

CORRELATION OF SOLVENT ACTIVITIES IN POLYMER SOLUTIONS: A COMPARISON OF MODELS

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Abstract

The activity coefficient models that have been proposed for correlation of Vapor-Liquid Equilibrium (VLE) of polymer solutions are often based on an ad-hoc coupling of the combinatorial (free-volume) and residual terms available in the literature. The goal of this work is to present a comparison of the performances of all the possible models that can be obtained based on some of the best and most used combinatorial (free volume) and residual terms. The combinatorial terms studied here are the Entropic free volume, p-free volume and Freed FH and the residual terms the NRF, UNIQUAC and Wu-NRTL along with a segment based UNIQUAC term, sUNIQUAC, here proposed for the first time. All the models investigated have two adjustable parameters and a two-parameter Flory-Huggins model was used as benchmark for comparative purposes. A database of 70 VLE data systems was used to evaluate the different models.

It is shown that models based on the p-free volume combinatorial term with a segment based residual part derived from either the NRTL or UNIQUAC models can provide an excellent correlation of VLE data for polymer systems and can describe a wide range of molecular weights using a single pair of interaction parameters. The NRF based models are shown to suffer from some deficiencies that limit their application to dilute solutions.

Keywords: Model, Activity coefficient, Vapor-liquid Equilibria, Polymer

Introduction

The knowledge of the vapour-liquid equilibrium (VLE) of polymer solutions is of great importance for the manufacturing and processing of polymeric materials. In the last few years a wide variety of excess free energy models has been proposed for the activity coefficient of solvents in polymer solutions, including many free volume activity coefficient models such as UNIFAC-FV ^[1] and Entropic-FV ^[2] among others. The activity coefficient models can be seen as a sum of two terms: a combinatorial-free volume term and a residual term.

$$\ln \gamma_i = \ln \gamma_i^{comb-fv} + \ln \gamma_i^{res} \quad (1)$$

The combinatorial part accounts for the entropic effects, mainly related to the size and shape differences of the molecules present in the solution, while the residual part accounts for the energetic interactions existent between the solvent and the polymer. From the several excess free energy models presented in the literature only those related to the work developed here will be discussed.

Chen et al. ^[3] developed a segment based local composition model that uses a combination of the Flory-Huggins expression for the entropy of mixing of molecules and the NRTL to account for the energetic interactions. More recently Wu and coworkers ^[4] developed a modified NRTL model to represent the Helmholtz free energy in polymer solutions that was coupled with the Freed et al ^[5, 6] (Freed FH) model truncated after the first correction to account for entropic contributions. Zafarani-Moattar and coworkers ^[7] proposed a modification to the non-random factor model earlier presented by Haghtalab and Vera ^[8] making it usable for polymer solutions to account for the energetic interactions. In the model developed by Zafarani-Moattar the Freed model is again used to account for the combinatorial contribution.

Although the concept of free volume can be traced back to the work of Flory its first explicit introduction into an activity coefficient model was done by Elbro and coworkers ^[2] when they proposed the Entropic free volume for size-asymmetric solutions such as polymer solutions. This model is very similar to the Flory-Huggins but free volume fractions are used instead of volume fractions and better results are achieved. The free volume itself is defined as:

$$V^{FV} = V - V_w \quad (2)$$

Where V_w is the van der Waals volume which represents the hard-core volume of the molecules. According to this model the free volume is the difference between the actual volume occupied by a molecule and its hard-core volume. Kontogeorgis et al.^[9] developed a correction to the Elbro model, accounting for the difference in size between the molecules of solvent and polymer, resulting in the p-free volume model.

Using these combinatorial and residual terms it is possible to combine them to form distinct models to correlate experimental data. In this work, the correlating capabilities of the models thus obtained are evaluated.

The advantage of the segment based models over conventional models for correlation of polymer solution experimental data is, unlike with the classical models, their ability to cover a wide range of polymer molecular weights with a single pair of interaction parameters, what confer them a predictive capability. A segment based UNIQUAC model, sUNIQUAC was here developed following the approach of Wu et al.^[4]. This residual term is here evaluated along with the other models

Since, as mentioned, the segment based models present some predictive capabilities their predictive character will also be evaluated for the accuracy and reliability to verify if they can be used outside the range of data used in the correlation of the interaction parameters.

Thermodynamic models

The solvent's activity coefficient calculation requires the contribution of two terms: a combinatorial (free volume) accounting for the differences in size and shape (and free volume) and a residual accounting for the energetic interactions between the molecules. In this work a comparison between the activity coefficient models resulting from the combination of the better and best-known combinatorial (free volume) and residual terms is performed.

Combinatorial terms

The models used for the combinatorial part of the activity coefficient model where the Entropic free volume^[2], the Freed *Flory-Huggins* model^[5, 6] and the p-free volume

model^[10]. Previous works have established the advantages of the free volume terms studied as well as their limitations^[10-12]. The Freed FH term was studied since it has been adopted in several recent polymer models^[4, 7].

Both the Entropic free volume and the p-free volume terms are based in the Flory-Huggins model with the difference that they use free volume fractions instead of volume fractions. The free volume is defined in Eq. (2).

In the p-free volume model a correction factor, p, defined as:

$$p = 1 - \frac{V_s}{V_p} \quad (3)$$

was introduced into the original Entropic free volume. With this parameter the free volume is now defined as:

$$V^{FV} = (V - V_w)^p \quad (4)$$

For both models, Entropic free volume and p-free volume, the free volume fraction is then defined as:

$$\phi_i^{FV} = \frac{x_i V_i^{FV}}{\sum_j x_j V_j^{FV}} \quad (5)$$

The combinatorial term based in these free volume fractions can be described as:

$$\ln \gamma_s^{comb-fv} = \ln \frac{\phi_s^{FV}}{x_s} + 1 - \frac{\phi_s^{FV}}{x_s} \quad (6)$$

The Freed *Flory-Huggins* model is a modification to the original Flory-Huggins in the sense that it is the exact solution for the Flory-Huggins lattice theory. The solution is a polynomial expansion in powers of a non-randomness factor similar to the factor present in NRTL. Freed only used the first correction. Hence:

$$\ln \gamma_s^{comb} = \ln \frac{\phi_s}{x_s} + \left(1 - \frac{r_s}{r_p}\right) \phi_p + \alpha \left(\frac{1}{r_s} - \frac{1}{r_p}\right)^2 \phi_p^2 \quad (7)$$

This combinatorial term, unlike the terms described previously, does not take into account the free volume contributions to the free energy.

Residual terms

The residual contribution term accounts for the energetic interactions between solvent and polymer. The residual terms used in this work were the original UNIQUAC^[13] and three segment based local composition models: NRF^[7], NRTL as proposed by Wu et al^[4], and sUNIQUAC a residual term based on UNIQUAC developed in this work. All these terms have two interaction parameters to be fitted to experimental data.

The NRF model used is a segment-based modification of the original NRF model made by Zafarani-Moattar^[7] and can be described as:

$$\ln \gamma_s^{res} = \frac{x_s^2 \lambda_s + 2r_p x_p x_s \lambda_s + r_p x_p^2 \lambda_{seg}}{(x_s + r_p x_p)^2} - \frac{r_p x_p^2 \lambda_{seg} e^{-\alpha \lambda_{seg}}}{(x_s + x_p e^{-\alpha \lambda_{seg}})^2} - \frac{x_s^2 \lambda_s + 2x_s x_p \lambda_s e^{-\alpha \lambda_s}}{(x_s + x_p e^{-\alpha \lambda_s})^2} \quad (8)$$

Being λ_s and λ_{seg} the energetic interaction parameters for the solvent and polymer segments respectively. Following Wu et al^[4] Zafarani-Moattar defined these parameters as functions of temperature, using only first a first order approach:

$$\lambda_s = a_{12} \frac{T_o}{T} \quad (9)$$

$$\lambda_{seg} = a_{21} \frac{T_o}{T} \quad (10)$$

The parameters, a_{12} and a_{21} , are temperature independent.

The model proposed by Wu and his coworkers^[4] is a segment-based modification of the original NRTL model with the following form:

$$\ln \gamma_s^{res} = q_s X_p^2 \left(\frac{\tau_{ps} G_{ps}^2}{(X_s + X_p G_{ps})^2} + \frac{\tau_{sp} G_{sp}}{(X_p + X_s G_{sp})^2} \right) \quad (11)$$

In which the energetic terms are expressed as in the NRTL model.

$$\tau_{ij} = e^{\frac{a_{ij}}{RT}} \quad (12)$$

$$G_{ij} = e^{-\alpha \tau_{ij}} \quad (13)$$

The term a_{ij} is the parameter fitted to the experimental data.

The composition used in the model is not the molar composition but the segment composition defined as

$$X_i = \frac{N_i q_i}{N_q}, \quad (14)$$

$$N_q = \sum_i N_i q_i \quad (15)$$

With N_i being the number of molecules of component i and N_q is the total number of segments present in the solution mixture. The q_i parameter is the actual number of segments for species i and is usually related to r_i by:

$$q_i = r_i \left(1 - 2\alpha \left(1 - \frac{1}{r_i} \right) \right) \quad (16)$$

The α parameter is the non-random factor defined in the same way as in the NRTL model, and was made equal to 0.4 throughout this work.

The value of r_i is equal to unity for the solvent and for the polymer it given by the ratio between the polymer and solvent volumes.

The UNIQUAC model was also studied as it generally provides a good description of the experimental data. The residual part of the UNIQUAC model for a binary mixture is presented below.

$$\ln \gamma_s^{res} = -q_s \ln(\theta_{s1} + \theta_p \tau_{ps}) + \theta_p q_s \left(\frac{\tau_{ps}}{\theta_s + \theta_p \tau_{ps}} - \frac{\tau_{sp}}{\theta_p + \theta_s \tau_{sp}} \right) \quad (17)$$

The parameters τ_{ij} and θ_i are defined as:

$$\tau_{ij} = e^{-\frac{a_{ij}}{T}} \quad (18)$$

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \quad (19)$$

With the a_{ij} being the energetic parameters to be fitted to the experimental data.

The sUNIQUAC model has been derived following the approach of Wu and coworkers for the development of a segment based model^[4]. In this model the segment composition is defined in the same way as in the Wu-NRTL model, and the same definitions of q_i and r_i also applies. The residual term has the following form:

$$\ln \gamma_s^{res} = -q_s \ln(X_s + X_p \tau_{ps}) + X_p q_s \left(\frac{\tau_{ps}}{X_s + X_p \tau_{ps}} - \frac{\tau_{sp}}{X_p + X_s \tau_{sp}} \right) \quad (20)$$

with the X_i being the segment fraction defined in Eqs. (14)-(15), and τ_{ij} defined as for the UNIQUAC model. A detailed derivation of this model is presented in Appendix A.

Results and discussion

The grouping of the combinatorial (free volume) and residual terms presented above lead to various activity coefficient models some of which have been previously proposed in the literature and others which are here studied for the first time. These models have been tested for their performance by fitting them to experimental VLE data. A total of 70 experimental data sets of polymer-solution systems from the literature^[14, 15] were used in this work to compare the overall performance of all models studied by correlating them to these sets of experimental data. As mentioned above all the models studied have two interaction energy parameters to be fitted to the experimental data. For the segment based models the α parameter was fixed to a value of 0.4.

The results obtained by the various models were compared to the results obtained with a two parameter Flory-Huggins model since this is a standard model for the correlation of phase behaviour of polymer solutions. The Flory-Huggins combinatorial term was coupled with a χ parameter residual term using a linear dependence on the inverse of the temperature^[9]:

$$\chi = a + \frac{b}{T} \quad (21)$$

The results obtained from the correlation of the experimental data for the various models studied are reported in Table 1 as percent improvement, defined as $AAD_{FH}/AAD-1$, over the Flory-Huggins model. These results show the advantage of the p-free volume over the other combinatorial free volume terms studied. For both NRF and sUNIQUAC residual terms it produces a description of the data that is consistently superior to the other combinatorial terms used. The p-free volume term suffers, however, from the limitation that it can only be applied to binary systems since there is no way to extend its validity to multicomponent systems. For these the use of the

combinatorial free volume term recently proposed by Kouskoumvekaki et al. ^[12] is suggested. On their work the authors state that the volume accessible to a molecule is smaller than the volume admitted by the Entropic free volume definition. Instead a volume larger than the molecules' hard-core is effectively inaccessible to the solvent and the free volume is defined as:

$$V^{FV} = V - cV_w \quad (22)$$

where the constant c has, according to the authors, the optimum value of 1.2 for the majority of the systems. This combinatorial term seems to have a behaviour close to the p-free volume with the advantage of an easy extension to multicomponent systems.

In what concerns the residual term the results reported in Table 1 clearly show the advantage of the UNIQUAC based models. The model indicated by this work to be recommended for VLE correlation would thus be a combination of an UNIQUAC residual term with the p-free volume combinatorial term. With an AAD% slightly above 1% for the ensemble of the database studied this model would provide a description of the data within their experimental uncertainty.

It should be kept on mind that the possibility of using a third adjusting parameter offered by the NRF or NRTL based models can be of importance in the description of LLE, for the correlation of VLE data, however, the UNIQUAC-p-free volume model seems to be more adequate.

A comparison with the performance of a predictive activity coefficient model was also carried. The UNIFAC-FV model ^[11] was used and a global AAD% of circa 8% was obtained. This is a deviation that although acceptable for many purposes is superior to the uncertainty of the experimental data. Deviations are particularly large polar for systems such as PDMS / Benzene (Mn = 3850) (24 %) and PEG / water (Mn = 43500) (55 %).

The behaviour of the models on the correlation of experimental data is shown in Figures 1 and 2 for the PS/1,4-Dioxane and PS/Diethyl Ketone systems. Figure 1 shows the deviations of the UNIFAC FV model to increase with the polymer concentration. Flory Huggins also displays some difficulty in describing the experimental behaviour being unable to provide the adequate trend of the data. Moreover the results for the NRF based model presented in Figure 2 also anticipate a problem at the high polymer concentration end of the phase diagram discussed below.

Predictive behaviour

More interesting than the capacity of a model to correlate a set of experimental data is its predictive capability. Once the energetic parameters have been fitted to experimental data it should be possible to use them to predict the activity coefficient of the solvent, for the same polymer/solvent system for any polymer molecular weight. The predictive capacities of the segment based residual terms used in this work, Wu-NRTL, NRF and sUNIQUAC, were investigated.

For the segment based residual terms the energetic parameters found do not represent for the energetic interaction between a molecule of the solvent and the polymer, but represent the interactions between the solvent, taken as the segment unity and the polymer segments. The polymer is considered to be composed by a number of segments proportional to the polymer size. Taking r_s as unity and estimating r_p from the following relation it is possible to count the number of segments in the polymer:

$$r_p = \frac{V_p}{V_s} \quad (23)$$

To compare the performance of the activity coefficients resulting from the segment based residual terms coupled with the p-free volume the systems for which a broad range of molecular weights was available were used. The systems chosen were PS/cyclohexane, PS/toluene, PDMS/benzene and PEG/water.

To investigate the predictive performance of these models, the energetic interaction parameters for each model were fitted to one of the sets of experimental data for a given binary and were used to predict the activities for the remaining sets with other polymer molecular weights. The results obtained are reported in Table 2. The models studied provide a good predictive description of the systems studied. Considering the range of the polymer's molecular weight the performance of the models is surprisingly good. As shown in Table 3 for the system PS/cyclohexane there is no degradation of the predictions with increasing molecular weight. The parameters presented, having been fitted to the system presented in the first row, were used for all the other molecular weights and the results are equally good for all the systems studied. The performance of the NRF model is generally somewhat inferior to the other two models and it was found

that it presents a surprisingly behaviour that is reflected on high error obtained for the data set with a molecular weight of 110000.

Although the overall performance of NRF is acceptable in what concerns the accuracy of the experimental data description, it displays an odd behaviour for very concentrate polymer solutions that make it unreliable for extrapolation in concentration or molecular weight outside the range of experimental used for parameter fitting. For regions of high polymer concentrations instead of a regular and smooth behaviour NRF displays a minimum followed by a sharp increase on the predicted activities as shown in Figure 3. This behaviour that was already suggested in Figure 2 is physically unsound and makes this model unreliable for use outside the range of experimental data used in the parameter fitting thus limiting its application.

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Conclusions

A comparison a number of two parameters activity coefficient models for the correlation of VLE data for polymer systems was performed. The models studied were obtained from the coupling of the best and better-known combinatorial (free volume) terms with residual terms from the local composition models NRF, NRTL and UNIQUAC. A number of these systems had already been proposed in the literature while others are here used for the first time. The comparison performed indicates the advantage of the segment based models derived from the NRTL and UNIQUAC formalisms. These models are able to produce the best correlations for the VLE experimental data and also present the capacity to describe the VLE behaviour of a broad range of polymer weights using a single pair of interaction parameters, when coupled to a good combinatorial free volume term, such as the p-free volume used here or other equivalent.

The results obtained also indicate that NRF based models display a physical unsound behaviour and while they may be adequately used for the correlation of VLE data the extrapolation of this data to higher polymer concentration or molecular weights other than the used in the correlation is not advisable.

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List of symbols

a	Adjustable energetic parameter
a	Activity of the solvent (Figures 1 to 3)
a, b	Parameter defining the FH parameter as function of temperature (eq. 21)
AAD	Average absolute deviation
c	Correction facto introduced in equation 22
FH	Flory-Huggins
FV	Free volume
G	Gibbs free energy (Appendix A)
G	Energetic parameter for the Wu-NRTL model
g	Energetic interaction parameter
k	Boltzmann constant
Mn	Number molecular weight of polymer
N	Number of molecules
NRF	Non random factor
p	Correcting parameter defined in equation 3
PDMS	Polydimethylsiloxane
PEG	Polyethyleneglycol
POD	Poly-1-octadecene
PS	Polystyrene
q	Area parameter
r	Number of segments
U, u	Energy
V	Molar volume
w	Mass fraction
x	Molar composition
X	Segment fraction

Greek letters

α	Non-randomness factor
γ	Molar activity coefficient
τ	Energetic parameter for the UNIQUAC, sUNIQUAC and Wu-NRTL models
λ	Energy parameter for the Zafarani-Moatar model
ϕ	volume fraction

θ	Area fraction
χ	Flory-Huggins parameter
Δ	difference

Subscripts

i	Component i
j	Component j
o	Reference
$2,p$	Polymer
q	segments
$1,s$	Solvent
seg	segment
w	Van der Waals

Superscripts

comb	combinatorial
comb-fv	Combinatorial free volume
E	Excess
FV	Free volume
P	Correcting parameter defined in equation 3
res	Residual

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Appendix A

According to the two-fluid theory a fluid results from the mixture of two hypothetical fluids: fluid 1 that has a molecule of type 1 surrounded by molecules of type 2 and fluid 2 that has a molecule of type 2 surrounded by molecules of type 1. In the system considered in this work there are no molecules but segments instead. In this system, and following Wu et al ^[4], the reference states are pure liquid for the solvent and a hypothetical aggregation state for the polymer segments.

Thus the excess free energy for this system is given by:

$$u^E = \frac{Z}{2} N_q (X_1 X_{21} (U_{21} - U_{11}) + X_2 X_{12} (U_{12} - U_{22})) \quad (\text{A1})$$

By the local composition theory the local composition of each component can be related to the global composition:

$$\frac{X_{ji}}{X_{ii}} = \frac{X_j}{X_i} e^{-\frac{Z U_{ji} - U_{ii}}{2 kT}} \quad (\text{A2})$$

Substituting equation A2 in equation A1 and arranging the final expression for the free energy becomes:

$$u^E = \frac{X_1 X_2 e^{-\frac{\Delta u_{21}}{T}} \Delta u_{21}}{X_1 + X_2 e^{-\frac{\Delta u_{21}}{T}}} + \frac{X_2 X_1 e^{-\frac{\Delta u_{12}}{T}} \Delta u_{12}}{X_2 + X_1 e^{-\frac{\Delta u_{12}}{T}}} \quad (\text{A3})$$

In which:

$$\Delta u_{ij} = \frac{Z (U_{ij} - U_{jj})}{2 k N_q} \quad (\text{A4})$$

To obtain the expression for the Helmholtz free energy the following relation is used:

$$\frac{d(a^E/T)}{d(1/T)} = u^E \quad (\text{A5})$$

Integrating equation A5:

$$\frac{a^E}{T} = \int_{1/T_0}^{1/T} u^E d(1/T) + C \quad (\text{A6})$$

The integration is made by letting $1/T_0 \rightarrow 0$. The constant of integration in equation A6 is the combinatorial term resulting from integration. But in this work the concern is on the residual term so the integration is made yielding:

$$\left[\frac{a^E}{N_q kT} \right]_{residual} = -X_1 \ln \left(X_1 + X_2 e^{-\frac{\Delta u_{21}}{T}} \right) - X_2 \ln \left(X_1 + X_2 e^{-\frac{\Delta u_{21}}{T}} \right) \quad (A7)$$

At the low pressures $(a^E)_{T,V} \approx (g^E)_{T,P}$ so by the definition of activity coefficient:

$$\frac{\partial \frac{G^E}{RT}}{\partial N_1} = \ln \gamma_1 = X_2 q_1 \left(\frac{\tau_{21}}{X_1 + X_2 \tau_{21}} - \frac{\tau_{12}}{X_2 + X_1 \tau_{12}} \right) \quad (A8)$$

with

$$G^E = \frac{N_q}{N_A} \times g^E \times N_A \quad (A9)$$

And with X_i and τ_{ij} being defined by equations 14 and 18 respectively.

Table 1 – Percent improvement achieved by the models studied over the two-parameter Flory-Huggins model

	Wu-NRTL	NRF	UNIQUAC	sUNIQUAC
Freed FH	-	44.4	-	104.4
p-free volume	96.0	70.8	139.8	114.7
Entropic free volume	-	51.3	-	89.3

Table 2 – Predictive performance expressed in average absolute deviations (%) for all models and systems considered, using p-free volume for the combinatorial part

System	M_n_p range	NRF	Wu-NRTL	sUNIQUAC
<i>PS / cyclohexane</i>	49000 – 500000	3.60	0.44	0.67
<i>PDMS / benzene</i>	1140 – 89000	4.80	5.67	5.91
<i>PS / toluene</i>	7500 – 600000	1.51	1.72	1.49
<i>PEG / Water</i>	200 – 20000	2.07	2.07	1.70

Table 3 – Average absolute deviations (%) obtained in predictive models using p-free volume for the combinatorial part for the different polymer molecular weights with the PS / cyclohexane system

Mn_p	NRF	Wu-NRTL	sUNQUAC
154000	0.237	0.041	0.027
49000	0.145	0.008	0.023
72000	0.164	0.036	0.030
110000	23.552	0.497	2.436
435000	0.021	0.003	0.003
440000	2.820	1.415	0.980
440000	0.101	0.013	0.013
500000	1.732	1.509	1.828
a ₁₂	-0.476	2.909	0.540
a ₂₁	-3.750	-0.249	0.452

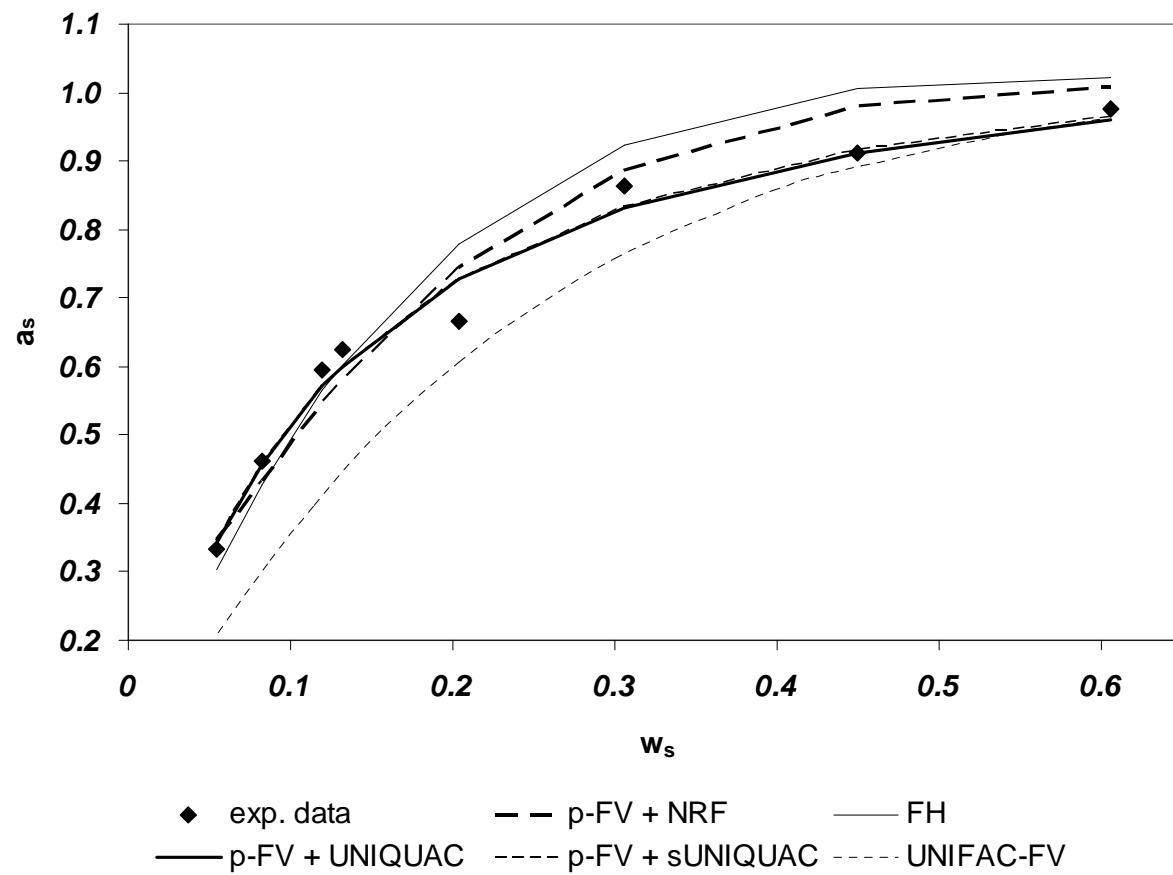
Figure Captions

Figure 1 – Experimental and correlated solvent activities for the PS/1,4-Dioxane system. ($M_{n_p} = 10300$, $T = 323.15$ K)

Figure 2 – Experimental and correlated solvent activities for the PS/Diethyl Ketone system. ($M_{n_p} = 500000$, $T = 293.15$ K)

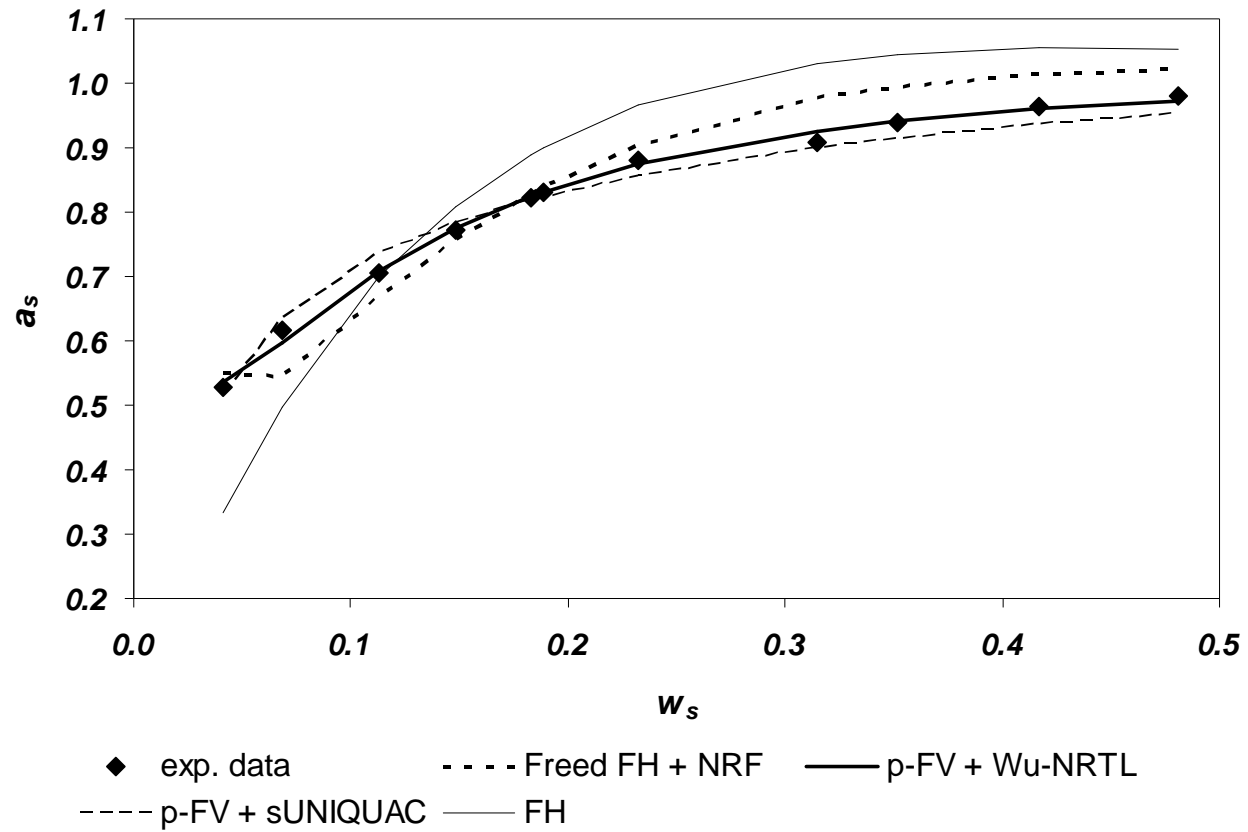
Figure 3 – Predictive behaviour of the p-free volume + NRF model for the PS / cyclohexane system: correlated model (—), predicted from model ($M_{n_{polymer}} = 110000$ (---), $M_n = 500000$ (-·-))

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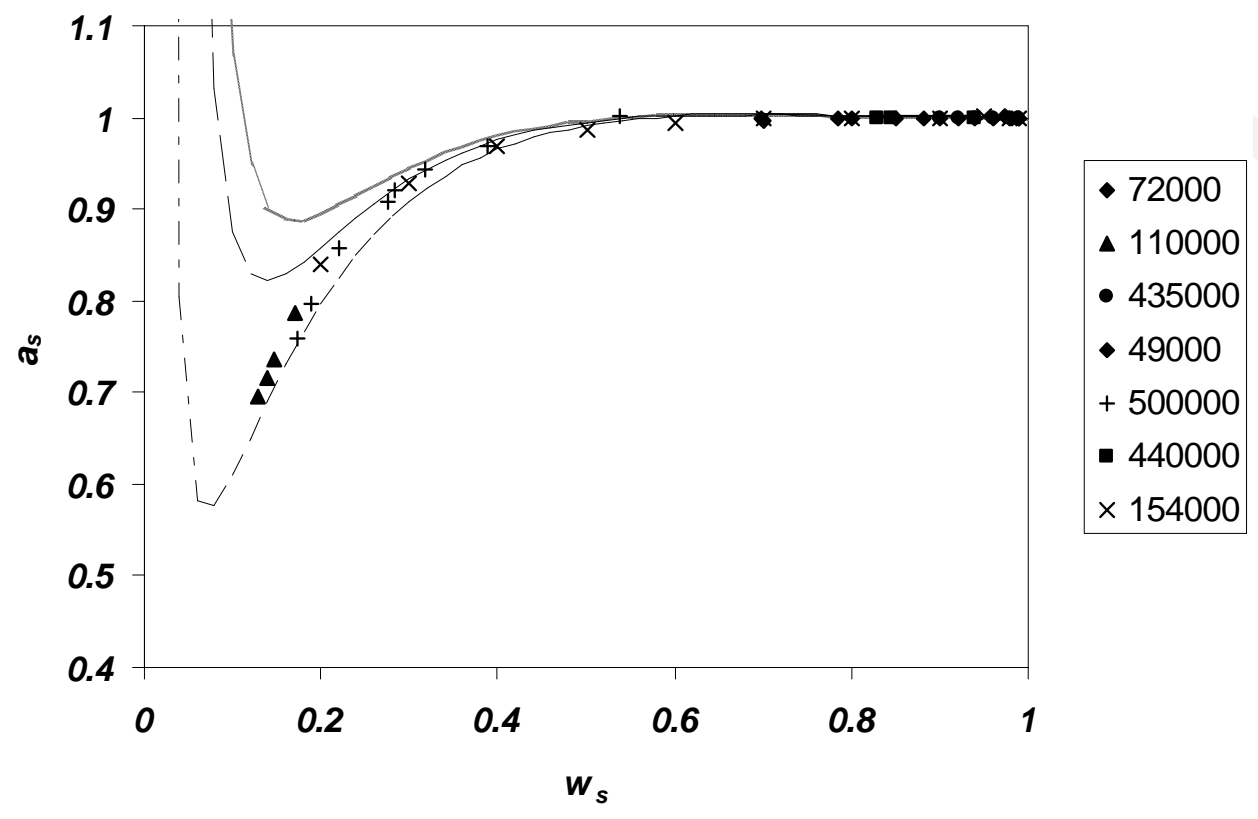
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