

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/228540409>

Prediction of Activity Coefficients in Polymer and Copolymer Solutions Using Simple Activity Coefficient Models

ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · DECEMBER 1999

Impact Factor: 2.59 · DOI: 10.1021/ie990265q

CITATIONS

28

READS

31

3 AUTHORS:



Georgia D. Pappa

National Technical University of Athens

23 PUBLICATIONS 373 CITATIONS

SEE PROFILE



Epaminondas Voutsas

National Technical University of Athens

72 PUBLICATIONS 1,943 CITATIONS

SEE PROFILE



Dimitrios P. Tassios

National Technical University of Athens

118 PUBLICATIONS 3,446 CITATIONS

SEE PROFILE

Prediction of Activity Coefficients in Polymer and Copolymer Solutions Using Simple Activity Coefficient Models

Georgia D. Pappa, Epaminondas C. Voutsas, and Dimitrios P. Tassios*

Laboratory of Thermodynamics and Transport Phenomena, Department of Chemical Engineering, National Technical University of Athens, 9 Heroon Polytechniou Str., Zographou Campus, 15780 Athens, Greece

Using an extensive database that covers activity coefficients in systems of polymers and copolymers with nonpolar and polar solvents, we test the predictive capabilities of two simple activity coefficient models: the Entropic-FV (free volume) and a recent modification of UNIFAC by Zhong et al. (*Fluid Phase Equilib.* **1996**, 123, 97). The only information required for their application is the structure of the components and in the case of Entropic-FV also their molar volumes. The results, which include solvent and polymer activity coefficient predictions (the latter based on data from molecular simulation), indicate that both models provide satisfactory predictions—except where association is present—considering their simplicity, with the Entropic-FV one being superior to the modified UNIFAC proposed by Zhong et al. The latter, however, is a very good alternative when no accurate molar volumes are available.

1. Introduction

The availability of solvent and polymer activity coefficients is of great importance in the design and operation of polymer processes. Polymerization often takes place in solvents, and it is quite important to know how the produced polymer will distribute between the polymer-rich and solvent-rich phases. In such cases liquid–liquid equilibrium (LLE) information is necessary, i.e., both polymer and solvent activity coefficients. On the other hand, the removal of solvents or nonpolymerized monomers from the produced polymer requires the knowledge of vapor–liquid equilibrium (VLE), i.e., the solvent activity coefficients.

Because experimental phase equilibrium data are often missing, the availability of fast and reliable predictive methods is a practical necessity for the design and optimization of polymer processes. A great amount of predictive equations of state and activity coefficient models capable of describing phase equilibria in polymer solutions is available today. These models can be divided into the following three major categories: (a) those based on the Flory equation of state² such as the group-contribution Flory (GC Flory) equation of state,^{3–5} (b) those based on the lattice-fluid theory of polymer solutions as proposed by Panayiotou and Vera^{6,7} such as the group-contribution lattice-fluid (GCLF) equation of state,^{8,9} and (c) group-contribution activity coefficient models such as the UNIFAC-free-volume (FV) model of Oishi and Prausnitz¹⁰ and the Entropic-FV model.^{11,12} The models of the last category have the disadvantage over those of the first two that they do not take into account the pressure effect on the polymer phase equilibria. On the other hand, because they can be coupled with the UNIFAC group-interaction parameter tables, they can be applied to more classes of low-pressure polymer solutions.

This study deals with models that belong to the third category while a comparison of models belonging to the

first two categories and UNIFAC-FV from the third one is given by Danner and High.¹³ More specifically, using an extensive database, we evaluate the accuracy of the Entropic-FV model and a recently proposed model by Zhong et al.,¹ hereafter referred to as the UNIFAC-ZM model, in the prediction of activity coefficients in polymer mixtures. This model implicitly takes into account the free-volume effects on the activity coefficients in polymer solutions through the introduction of modified van der Waals volume parameters for the polymer. The UNIFAC-ZM model has the advantage over the Entropic-FV model that it does not require the knowledge of the molar volumes of the system components.

The two models employ the residual term of UNIFAC using, though, different group-interaction parameters. The Entropic-FV model uses the temperature-dependent parameters proposed by Hansen et al.¹⁴ and the UNIFAC-ZM the temperature-independent ones proposed by Hansen et al.¹⁵ Both sets of parameters were obtained from VLE data of low molecular weight compounds. In this study, we examine the use of both temperature-dependent and -independent interaction parameters in the two models.

The rest of the paper is organized as follows: First, the database used is presented, followed by a brief description of the models. Then, given that the Entropic-FV model requires the knowledge of the components' molar volumes, two methods for estimating polymer densities are compared: the GCVOL method¹⁶ and the Tait correlation.¹⁷ The two models are then applied in the prediction of activity coefficients in polymer/solvent mixtures. We close with our conclusions.

2. Database

To evaluate the accuracy of the two models studied here in the prediction of activity coefficients in all cases encountered in practice, an extensive database is used, which we classify into four categories:

a. Activity coefficients in athermal systems, i.e., systems where the residual term of UNIFAC is assumed to be equal to zero, that include the following:

* Corresponding author. E-mail: dtassios@orfeas.chemeng.ntua.gr.

- (i) Solvent activity coefficients at infinite dilution.
- (ii) Solvent and polymer activity coefficients at infinite dilution obtained from molecular simulation (MS).
- (iii) Solvent activity coefficients at intermediate concentrations.
- b. Activity coefficients in polymer systems with polar solvents where association is not present, that include the following:
 - (i) Solvent activity coefficients at infinite dilution.
 - (ii) Solvent activity coefficients at intermediate concentrations.
- c. Activity coefficients in systems where association is present that include the following:
 - (i) Solvent activity coefficients at infinite dilution.
 - (ii) Solvent activity coefficients at intermediate concentrations.
- d. Activity coefficients in copolymer/solvent systems that include the following:
 - (i) Solvent activity coefficients at infinite dilution.
 - (ii) Solvent activity coefficients at intermediate concentrations.

3. Activity Coefficient Models Considered

a. The Entropic-FV Model. The Entropic-FV model was proposed by Elbro et al.¹¹ and Kontogeorgis et al.¹² In contrast with the UNIFAC-FV model proposed by Oishi and Prausnitz,¹⁰ Entropic-FV does not include an additional term to the combinatorial one to account for the free-volume differences between solvents and polymers. In the Entropic-FV model the combinatorial and free-volume effects are both included in a combinatorial-FV expression, similar to the Flory–Huggins one, where free-volume fractions are used instead of volume fractions:

$$\ln \gamma_i^{\text{comb-fv}} = \ln \frac{\varphi_i^{\text{fv}}}{x_i} + 1 - \frac{\varphi_i^{\text{fv}}}{x_i} \quad (1)$$

where φ_i^{fv} is the fraction of free volumes:

$$\varphi_i^{\text{fv}} = \frac{x_i V_{fi}}{\sum_i x_i V_{fi}} \quad (2)$$

The free volume (V_f), which is the inaccessible to other molecules volumes, was assumed to be equal to

$$V_{fi} = V_i - V_{wi} \quad (3)$$

where V_i is the molar volume of the component i and V_{wi} the van der Waals volume as calculated by the method of Bondi.¹⁸

The Entropic-FV model uses the classical UNIFAC residual term with the linearly temperature-dependent interaction parameters proposed by Hansen et al.¹⁴

b. The UNIFAC-ZM Model. In a recent publication, Zhong et al.¹ used a UNIFAC-type model for VLE predictions in polymer/solvent mixtures. They introduced a modified van der Waals volume parameter (r) value for the polymer in the Flory–Huggins term of UNIFAC, which, according to the authors, is able to account for the free-volume effect, though no explicit free-volume term is involved.

For an n -mer chain molecule the volume parameter was set equal to:

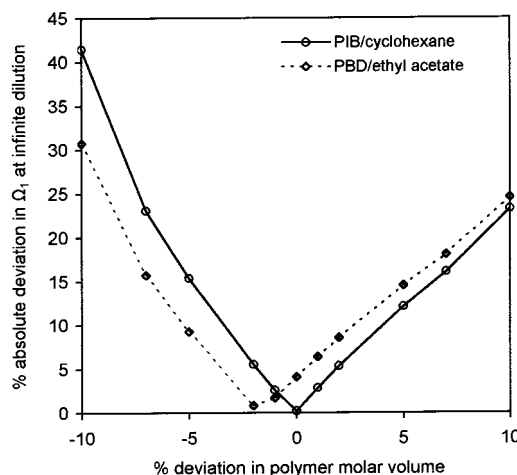


Figure 1. Sensitivity of the predictions obtained with Entropic-FV to errors in the polymer molar volumes.

$$r(n) = 0.6583nr(1) \quad (4)$$

where $r(1)$ is the volume parameter of the monomer.

Thus, the modified combinatorial term is given by

$$\ln \gamma_i^{\text{comb}} = \ln \frac{\phi_i'}{x_i} + 1 - \frac{\phi_i'}{x_i} - \frac{zq_i}{2} \left[\ln \frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i} \right] \quad (5)$$

where

$$\phi_1' = \frac{x_1 r_1}{x_1 r_1 + x_2 [0.6583nr(1)]}; \quad \phi_2' = \frac{x_2 [0.6583nr(1)]}{x_1 r_1 + x_2 [0.6583nr(1)]} \quad (6)$$

and

$$\phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 [nr(1)]}; \quad \phi_2 = \frac{x_2 [nr(1)]}{x_1 r_1 + x_2 [nr(1)]} \quad (7)$$

The UNIFAC-ZM model uses the classical UNIFAC residual term with the temperature-independent interaction parameters proposed by Hansen et al.¹⁵

4. Estimation of Densities

Application of the Entropic-FV model requires accurate knowledge of the molar volumes of both solvent and polymer because the obtained results are very sensitive to their values, as demonstrated in Figure 1 for two systems, one athermal (PIB/cyclohexane) and one with a polar solvent (PBD/ethyl acetate). Notice that the percent error in the Ω_1^∞ is about 2–3 times that of the volume. Reliable molar volume values for the typical solvents are available in the DIPPR correlation of experimental data.¹⁹ For polymers we examine two methods for the calculation of molar volumes: the Tait correlation¹⁷ and the predictive group-contribution method GCVOL.¹⁶

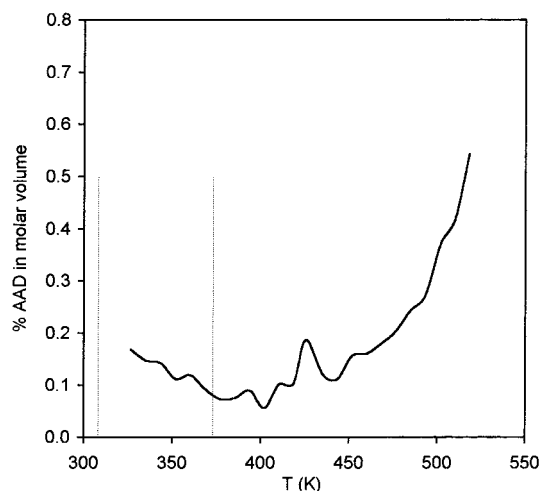
4.1. Polymers. The temperature range of applicability of the Tait correlation with the available by Rodgers¹⁷ parameters is rather narrow for the majority of polymers and, thus, we examined its extrapolation to a wider temperature range. On the other hand, GCVOL is applicable from the glass transition temperature up to the degradation one.

Table 1. Absolute Percent Average Deviation (% AAD) between Experimental²⁰ and Calculated Polymer Molar Volumes

| polymer | Trange of experimental data | Trange of applicability of Tait | % AAD ^a | |
|------------------|-----------------------------|---------------------------------|--|-------|
| | | | Tait | GCVOL |
| HDPE | 413–543 | 413–476 | 1.07 | 0.29 |
| PIB | 303–579 | 326–383 | 0.95 | 6.60 |
| PBD(cis) | 303–510 | 277–328 | 0.12 | 5.75 |
| PBD ^b | 304–495 | 277–328 | 1.00 | 4.44 |
| PS | 373–524 | 388–469 | 0.65 | 3.83 |
| PVAc | 327–518 | 308–373 | 0.18 | 3.23 |
| PEO | 323–483 | 361–497 | 0.61 | 3.41 |
| PEA | 303–489 | 310–490 | 0.14 | 6.63 |
| PBA | 303–482 | ^c | ^c | 4.12 |
| PMMA | 392–505 | 387–432 | 0.04 | 1.35 |
| PEMA | 303–456 | 386–434 | 0.48 | 1.31 |
| PBMA | 303–444 | 307–473 | 6.83 ^d (0.32 ^e) | 2.00 |
| PMA | 303–493 | 310–493 | 3.72 ^d (0.09 ^e) | 11.94 |

^a

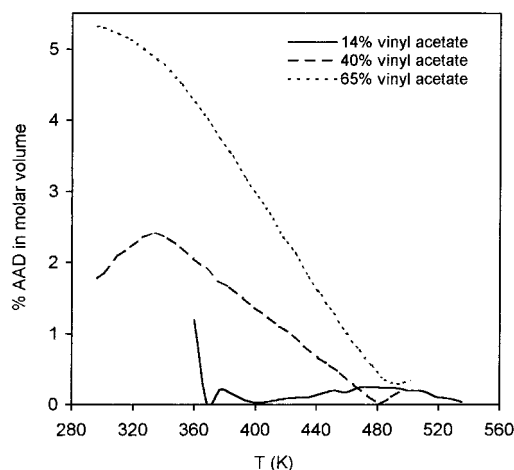
$$\% \text{AAD} = \frac{1}{\text{NP}} \sum_{i=1}^{\text{NP}} \frac{|V_i^{\text{calc}} - V_i^{\text{exp}}|}{V_i^{\text{exp}}} \times 100.$$

^b The Tait correlation was applied with the parameters of PBD(cis).^c Parameters for the Tait correlation are not available. ^d Using the old Tait parameters.¹⁷ ^e Using the parameters estimated in this work.**Figure 2.** % AAD in the molar volume of PVAc obtained with the Tait correlation (the dashed lines indicate the temperature range of applicability of the Tait correlation).**Table 2. Absolute Percent Average Deviation (% AAD) between Experimental and Calculated Copolymer Molar Volumes**

| copolymer | % composition | NP | Trange (K) | % AAD |
|------------------------------|-----------------------|----|------------|-------|
| poly(E-co-VAc) ^a | 14% vinyl acetate | 23 | 360–535 | 0.2 |
| | 40% vinyl acetate | 27 | 297–497 | 1.3 |
| | 65% vinyl acetate | 27 | 297–502 | 3.0 |
| poly(E-co-VA) ^a | 56% vinyl alcohol | 15 | 418–535 | 3.4 |
| | 70% vinyl alcohol | 9 | 469–536 | 3.7 |
| poly(E-co-P) ^a | 23% propylene | 29 | 295–581 | 0.8 |
| | 57% propylene | 36 | 295–582 | 1.0 |
| | 84% propylene | 28 | 296–575 | 1.2 |
| poly(EO-co-PO) ^b | 5–27% propylene oxide | 25 | 298–306 | 5.4 |
| poly(S-co-BD) ^c | 38.8–75% butadiene | 11 | 295–373 | 2.4 |
| poly(VE-co-BD) ^c | 67.7% butadiene | 1 | 298.2 | 4.3 |
| poly(VC-co-VAc) ^c | 15% vinyl acetate | 1 | 293.2 | 3.9 |
| poly(E-co-BD) ^c | 60% butadiene | 1 | 298.3 | 7.8 |

^a Experimental data from ref 20. ^b Experimental data from refs 22 and 23. ^c Experimental data from ref 24.

Table 1 presents the absolute average percent deviation (% AAD) obtained with the Tait correlation and the

**Figure 3.** % AAD in the molar volume of poly(ethylene-co-vinyl acetate) obtained with the GCVOL method for various concentrations in ethylene.**Table 3. Absolute Percent Average Deviation (% AAD) between Experimental²⁵ and Predicted Solvent Weight Fraction Based Activity Coefficients at Infinite Dilution for Athermal Systems**

| system | T (K) | NP | % AAD ^a | |
|---------------------------------|-------------|----|--------------------|-----------|
| | | | Entropic-FV | UNIFAC-ZM |
| LDPE(35000)/c-C ₆ | 383.2–473.2 | 5 | 4.9 | 3.9 |
| LDPE(35000)/C ₆ | 383.2–473.2 | 5 | 7.9 | 20.6 |
| LDPE(35000)/C ₇ | 383.2–473.2 | 5 | 6.1 | 12.6 |
| LDPE(35000)/C ₈ | 383.2–473.2 | 5 | 5.6 | 6.6 |
| PE(16600)/C ₄ | 397.2–423.2 | 2 | 35.9 | 33.9 |
| PE(15000)/C ₆ | 413.0–443.0 | 2 | 7.0 | 23.3 |
| PE(16600)/C ₆ | 397.2–473.2 | 3 | 10.4 | 14.5 |
| PE(82000)/3-C ₆ | 393.2–418.3 | 2 | 6.4 | 7.9 |
| PE(105000)/3-C ₆ | 418.6–425.8 | 2 | 14.1 | 18.0 |
| PE(82000)/2-C ₇ | 393.2–418.3 | 2 | 3.7 | 12.5 |
| PE(105000)/2-C ₇ | 418.6–425.8 | 2 | 7.9 | 18.5 |
| PE(82000)/3-C ₇ | 393.2–418.3 | 2 | 4.2 | 10.1 |
| PE(105000)/3-C ₇ | 418.6–425.8 | 2 | 8.6 | 16.2 |
| PE(82000)/2,4-C ₆ | 393.2–418.3 | 2 | 5.4 | 7.4 |
| PE(105000)/2,4-C ₆ | 418.6–425.8 | 2 | 7.6 | 12.2 |
| PE(82000)/2,5-C ₆ | 393.2–418.3 | 2 | 8.0 | 10.5 |
| PE(105000)/2,5-C ₆ | 418.6–425.8 | 2 | 10.4 | 15.4 |
| PE(82000)/3,4-C ₆ | 393.2–418.3 | 2 | 3.7 | 3.8 |
| PE(105000)/3,4-C ₆ | 418.6–425.8 | 2 | 7.6 | 3.0 |
| PE(15000)/C ₈ | 413.0–443.0 | 2 | 24.0 | 22.0 |
| PE(16600)/C ₈ | 397.2–523.2 | 4 | 10.7 | 2.0 |
| PE(82000)/C ₈ | 393.2–418.3 | 2 | 5.8 | 4.1 |
| PE(105000)/C ₈ | 418.6–425.8 | 2 | 8.5 | 7.3 |
| PE(82000)/C ₉ | 393.2–418.3 | 2 | 6.5 | 0.8 |
| PE(105000)/C ₉ | 418.6–425.8 | 2 | 10.1 | 6.1 |
| PE(82000)/C ₁₀ | 393.2–418.3 | 2 | 1.0 | 9.3 |
| PE(105000)/C ₁₀ | 418.6–426.5 | 2 | 9.9 | 2.6 |
| PE(82000)/C ₁₂ | 393.2–418.3 | 2 | 7.4 | 7.9 |
| PE(105000)/C ₁₂ | 418.6–426.5 | 2 | 10.6 | 2.6 |
| PE(82000)/2,2,4-C ₅ | 393.2–418.3 | 2 | 5.8 | 6.4 |
| PE(105000)/2,2,4-C ₅ | 418.6–426.5 | 2 | 9.2 | 12.5 |
| PIB(53000)/c-C ₆ | 323.2–423.2 | 5 | 2.7 | 11.9 |
| PIB(860000)/c-C ₆ | 313.1–323.1 | 2 | 9.4 | 13.2 |
| PIB(860000)/C ₅ | 313.1–323.1 | 2 | 13.6 | 36.4 |
| PIB(53000)/C ₆ | 323.2–423.2 | 4 | 6.4 | 31.0 |
| overall | | 90 | 8.2 | 12.2 |

$$\% \text{AAD} = \frac{1}{\text{NP}} \sum_{i=1}^{\text{NP}} \frac{|\Omega_{1,i}^{\infty}(\text{predicted}) - \Omega_{1,i}^{\infty}(\text{experimental})|}{\Omega_{1,i}^{\infty}(\text{experimental})} \times 100.$$

GCVOL method for 12 of the polymers examined in this study using the experimental data of Zoller and Walsh.²⁰ It is shown that Tait gives reliable results, with the exception of PBMA and PMA, even for temperatures

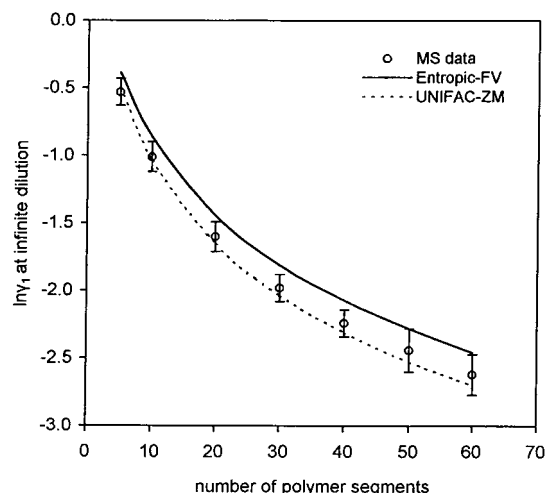


Figure 4. Predicted logarithms of monomer activity coefficient at infinite dilution for polymer–monomer systems compared with MS data.

outside its range of applicability, as demonstrated in Figure 2 for PVAc.

Especially for PBMA, the Tait correlation fails even in describing the experimental specific volumes of Olabisi and Simha²¹ used for the calculation of its parameters, yielding an overall error larger than 7%. Thus, we reestimate the parameters for the $V(0, T)$ term of the Tait equation:

$$V(0, T) = \sum_{i=0}^3 a_i t^i \quad (8)$$

where t is the temperature in degrees Celsius.

An a_2 value equal to 6.5803×10^{-7} was calculated instead of the 6.5803×10^{-6} one given by Olabisi and Simha²¹ and by Rodgers,¹⁷ while the values of the other three parameters α_0 , α_1 , and α_3 were the same as the originally proposed ones^{17,21} i.e., $\alpha_0 = 0.9341$, $\alpha_1 = 5.5254 \times 10^{-4}$, and $\alpha_3 = 1.5691 \times 10^{-10}$. With this set of parameters the overall error in the specific volumes of PBMA is less than 0.5% (Table 1).

Furthermore, we reestimated the Tait parameters for PMA using the experimental specific volumes of Zoller and Walsh.²⁰ For this polymer the $V(0, T)$ term of the Tait equation is

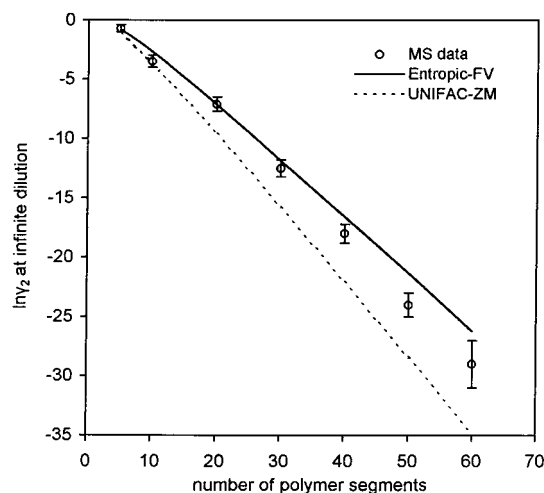


Figure 5. Predicted logarithms of polymer activity coefficient at infinite dilution for polymer–monomer systems compared with MS data.

$$V(0, T) = a_0 \exp(a_1 t) \quad (9)$$

where t is the temperature in degrees Celsius. The new values are $\alpha_0 = 0.8073$ and $\alpha_1 = 6.723 \times 10^{-4}$. With the new set of parameters the overall error obtained is less than 0.1% (Table 1).

The errors, on the other hand, obtained with GCVOL can be quite high as in the case of poly(acrylates) and poly(isobutylene).

From the results presented in Table 1 and Figures 1 and 2 it is obvious that the Tait correlation should be preferred over GCVOL in the application of the Entropic-FV model. On the other hand, GCVOL offers a good alternative for polymers where the parameters for the Tait correlation are not available, e.g., for PBA.

4.2. Copolymers. Here we examine only the GCVOL method because it can be applied directly in the prediction of copolymer molar volumes. Prediction results for eight copolymers with various concentrations are shown in Table 2. GCVOL performs satisfactorily when non-polar polymers are present except for the case of poly(E-co-BD), where the high error is due to the poor prediction of PBD molar volume (Table 1). Higher errors are obtained when polar polymers are present, e.g., poly(E-co-VAc) and poly(E-co-VA), especially at high concentrations, as shown in Figure 3. The latter has to be

Table 4. % AAD between Experimental²⁵ and Predicted Solvent Activity Coefficients at Intermediate Concentrations for Athermal Systems

| system | T range (K) | w_1 range | NP | % AAD | |
|--------------------------------------|-------------|---------------|-----|-------------|-----------|
| | | | | Entropic-FV | UNIFAC-ZM |
| PIB(1000000)/butane | 298.2–319.7 | 0.0182–0.1040 | 22 | 16.7 | 40.3 |
| PIB(1000000)/isobutane | 298.2–318.2 | 0.0068–0.0675 | 20 | 19.6 | 46.8 |
| PIB(2250000)/pentane | 298.2–328.2 | 0.185–0.888 | 33 | 4.9 | 8.8 |
| PIB(1000000)/isopentane | 298.2–319.7 | 0.008–0.152 | 24 | 19.7 | 38.6 |
| PIB(1000000)/neopentane | 298.2–319.7 | 0.0158–0.1315 | 10 | 23.6 | 43.3 |
| PIB(50000)/hexane | 298.2–338.2 | 0.0517–0.3363 | 23 | 3.2 | 11.9 |
| PIB(4700000)/2,2-dimethylbutane | 296.2 | 0.1139–0.1942 | 4 | 6.8 | 17.4 |
| PIB(4700000)/cyclopentane | 296.2 | 0.916–0.153 | 6 | 0.6 | 5.6 |
| PIB(40000)/cyclohexane | 298.2 | 0.1282–0.5686 | 8 | 7.3 | 8.1 |
| PIB(90000)/cyclohexane | 281.2–330.2 | 0.752–0.995 | 21 | 0.3 | 0.3 |
| PIB(100000)/cyclohexane | 298.2–338.2 | 0.082–0.827 | 29 | 4.3 | 5.2 |
| HDPE(50000)/hexane ^a | 353.2 | 0.0124–0.0953 | 7 | 17.6 | 19.0 |
| HDPE(50000)/hexane ^b | 410.2 | 0.0059–0.0828 | 8 | 19.7 | 28.9 |
| HDPE(50000)/cyclohexane ^a | 373.2 | 0.0069–0.0478 | 6 | 19.7 | 11.6 |
| overall | | | 221 | 10.5 | 20.4 |

^a Experimental data from ref 27. ^b Experimental data from ref 27.

Table 5. % AAD between Experimental²⁵ and Predicted Solvent Weight Fraction Based Activity Coefficients at Infinite Dilution for Systems Involving Polar Solvents

| system | T range (K) | NP | % AAD | | | |
|--------------------------------|-------------|----|---------------|-----------|-------------|-----------|
| | | | T-independent | | T-dependent | |
| | | | Entropic-FV | UNIFAC-ZM | Entropic-FV | UNIFAC-ZM |
| PVAc(83350)/ethyl acetate | 398–473 | 4 | 4.8 | 15.7 | 5.0 | 18.0 |
| PBD(22600)/ethylacetate | 353–373 | 3 | 1.6 | 8.4 | 2.8 | 7.0 |
| PMMA(85100)/methylacetate | 399–434 | 4 | 6.9 | 35.5 | 6.8 | 36.5 |
| PEMA(144000)/butylacetate | 418 | 1 | 16.4 | 32.5 | 17.0 | 33.0 |
| PEMA(40000)/ethylacetate | 418 | 1 | 18.0 | 37.3 | 18.8 | 37.9 |
| PBMA(8716)/ethylacetate | 373–413 | 3 | 15.6 | 23.2 | 18.6 | 25.9 |
| PVAc(83350)/MEK | 398–473 | 4 | 27.6 | 10.5 | 17.7 | 3.3 |
| PS(96200)/MEK | 397–448 | 3 | 11.8 | 8.2 | 9.7 | 14.3 |
| PBD(93000)/MEK | 339–369 | 4 | 9.4 | 23.8 | 22.9 | 39.1 |
| PBD(22600)/MiBK | 353–373 | 3 | 10.0 | 4.1 | 2.5 | 18.6 |
| PBD(22600)/acetone | 353–373 | 3 | 55.7 | 10.0 | 10.1 | 14.2 |
| PBMA(8716)/acetone | 373–413 | 3 | 11.5 | 21.6 | 14.4 | 19.6 |
| PEMA(144000)/acetone | 418 | 1 | 14.9 | 32.3 | 31.0 | 22.9 |
| PBMA(73500)/chlorobutane | 393–413 | 3 | 7.0 | 22.6 | 17.4 | 15.1 |
| PMMA(6107)/dichloromethane | 423–473 | 3 | 6.7 | 55.4 | 19.0 | 47.5 |
| PBMA(73500)/dichloromethane | 393–413 | 3 | 24.6 | 34.7 | 9.3 | 21.4 |
| PS(96200)/chlorobenzene | 397–448 | 3 | 4.4 | 19.6 | 9.9 | 32.5 |
| PBD(22600)/carbontetrachloride | 353–373 | 3 | 12.1 | 15.7 | 7.1 | 8.9 |
| PMA(63200)/benzene | 363–383 | 3 | 19.9 | 18.5 | 5.6 | 28.2 |
| PBD(22600)/benzene | 353–373 | 3 | 22.2 | 27.1 | 5.7 | 10.0 |
| PMA(63200)/toluene | 363–383 | 3 | 1.9 | 24.6 | 6.8 | 21.0 |
| PS(76000)/toluene | 413–473 | 4 | 6.3 | 14.2 | 5.9 | 13.8 |
| PEMA(144000)/toluene | 418 | 1 | 10.8 | 30.1 | 13.0 | 31.9 |
| overall | | 66 | 12.6 | 21.4 | 11.3 | 21.5 |

Table 6. % AAD between Experimental²⁹ and Predicted Solvent Activity Coefficients at Intermediate Concentrations for Systems Involving Polar Solvents

| system | T range (K) | w ₁ range | NP | T-independent | | T-dependent | |
|---------------------------------------|-------------|----------------------|-----|-------------------|-----------|-------------------|-----------|
| | | | | EntropicFV | UNIFAC-ZM | EntropicFV | UNIFAC-ZM |
| PS(15700)/acetone ^a | 298.2–323.2 | 0.042–0.429 | 14 | 16.1 | 5.9 | 13.9 | 4.5 |
| PS(290000)/MEK ^a | 298.2–343.2 | 0.052–0.529 | 17 | 15.6 | 5.3 | 10.8 | 10.7 |
| PS(290000)/propylacetate ^a | 298.2–343.2 | 0.063–0.524 | 19 | 18.5 | 2.2 | 23.9 | 6.6 |
| PS(290000)/toluene ^a | 298.2–353.2 | 0.102–0.918 | 14 | 7.1 | 3.0 | 5.6 | 1.7 |
| PS(600000)/toluene | 296.7 | 0.1427–0.2911 | 5 | 4.0 | 3.3 | 1.7 | 5.0 |
| PS(290000)/chloroform | 298.2–323.2 | 0.051–0.869 | 22 | 9.2 | 5.3 | 5.7 | 4.3 |
| PS(21800)/cyclohexane | 313.2–353.2 | 0.0238–0.3820 | 28 | 15.6 | 6.0 | 16.1 | 6.5 |
| PMA(63200)/toluene | 296.7 | 0.0840–0.1943 | 5 | 11.8 | 4.8 | 37.8 | 17.3 |
| PMA(63200)/benzene | 296.7 | 0.1141–0.2758 | 7 | 15.3 | 2.6 | 5.0 | 19.7 |
| PMMA(33200)/chloroform | 296.7 | 0.2459–0.5507 | 8 | 5.0 | 10.9 | 2.2 | 15.1 |
| PMMA(33200)/dichloromethane | 296.7 | 0.2105–0.4594 | 7 | 13.2 | 6.5 | 12.3 | 7.4 |
| PBA(33000)/benzene | 296.7 | 0.1762–0.3643 | 7 | 13.5 ^b | 7.6 | 3.1 ^b | 4.4 |
| PBA(33000)/toluene | 296.7 | 0.1407–0.3069 | 6 | 10.1 ^b | 7.3 | 27.8 ^b | 24.5 |
| PEA(38600)/benzene | 296.7 | 0.1798–0.3441 | 5 | 12.6 | 5.2 | 2.4 | 8.6 |
| PEA(38600)/toluene | 296.7 | 0.1126–0.3099 | 6 | 7.0 | 2.7 | 27.2 | 21.4 |
| PEMA(144000)/benzene | 296.7 | 0.1825–0.3034 | 5 | 17.1 | 5.0 | 3.0 | 8.3 |
| PEMA(144000)/toluene | 296.7 | 0.1126–0.3099 | 6 | 8.0 | 1.5 | 27.2 | 16.0 |
| PEO(5700)/benzene | 319.0–343.2 | 0.0290–0.7389 | 14 | 1.1 | 5.5 | 3.4 | 6.1 |
| PEO(600000)/benzene | 323.5–343.2 | 0.0967–0.7412 | 13 | 1.7 | 5.8 | 3.0 | 5.6 |
| PBD(65200)/cyclohexane | 296.7 | 0.1480–0.2274 | 4 | 6.6 | 3.6 | 11.9 | 2.4 |
| PBD(65200)/hexane | 296.7 | 0.0913–0.1644 | 4 | 9.1 | 4.6 | 15.9 | 11.7 |
| PBD(65200)/toluene | 296.7 | 0.1308–0.2853 | 4 | 1.1 | 9.2 | 12.0 | 3.4 |
| PIB(40000)/benzene ^a | 298.2 | 0.0437–0.3730 | 11 | 10.1 | 13.0 | 6.8 | 9.4 |
| PIB(50000)/ethylbenzene | 298.2–338.2 | 0.0184–0.3643 | 16 | 6.4 | 8.2 | 6.2 | 8.4 |
| PIB(50000)/toluene | 298.2–338.2 | 0.0114–0.2949 | 14 | 3.3 | 3.4 | 6.3 | 7.0 |
| overall | | | 261 | 10.2 | 5.6 | 11.0 | 8.2 |

^a Experimental data from ref 25. ^b PBA liquid densities were calculated by GCVOL.

taken under consideration when Entropic-FV is applied in the prediction of activity coefficients coupled with molar copolymer volumes from GCVOL.

5. Results: Polymer Systems

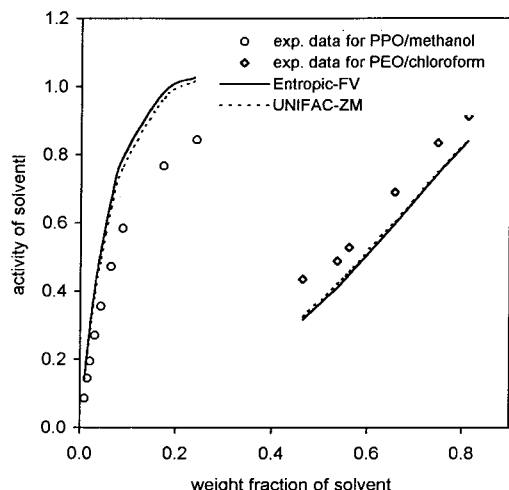
5.1. Athermal Systems. a. Infinite Dilution Region. Prediction results are shown in Table 3. The best overall results are obtained with the Entropic-FV model using polymer densities from the Tait correlation, with

typical errors in the range of 5–15%. Similar results are obtained with the Entropic-FV model employing polymer densities from GCVOL, except for the PIB systems because of the high errors obtained from GCVOL in the prediction of the PIB density (Table 1).

The performance of the UNIFAC-ZM model is remarkably good considering its simplicity. As expected, however, it has two main drawbacks. First, it cannot account for the temperature effect and, thus, for athermal mixtures it yields increased errors with increasing

Table 7. % Deviation between Experimental²⁵ and Predicted Solvent Weight Fraction Based Activity Coefficients at Infinite Dilution for Associated Systems

| system | T range (K) | NP | % AAD | | | |
|------------------------|-------------|----|---------------|-----------|-------------|-----------|
| | | | T-independent | | T-dependent | |
| | | | Entropic-FV | UNIFAC-ZM | Entropic-FV | UNIFAC-ZM |
| PEO(2000)/butanol | 348–392 | 3 | 43.0 | 72.7 | 15.1 | 39.1 |
| PEO(10700)/propanol | 343–393 | 3 | 31.0 | 29.5 | 4.3 | 6.0 |
| PEO(10700)/ethanol | 348–393 | 3 | 40.4 | 57.7 | 7.6 | 21.2 |
| PVAc(84300)/2-propanol | 398–473 | 4 | 81.5 | 58.0 | 2.1 | 13.1 |
| PS(20000)/1-propanol | 436–503 | 4 | 55.0 | 47.3 | 40.7 | 35.0 |
| PBD(93000)/1-propanol | 339–369 | 4 | 15.6 | 10.0 | 17.4 | 3.8 |
| PMMA(6107)/methanol | 423–473 | 3 | 94.7 | 3.8 | 78.2 | 7.1 |
| PS(20000)/acetic acid | 436–503 | 4 | 46.7 | 27.4 | 47.0 | 76.2 |
| overall | | 28 | 50.8 | 37.9 | 26.6 | 26.2 |

**Figure 6.** Experimental and predicted solvent activities in the systems PEO(6000)/chloroform at 298 K and PPO(2000)/methanol at 313 K.

temperature. Second, it cannot predict the branching effects as shown, for example, with the results obtained for PIB with respect to those for PE.

b. Molecular Simulation (MS) Data. MS data provide a means for investigating the performance of an activity coefficient model in areas where actual experimental data are not available. Sheng et al.²⁶ performed constant-pressure Monte Carlo simulations to obtain activity coefficient data at infinite dilution for both small and large molecules in mixtures with asymmetries varying from 5 to 60.

Figures 4 and 5 show a comparison between the predictions of the Entropic-FV and UNIFAC-ZM models with the MS data for monomer (solvent) and polymer activity coefficients. Given the uncertainty of the MS data denoted by the error bars of Figure 4, the two models give similarly good monomer activity coefficient predictions while Entropic-FV gives somewhat better results for polymer activity coefficients (Figure 5). It must be noted that the MS data include a degree of uncertainty because Sheng et al.²⁶ have estimated a higher than expected solvent free-volume percentage (66% instead of 40–50%).

c. Intermediate Concentrations. Solvent activity coefficient prediction results with the Entropic-FV and the UNIFAC-ZM models at intermediate concentrations for athermal systems are shown in Table 4. Because of the presence of a large number of PIB systems here, the performance of Entropic-FV—with polymer molar volumes from Tait—is substantially better than that of UNIFAC-ZM. Entropic-FV gives better results than

Table 8. % AAD between Experimental²⁹ and Predicted Solvent Weight Fraction Based Activity Coefficients at Infinite Dilution for Copolymer–Solvent Systems^a

| system | <i>T</i> range (K) | NP | % AAD | |
|---|--------------------|----|-------------|-----------|
| | | | Entropic-FV | UNIFAC/ZM |
| Styrene- <i>co</i> -isobutyl Methacrylate (70000) with 80% wt Styrene | | | | |
| benzene | 413.2 | 1 | 31.2 | 0.3 |
| chloroform | 413.2 | 1 | 42.1 | 14.5 |
| cyclohexane | 413.2 | 1 | 6.7 | 18.4 |
| Styrene- <i>co</i> -butadiene (107700) with 30% wt Styrene | | | | |
| benzene | 423.2–498.2 | 4 | 0.9 | 5.5 |
| cyclohexane | 423.2–498.2 | 4 | 24.9 | 25.5 |
| hexane | 423.2–473.2 | 3 | 26.4 | 10.4 |
| Ethylene- <i>co</i> -vinyl Acetate (43200) with 29% wt Vinyl Acetate | | | | |
| benzene | 423.6–433.7 | 2 | 7.9 | 3.9 |
| ethylacetate | 423.6–433.7 | 2 | 9.7 | 2.4 |
| cyclohexane | 423.6–433.7 | 2 | 28.1 | 28.3 |
| acetic acid | 423.6–433.7 | 2 | 65.3 | 109.7 |
| overall | | 22 | 22.0 | 21.7 |

^a Copolymer molar volumes were calculated by the GCVOL method.¹⁶

UNIFAC-ZM even when it uses polymer molar volumes from GCVOL (overall % AAD = 16.7).

5.2. Polymer Systems with Polar Solvents Where Association Is Not Present. a. Infinite Dilution Region. The Entropic-FV and UNIFAC-ZM models, combined either with the *T*-independent group interaction parameters of Hansen et al.¹⁵ or with the *T*-dependent ones of Hansen et al.,¹⁴ were applied in polymer systems with polar solvents such as some chlorinated hydrocarbons, aromatic hydrocarbons, ketones, esters, etc. The results shown in Table 5 indicate that the Entropic-FV model coupled with *T*-dependent group interaction parameters and polymer molar volumes from Tait gives the best results with typical errors in the range of 5–15%.

The UNIFAC-ZM results are poorer, with no improvement realized by the use of *T*-dependent parameters probably because it is counterbalanced by the insensitivity to temperature changes combinatorial term.

b. Intermediate Concentrations. The results presented in Table 6 indicate that both models give similar satisfactory results, which are not affected by the use of *T*-dependent parameters because of the low-temperature ranges involved.

5.3. Polymer Systems with Polar Solvents Where Association Is Present. In systems involving polymers such as PEO, PPO, etc., or solvents such as alcohols, acids, or CHCl₃, hydrogen bonding has a significant effect on the activity coefficients. Such systems can present only self-association like the system PS/propanol, both self- and cross-association like the system

Table 9. % AAD between Experimental and Predicted Solvent Activity Coefficients at Intermediate Concentrations for Copolymer-Solvent Systems

| system | T range (K) | w_1 range | NP | % AAD | UNIFAC-ZM |
|---|---------------|-------------|-----|-------------|-----------|
| | | | | Entropic-FV | |
| Ethylene- <i>co</i> -vinyl Acetate (30000) with 96.4% Ethylene ^a | | | | | |
| 2-methylheptane | 383 | 0.036–0.184 | 4 | 0.7 | 9.8 |
| cyclohexane | 383 | 0.007–0.141 | 8 | 19.8 | 25.0 |
| Ethylene- <i>co</i> -vinyl Acetate (14550) with 58.2% Ethylene ^b | | | | | |
| benzene | 323–343 | 0.251–0.693 | 22 | 6.2 | 6.9 |
| toluene | 323–363 | 0.205–0.625 | 32 | 5.8 | 8.5 |
| Ethylene- <i>co</i> -vinyl Acetate (4620) with 58.6% Ethylene ^b | | | | | |
| methyl acetate | 303 | 0.387–0.735 | 8 | 5.7 | 0.7 |
| ethyl acetate | 303–343 | 0.233–0.770 | 21 | 4.2 | 1.8 |
| propyl acetate | 303–363 | 0.190–0.802 | 32 | 12.0 | 9.3 |
| Styrene- <i>co</i> -butyl Methacrylate (200000) with 50% Styrene ^c | | | | | |
| acetone | 333 | 0.005–0.254 | 14 | 9.9 | 15.5 |
| chloroform | 343 | 0.078–0.512 | 7 | 39.2 | 25.0 |
| overall | | | 148 | 9.5 | 9.4 |

^a Experimental data from ref 25. ^b Experimental data from ref 29. ^c Experimental data from ref 30.

Table 10. % AAD between Experimental³¹ and Predicted Solvent Activity Coefficients at Intermediate Concentrations for Systems of Substituted PSMA with Various Solvents

| system | <i>T</i> (K) | <i>w</i> ₁ range | NP | % AAD | | |
|---|--------------|-----------------------------|----|-------------|--------------------------------|-----------|
| | | | | Entropic-FV | | UNIFAC-ZM |
| | | | | GCVOL | pol.den. = 1 g/cm ³ | |
| PSMA-C ₅ comb(116000)/acetone | 323 | 0.043–0.369 | 10 | 41.1 | 6.1 | 17.8 |
| PSMA-C ₁₂ comb(154000)/acetone | 323 | 0.035–0.335 | 10 | 32.9 | 10.6 | 19.0 |
| PSMA-C ₂₂ comb(213400)/acetone | 323 | 0.026–0.231 | 10 | 16.7 | 12.3 | 8.9 |
| PSMA-C ₁₂ comb(154000)/cyclohexane | 333 | 0.010–0.308 | 11 | 11.8 | 17.4 | 11.6 |
| PSMA-C ₂₂ comb(213400)/cyclohexane | 333 | 0.024–0.370 | 10 | 4.6 | 4.0 | 3.9 |
| overall | | | 51 | 21.2 | 10.2 | 12.2 |

PEO/propanol, or cross-association only as in the case of PEO/CHCl₃.

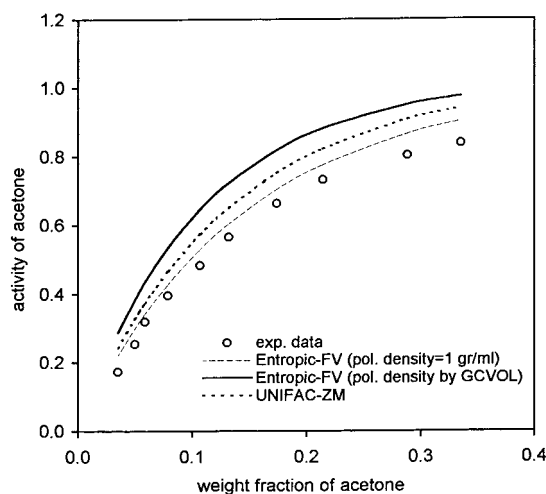
In the case of alcohols, the free volumes involved in the combinatorial term of Entropic-FV were calculated using the physical values for the van der Waals (vdW) volume parameters as suggested by Elbro et al.¹¹ For the UNIFAC-ZM model we examined the use of (a) physical vdW volume (*R*) and surface area (*Q*) parameters for the hydroxyl (OH) group and (b) the fitted ones calculated from the UNIFAC tables. It was found that use of the physical *R* and *Q* values for the OH group (*R*_{OH} = 0.53, *Q*_{OH} = 0.584) gives substantially better results, leading to an overall error equal to 19.4%, while by using the fitted ones (*R*_{OH} = 1.0, *Q*_{OH} = 1.2), the overall error is 43.8%.

Table 7 presents activity coefficient prediction results at infinite dilution for systems where hydrogen bonding is present. Use of the *T*-dependent group interaction parameters with the two models leads to better results. The relatively high errors observed are attributed to the fact that the two models do not take into account the association effect on the activity coefficients.

Typical predictions of solvent activities at intermediate concentrations are presented graphically in Figure 6. Again the predictions obtained with the two models deviate substantially from the experimental data.

6. Results: Copolymer Systems

6.1. Infinite Dilution Region. Table 8 presents solvent activity coefficient prediction results at infinite dilution with the Entropic-FV and the UNIFAC-ZM models for solvent/copolymer systems. The molar volumes needed for the Entropic-FV model were calculated with GCVOL. Furthermore, in all calculations the two

**Figure 7.** Experimental and predicted activities of acetone in the system PSMA-C₁₂ comb(213000)/acetone at 323 K.

models were applied coupled with the *T*-dependent parameters of Hansen et al.¹⁴ because of the high temperatures involved. The two models give satisfactory results except for the system with acetic acid where strong association effects are involved.

6.2. Intermediate Concentrations. Prediction results of the solvent activity coefficient at intermediate concentrations for ethylene/vinyl acetate and styrene/butyl methacrylate copolymers are shown in Table 9 where *T*-dependent parameters of Hansen et al.¹⁴ were used. As shown the two models give satisfactory results.

The two models were also applied to some systems containing very complex copolymers, as is the case of the substituted polystyrene/maleic anhydride (PSMA)

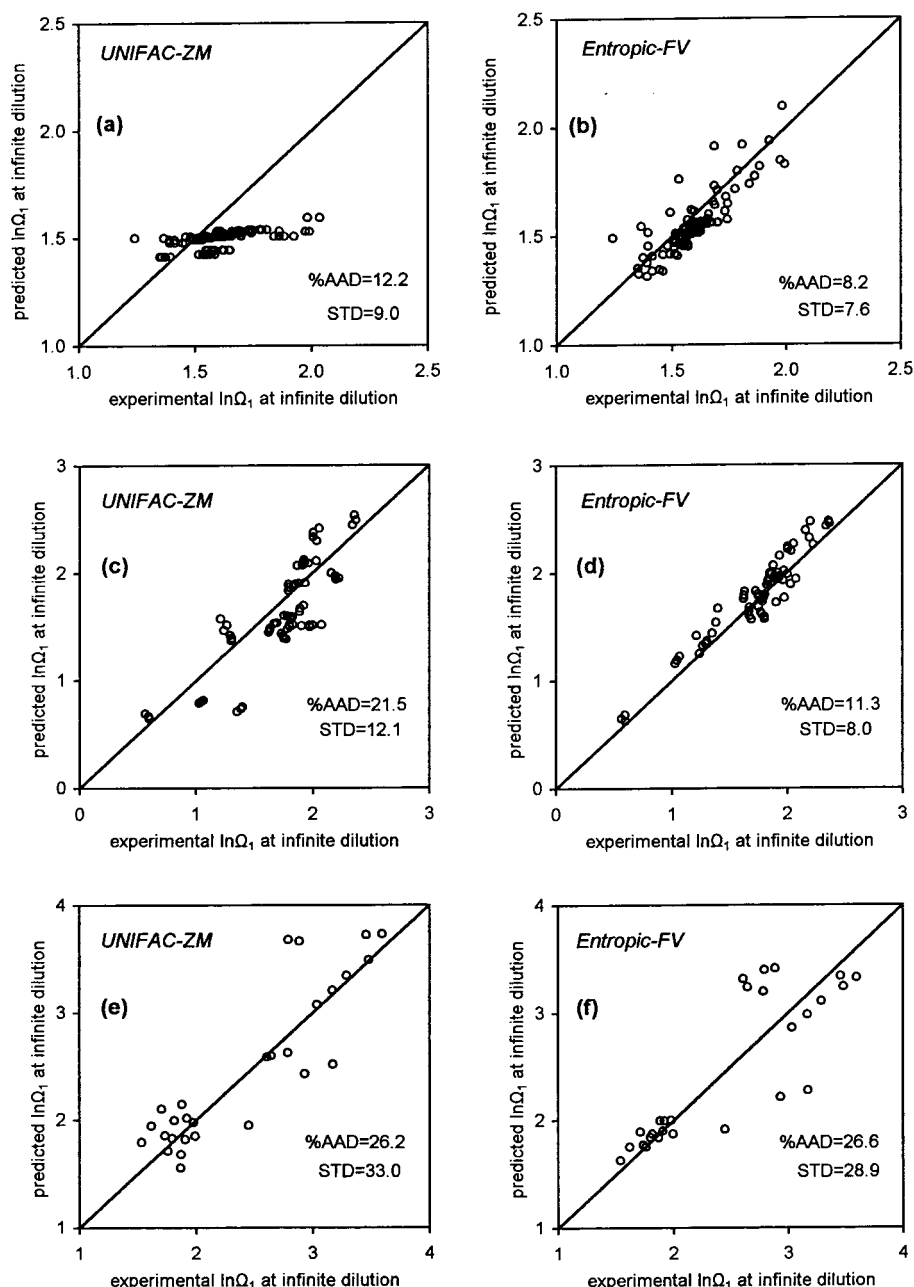


Figure 8. Logarithms of experimental and predicted solvent weight fraction activity coefficients at infinite dilution in (a and b) athermal systems, (c and d) systems containing polar solvents where hydrogen bonding is not present, and (e and f) systems where hydrogen bonding is present

$$\text{STD} = \frac{\sum_{i=1}^{\text{NP}} |\text{AAD} - \text{average}(\text{AAD})|}{\text{NP} - 1} \times 100$$

copolymers,³¹ hereafter referred to as combs. Alcohols (1-pentanol, 1-dodecanol, and 1-docosanol) were attached to the copolymer with esterification, and three different combs—PSMA-C₅, PSMA-C₁₂, and PSMA-C₂₂, respectively—were produced.

The necessary R and Q values for the CHC=O anhydride group of these copolymers are not available in the UNIFAC tables. Thus, we estimated these values as

$$R_{\text{CHCO}} = R_{\text{CH}_2\text{CHO}} - (R_{\text{CH}_2} - R_{\text{CH}})$$

$$Q_{\text{CHCO}} = Q_{\text{CH}_2\text{CHO}} - (Q_{\text{CH}_2} - Q_{\text{CH}})$$

and we used for this group the interaction parameters of the carbonyl group (CH_2CO).

The Entropic-FV model was applied with copolymer molar volumes predicted with the GCVOL method as well as by setting the copolymer density equal to 1 g/cm^3 as proposed by Mio et al.³¹

Table 10 presents prediction results for these systems with the two models while typical ones for the PSMA-C₁₂ comb/acetone system are shown in Figure 7. Both models perform satisfactorily, especially considering the complexity of the polymer and the simplified assumptions made for their application. The performance of the UNIFAC-ZM model is getting better as the copolymer side chains increase. Entropic-FV gives much better predictions when the copolymer density is set equal to 1 g/cm^3 .

7. Discussion

The following comments summarize our observations on the obtained results:

1. The predictions obtained with the Entropic-FV model are very sensitive to the values of the components' molar volumes. It should be, thus, used with reliable molar volume values such as those from the DIPPR correlation for the solvents¹⁹ and the Tait correlation for polymers.¹⁷ Note that as shown the latter provides reliable polymer molar values even when used outside the temperature range it was developed for.

2. The erratic performance of GCVOL in certain cases (Table 1) combined with the aforementioned sensitivity of Entropic-FV to the molar volumes does not make its use a reliable alternative to the simple UNIFAC-ZM approach, which does not require molar volumes.

3. This absence of molar volumes from the combinatorial term of the UNIFAC-ZM model leads, however, to two important limitations: a *T*-independent combinatorial and insignificant differentiation among isomers.

4. Use of the temperature-dependent group interaction parameters of Hansen et al.¹⁴ is recommended especially when high temperatures are involved.

5. The overall evaluation of the Entropic-FV and UNIFAC-ZM models in the prediction of solvent activity coefficients at infinite dilution is presented graphically in Figure 8a–f where the overall % AAD and the standard deviation (STD) of the predicted activity coefficient values are also shown. As demonstrated, the Entropic-FV model is overall better than the UNIFAC-ZM one. Satisfactory results are obtained, except for the cases where association is present.

6. It should be noted, finally, that as demonstrated by Bogdanic and Fredenslund³² polymer polydispersity has a very small effect on solvent activity coefficient predicted by the Entropic-FV model. This is in agreement with the experimental evidence.

8. Conclusions

Two simple activity coefficient models, the Entropic-FV and the UNIFAC-ZM, were evaluated in the prediction of activity coefficients using an extensive database involving solvent activity coefficients in polymer and copolymer systems.

The Entropic-FV model with polymer molar volumes from the Tait correlation provides the best results, but the performance of the UNIFAC-ZM must be considered satisfactory considering its simplicity. In the absence of experimental polymer molar volume values or parameters for the Tait correlation, the GCVOL method does not appear to offer a good alternative for the application of Entropic-FV. In these cases use of the UNIFAC-ZM model is recommended.

Use of the temperature-dependent group interaction parameters of Hansen et al.¹⁴ is recommended especially when high temperatures are involved. Finally, the two models in their present form do not give good results when association is present.

Acknowledgment

We thank C. Giannaris, senior at NTUA, who performed some of the calculations.

Nomenclature

n = number of monomers in a chain polymer
Q = group surface area parameter

R = group volume parameter

V = molar volume

V_f = free volume

V_w = van der Waals volume

x = mole fraction

w = weight fraction

z = coordination number (equal to 10)

% AAD = average percent absolute deviation

STD = standard deviation

Greek Letters

γ = activity coefficient

θ = surface area fraction

φ = volume fraction

φ' = modified volume fraction

φ^{fv} = free-volume fraction

Ω = weight fraction based activity coefficient

Ω^∞ = weight fraction based activity coefficient at infinite dilution

Subscripts

1 = solvent

2 = polymer

i = component

Polymers

HDPE = high-density polyethylene

LDPE = low-density polyethylene

PAA = poly(acrylic acid)

PBA = poly(butyl acrylate)

PBD = poly(butadiene)

PBMA = poly(butyl methacrylate)

PE = poly(ethylene)

PEA = poly(ethyl acrylate)

PEMA = poly(ethyl methacrylate)

PEO = poly(ethylene oxide)

PIB = poly(isobutylene)

PMA = poly(methyl acrylate)

PMMA = poly(methyl methacrylate)

PPO = poly(propylene oxide)

PS = poly(styrene)

PVAc = poly(vinyl acetate)

Poly(E-*co*-BD) = poly(ethylene-*co*-butadiene)

Poly(E-*co*-P) = poly(ethylene-*co*-propylene)

Poly(E-*co*-VA) = poly(ethylene-*co*-vinyl alcohol)

Poly(E-*co*-VAc) = poly(ethylene-*co*-vinyl acetate)

Poly(EO-*co*-PO) = poly(ethylene oxide-*co*-propylene oxide)

Poly(S-*co*-BD) = poly(styrene-*co*-butadiene)

Poly(S-*co*-BMA) = poly(styrene-*co*-butyl methacrylate)

Poly(S-*co*-iBMA) = poly(styrene-*co*-isobutyl methacrylate)

Poly(VC-*co*-VAc) = poly(vinyl chloride-*co*-vinyl acetate)

Poly(VE-*co*-BD) = poly(vinyl ethylene-*co*-butadiene)

PSMA-C₅ comb = poly(styrene-*co*-maleic anhydride) substituted with 1-pentanol

PSMA-C₁₂ comb = poly(styrene-*co*-maleic anhydride) substituted with 1-dodecanol

PSMA-C₂₂ comb = poly(styrene-*co*-maleic anhydride) substituted with 1-docosanol

Literature Cited

- (1) Zhong, C.; Sato, Y.; Masuoka, H.; Chen, X. Improvement of Predictive Accuracy of the UNIFAC Model for Vapor–Liquid Equilibria of Polymer Solutions. *Fluid Phase Equilib.* **1996**, *123*, 97.
- (2) Flory, P. J.; Oriji, R. A.; Vrij, A. Statistical Thermodynamics of Chain Molecule Liquids. I. An Equation of State for Normal Paraffin Hydrocarbons. *J. Am. Chem. Soc.* **1964**, *86*, 3507.
- (3) Holten-Andersen, J.; Fredenslund, A.; Rasmussen, P.; Carvoli, G. Phase Equilibria in Polymer Solutions by Group-Contribution. *Fluid Phase Equilib.* **1986**, *29*, 357.

- (4) Chen, F.; Fredenslund, Aa.; Rasmussen, P. Group-Contribution Flory Equation of State for Vapor-Liquid Equilibria in Mixtures with Polymers. *Ind. Eng. Chem. Res.* **1990**, *29*, 875.
- (5) Bogdanic, G.; Fredenslund, Aa. Revision of the Group-Contribution Flory Equation of State for Phase Equilibria Calculations in Mixtures with Polymers. 1. Prediction of Vapor-Liquid Equilibria for Polymer Solutions. *Ind. Eng. Chem. Res.* **1994**, *33*, 1331.
- (6) Panayiotou, C.; Vera, J. H. An Improved Lattice-fluid Equation of State for Pure Component Polymeric Fluids. *Polym. Eng. Sci.* **1982**, *22*, 345.
- (7) Panayiotou, C.; Vera, J. H. Statistical Thermodynamics of n -mer Fluids and their Mixtures. *Polym. J.* **1982**, *14*, 681.
- (8) High, M. S.; Danner, R. P. Application of the Group-Contribution Lattice-Fluid EoS to Polymer Solutions. *AIChE J.* **1990**, *36*, 1625.
- (9) Lee, B.-C.; Danner, R. P. Prediction of Polymer-Solvent Phase Equilibria by a Modified Group-Contribution EoS. *AIChE J.* **1996**, *42*, 837.
- (10) Oishi, T.; Prausnitz, J. M. Estimation of Solvent Activities in Polymer Solutions Using a Group-Contribution Method. *Ind. Eng. Chem. Process Des. Dev.* **1978**, *17*, 333.
- (11) Elbro, H. S.; Fredenslund, Aa.; Rasmussen, P. A New Simple Equation for the Prediction of Solvent Activities in Polymer Solutions. *Macromolecules* **1990**, *23* (21), 4707.
- (12) Kontogeorgis, G. M.; Fredenslund, Aa.; Tassios, D. P. Simple Activity Coefficient Models for the Prediction of Solvent Activities in Polymer Solutions. *Ind. Eng. Chem. Res.* **1993**, *32* (2), 362-372.
- (13) Danner, R. P.; High, M. S. *Handbook of Polymer Solution Thermodynamics*; Design Institute for Physical Property Data, AIChE: New York, 1993.
- (14) Hansen, H. K.; Coto, B.; Kuhlmann, B. UNIFAC with Linearly-Dependent Group-Interaction Parameters. Technical Report, IVC-SEP-9212; Research Engineering Center, Institut for Kemiteknik, The Technical University of Denmark: Lyngby, Denmark, 1992.
- (15) Hansen, H. K.; Rasmussen, P.; Fredenslund, Aa.; Schiller, M.; Gmehling, J. Vapor-Liquid Equilibria by UNIFAC Group Contribution. 5. Revision and Extension. *Ind. Eng. Chem. Res.* **1991**, *30*, 2352.
- (16) Elbro, H. S.; Fredenslund, Aa.; Rasmussen, P. Group Contribution Method for the Prediction of Liquid Densities as a Function of Temperature for Solvents, Oligomers and Polymers. *Ind. Eng. Chem. Res.* **1991**, *30* (12), 2576.
- (17) Rodgers, P. A. Pressure-Volume-Temperature Relationships for Polymeric Liquids: A Review of Equations of State and their Characteristic Parameters for 56 Polymers. *J. Appl. Polym. Sci.* **1993**, *48*, 1061.
- (18) Bondi, A. *Physical Properties of Molecular Crystals, Liquids and Glasses*; John Wiley & Sons: New York, 1968.
- (19) Daubert, T. E.; Danner, R. P. *Physical and Thermodynamic Properties of Pure Compounds: Data Compilation*; Hemisphere: New York, 1989.
- (20) Zoller, P.; Walsh, D. *Standard Pressure-Volume-Temperature Data for Polymers*; Technomic: Lancaster, PA, 1995.
- (21) Olabisi, O.; Simha, R. Pressure-Volume-Temperature Studies of Amorphous and Crystallizable Polymers. I. Experimental. *Macromolecules* **1975**, *8*, 206.
- (22) Ashman, P. C.; Booth, C. Crystallinity and Fusion of Ethylene Oxide/Propylene Oxide Block Copolymers: 1. Type PE Copolymers. *Polymer* **1975**, *16*, 889.
- (23) Ashman, P. C.; Booth, C.; Cooper, D. R.; Price, C. Crystallinity and Fusion of Ethylene Oxide/Propylene Oxide Block Copolymers: 2. Type PEP Copolymers. *Polymer* **1975**, *16*, 897.
- (24) Bogdanic, G.; Fredenslund, Aa. Prediction of Vapor-Liquid Equilibria for Mixtures with Copolymers. *Ind. Eng. Chem. Res.* **1995**, *34*, 324.
- (25) Wen, H.; Elbro, H. S.; Alessi, P. *Polymer Solution Data Collection*; DECHEMA Chemistry Data Series; DECHEMA: Frankfurt/Main, Germany, 1992.
- (26) Sheng, Y.-J.; Panagiotopoulos, A. Z.; Tassios, D. P. Activity Coefficients in Nearly Athermal Model Polymer/Solvent Systems. *AIChE* **1995**, *41* (10), 2306.
- (27) Brockmeier, N. F.; McCoy, R. W.; Meyer, J. A. Gas Chromatographic Determination of Thermodynamic Properties of Polymer Solutions. II. Semicrystalline Polymer Systems. *Macromolecules* **1973**, *6*, 176.
- (28) Bonner, D. C.; Brockmeier, N. F.; Cheng, Y.-I. Thermodynamics of Some Concentrated High Polymer Solutions. *Ind. Eng. Chem. Process Des. Dev.* **1974**, *13*, 437.
- (29) Wohlfarth, C. *Vapour-Liquid Equilibrium Data of Binary Polymer Solutions*; Physical Sciences Data 44; Elsevier: New York, 1994.
- (30) Gupta, R. B.; Prausnitz, J. M. Vapor-Liquid Equilibria of Copolymer + Solvent and Homopolymer + Solvent Binaries: New Experimental Data and Their Correlation. *J. Chem. Eng. Data* **1995**, *40*, 784.
- (31) Mio, C.; Jayachandran, K. N.; Prausnitz, J. M. Vapor-Liquid Equilibria for Binary Solutions of Some Comb Polymers Based on Poly(styrene-co-maleic anhydride) in Acetone, Methanol and Cyclohexane. *Fluid Phase Equilib.* **1997**, *141*, 165.
- (32) Bogdanic, G.; Fredenslund, Aa. Prediction of Vapor-Liquid Equilibria for Mixtures with Copolymers. *Ind. Eng. Chem. Res.* **1995**, *34*, 324.

Received for review April 13, 1999

Revised manuscript received September 10, 1999

Accepted September 17, 1999

IE990265Q