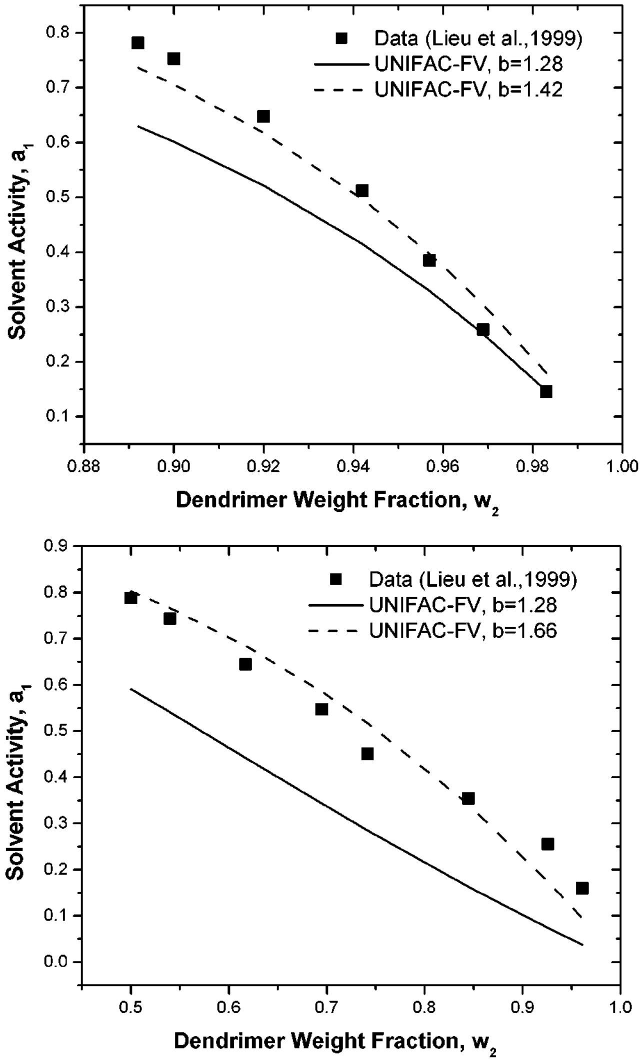

Figure 1. (a) Acetone activity in solution with the A4 dendrimer at 50 °C.[2] (b) Chloroform activity in solution with the B4 dendrimer at 70 °C.[2]

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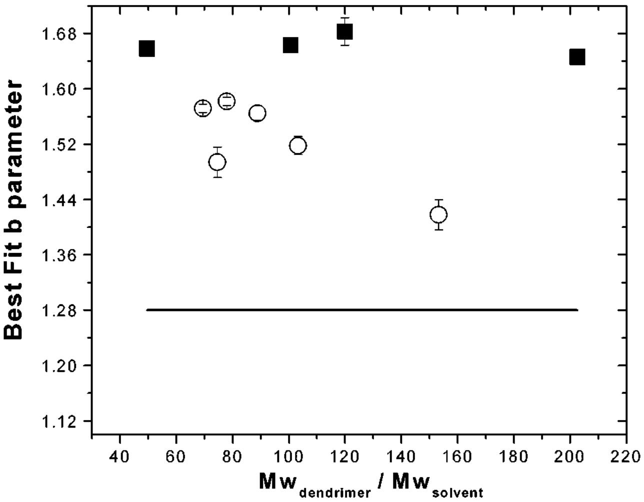

Figure 2. UNIFAC-FV best-fit *b* parameters obtained from fits to the solvent activity data of Lieu et al. plotted in terms of the molecular weight ratio of polymer to solvent. Open symbols represent the A series dendrimers; filled symbols represent the B series dendrimers. The solid line represents the recommended *b* parameter for linear polymers from ref 14.

molecular architecture.

The UNIFAC-FV model is applied to the data of Lieu et al., where we focus on the systems that were difficult to fit with the two-parameter, modified lattice cluster theory. Specifically, the model is applied to the fourth generation of poly(propylene imine) dendrimers fully surface-functionalized with C_{12} to C_{18} alkanes in acetone and C_6 to C_9 *n*-alkanes. The UNIFAC group parameters are taken from ref 17, and the modified Rackett technique[17] was used to estimate liquid densities as a function of temperature. The density of the dendrimer is set to 1.0 g/cm^3, consistent with that of Lieu et al.[2] Figure 1a shows a *prediction* of the solvent activity from the UNIFAC-FV model (with $b = 1.28$) as compared to representative solvent activity data for the A4 dendrimer in acetone. The theory underpredicts the data. However, an excellent *correlation* of the data can be obtained by adjusting $b = 1.42 \pm 0.02$, also shown in Figure 1a. Figure 1b shows the results for B4 in chloroform, where a good fit is achieved with a higher *b* value ($b = 1.66 \pm 0.03$). The results are similar for the other solvents, but with different values of the *b* parameter. The best-fit values of the *b* parameter are shown in Figure 2, where they are plotted as a function of the ratio of polymer to solvent molecular weight. The *b* values are all greater than the optimum value determined for Gaussian chains in a good solvent ($b = 1.28$). For the A4 series, there is a clear trend that tends toward the value expected for linear chains with decreasing solvent molecular weight. For the B3 to B5 series in chloroform, *b* is approximately 1.65, independent of generation number. The greater value in chloroform is not unexpected, as the bulky solvent is known not to penetrate inverse micelles[18] and dendrimers.[19] The values for B4 in *n*-heptane are also in this range and are slightly greater than those for A4 in *n*-heptane ($b = 1.57 \pm 0.01$).

Considerations of molecular structure suggest that the *b* parameter (molecular hard-core excluded volume) might be a function of polymer and solvent molecular architecture and molecular weight. Our observation suggests that, in predicting dendrimer solution thermodynamics, it is relevant to consider the penetrability of the solvent into the dendrimer and that this may be correlated to the molecular weight ratio of polymer to solvent for a given polymer architecture. We draw attention to this approach as a fruitful arena for molecular simulations and theory to address the influence of macromolecular hyperbranching on polymer solution thermodynamics.

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