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A new segmental local composition model for calculation of thermodynamic properties of binary polymer solutions

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Abstract. A new local composition model, Segmental-Wilson-Non-Random Factor (S-Wilson-NRF), based on volume fraction is developed. The new activity coefficient model consists of the combinatorial (entropy) Flory-Huggins term and the residual (enthalpy) S-Wilson-NRF term. This model, for non-polymeric systems, reduces to nonelectrolyte-Wilson-NRF model. The present model with two dependent adjustable energy parameters is applied to correlation of the activity of solvent for 24 binary polymer systems at various number-average molar masses of polymer and temperatures. Moreover, the results of the present model are compared with the other local composition models such as None-random Two-Liquid (NRTL), NRTL-None-random Factor (NRTL-NRF) models and the Flory-Huggins χ model. Finally, the new model is applied for correlation of the excess molar enthalpy of the binary polymer solutions at different conditions. As a conclusion, the results of the new model are in good agreement with the experiment.

1. Introduction

Phase equilibrium calculation of polymeric systems plays an important role in designing of industrial processes such as polymerization, separation and extraction of proteins. The two general approaches of activity coefficient and equation of state methods are used for calculation of phase equilibrium of polymer-solvent systems. Various activity coefficient models and equations of state have been introduced, so far, regarding the calculation of the thermodynamic properties of polymer solutions. Gibbs energy functions are easy to use, flexible and give acceptable results. In the beginning, polymeric solutions were treated as an athermal mixture, where the celebrated combinatorial Flory-Huggins equation [1,2] is widely applied for entropic effects. For enthalpy effects, several activity coefficient models have been introduced for computation of the thermodynamic properties of polymer solutions; however, the combinatorial Flory-Huggins is always the leading term for most of excess Gibbs functions, which have been proposed so far. To take into account the enthalpy effects, the various version of segmental-based local composition models, such as None-Random Two-Liquid (NRTL) local composition model, have been developed by Chen [3] and Vetere [4], and the combinatorial Flory-Huggins equation is used for the entropy term.

The various versions of segmental-based local composition models have been developed to take into account the enthalpy effects, such as Chen [3] and Vetere [4] models in which the None-Random Two-Liquid (NRTL) local composition model was used for the residual term and combinatorial Flory- Huggins equation for the entropy term. Wu et al. [5] applied the modified NRTL model for derivation of a

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Helmholtz energy function for calculation of the phase equilibrium of homologous polymer solutions with or without orientated interactions. Sadeghi [6,7] modified the Wilson local composition model for phase equilibrium calculation of polymer solutions. Haghtalab and Espanani [8] applied the NRTL-None-Random Factor (NRTL-NRF) model [9] for VLE calculation of binary polymer solutions. Sadeghi and Zaffarani-Moatar [10] extended the NRTL and NRTL-NRF models to multicomponent polymer solutions. Radfarnia et al. [11] used UNIQUAC-NRF model, proposed by Haghtalab and Asadollahi [12], for correlation and prediction of thermodynamic properties of polymer solutions.

In this work, following Nonelectrolyte-Wilson-NRF (N-Wilson-NRF) model [13,14], a new segmental based-G^E model is developed to correlate thermodynamic properties of polymer solutions. The results of the present work are compared with those obtained using the local composition models such as NRTL, NRTL-NRF and Flory-Huggins χ models.

2. Thermodynamic framework

The excess Gibbs energy of solutions can be expressed as sum of the combinatorial and residual terms as:

$$\frac{g^E}{RT}=\left(\frac{g^E}{RT}\right)^C+\left(\frac{g^E}{RT}\right)^R, \tag{1}$$

where the superscripts C and R stand for the combinatorial and residual contributions, respectively. In this work, the combinatorial Flory-Huggins excess Gibbs energy function is used as:

$$\left(\frac{g^E}{RT}\right)^C=x_1\ln\frac{\phi_1}{x_1}+x_2\ln\frac{\phi_2}{x_2}, \tag{2}$$

where subscripts 1 and 2 denote solvent and polymer, respectively, and ϕ_i is the bulk volume fraction of component i as:

$$\phi_i=\frac{x_ir_i}{\sum\limits_j x_jr_j}, \tag{3}$$

where x is mole fraction and r presents segment numbers of a polymeric chain that is obtained as [15]:

$$r_2=\frac{MW_n}{MW_1}, \tag{4}$$

in which MW_n and MW_1 stand for the number-average molar mass of polymer and molar mass of solvent, respectively.

For residual term, based on the local composition concept, a new function is obtained for the excess Gibbs energy of solutions. Thus, following Nonelectrolyte-Wilson-NRF excess Gibbs energy model [13] and using Non-Random Two-Liquid theory [9], one can assume presence of two types of central cells in a binary polymer solution. The cells 1 and 2 show a central solvent molecule and a central polymer segment, respectively. Assuming the solvent molecules and polymer segments in surrounding of the central molecules, one can write the molar excess enthalpy energy for a binary polymer solution as:

$$\frac{h^E}{RT}=\frac{x_1h_1^E}{RT}+\frac{x_2h_2^E}{RT}, \tag{5}$$

where h_1^E and h_2^E stand for the excess enthalpy of the cells 1 and 2, respectively. Assuming the random state as a reference state, the excess enthalpy of each cell is written as:

$$\frac{h_1^E}{RT}=\frac{h_1}{RT}-\frac{h_1^0}{RT}, \tag{6}$$

$$\frac{h_2^E}{RT}=\frac{h_2}{RT}-\frac{h_2^0}{RT}, \tag{7}$$

where h and h^0 denote the enthalpy of the cells and reference cells, respectively. For the two cells one can write them down as:

$$\frac{h_1}{RT}=\frac{(\phi_{11}h_{11}+\phi_{21}h_{21})}{RT}, \tag{8}$$

$$\frac{h_2}{RT}=\frac{(\phi_{22}h_{22}+\phi_{12}h_{12})}{RT}, \tag{9}$$

where h_{ij} is enthalpic interaction energy between species i and j, and ϕ_{ij} is local volume fraction of species i surrounding central species j. For the reference random state, one can assume that ϕ_{ij} reduces to bulk volume fraction ϕ_j, so that the enthalpies of the two cells at the reference state are expressed as:

$$\frac{h_1^0}{RT}=\frac{(\phi_1h_{11}+\phi_2h_{21})}{RT}, \tag{10}$$

$$\frac{h_2^0}{RT}=\frac{(\phi_2h_{22}+\phi_1h_{12})}{RT}. \tag{11}$$

The relation between the local and bulk volume fractions is determined by means of Non-Random Factor (NRF) as:

$$\phi_{ij}=\phi_i\Gamma_{ij}. \tag{12}$$

Similarly, we have:

$$\phi_{jj}=\phi_j\Gamma_{jj}, \tag{13}$$

where by dividing Eq. (12) to (13), one can write as:

$$\frac{\phi_{ij}}{\phi_{jj}}=\frac{\phi_i}{\phi_j}\tau_{ij}, \tag{14}$$

with τ_{ij} being the Boltzman factor expressible as:

$$\tau_{ij} = \frac{\Gamma_{ij}}{\Gamma_{jj}} = \exp\left(-\frac{h_{ij} - h_{jj}}{ZRT}\right) = \exp\left(-\frac{\lambda_{ij}}{Z}\right). \tag{15}$$

Here, $\tau_{ij} \neq \tau_{ji}$; $\tau_{ii} = \tau_{jj} = 1$, Z is coordination number, and λ_{ij} is the adjustable binary parameter. Local volume balances for the central cells can be written as:

$$\phi_{11} + \phi_{21} = 1, \tag{16}$$

$$\phi_{12} + \phi_{22} = 1. \tag{17}$$

Combining Eqs. (12), (13), (16) and (17), the non-random factors are obtained as:

$$\Gamma_{21} = \frac{\tau_{21}}{\phi_1 + \phi_2\tau_{21}}, \tag{18}$$

$$\Gamma_{12} = \frac{\tau_{12}}{\phi_2 + \phi_1\tau_{12}}, \tag{19}$$

where $\tau_{12} \neq \tau_{21}$; then as indicated by Panayiotou and Vera [16,17] $\Gamma_{12} \neq \Gamma_{21}$. Thus, one may conclude that conservation equation $\phi_i\phi_{ji} = \phi_j\phi_{ij}$ is not valid in the case of Wilson type local composition, so that the intermolecular or intermolecular contact conservation requirements are only true in the case of quasichemical local composition theory.

Finally, combining Eqs. (5)-(11) and using Eqs. (15)-(19), the excess molar enthalpy for a binary polymer solution is obtained as:

$$\frac{h^E}{RT} = x_1\phi_2\lambda_{21}(\Gamma_{21} - 1) + x_2\phi_1\lambda_{12}(\Gamma_{12} - 1). \tag{20}$$

The excess Gibbs energy function is obtained by integration of Eq. (20) through the Gibbs-Helmholtz equation as:

$$\frac{g^E}{RT} = \int_{T_0=\infty}^{T} \frac{h^E}{R} d\left(\frac{1}{T}\right), \tag{21}$$

where the lower limit corresponds to the combinatorial excess Gibbs energy that at very high (infinite) temperature, we assume that components 1 and 2 form an athermal mixture. Assuming λ_{12} and λ_{21} independent of temperature, the integration of Eq. (21) at upper limit results the residual excess Gibbs energy as:

$$\left(\frac{g^E}{RT}\right)_{\text{S-Wilson-NRF}} = Z\left[x_1\ln\Gamma_{11} + x_2\ln\Gamma_{22} + \frac{x_1x_2}{x_1r_1 + x_2r_2}\ln(\tau_{12}^{r_1}\tau_{21}^{r_2})\right], \tag{22}$$

where r_1 and r_2 are the segmental number of solvent and polymer, respectively. By proper differentiation of Eq. (22), the residual term of the activity coefficient function can be obtained for a solvent in a binary mixture as:

$$(\ln\gamma_1)^R_{\text{S-Wilson-NRF}} = Z\left[\ln\Gamma_{11} + \phi_2\left(\Gamma_{21} - \frac{r_1}{r_2}\Gamma_{12} + \frac{r_1}{r_2} - 1\right) + x_2\phi_2\ln(\tau_{12}^{r_1}\tau_{21}^{r_2})\right]. \tag{23}$$

The above expression presents the segmental-Wilson-NRF activity coefficient equation. For the case $r_1 = r_2 = 1$, the S-Wilson-NRF model Eqs. (22) and (23) reduce to the N-Wilson-NRF model as [13]:

$$\left(\frac{g^E}{RT}\right)_{\text{N-Wilson-NRF}} = Z\left[x_1\ln\Gamma_{11} + x_2\ln\Gamma_{22} + x_1x_2\ln(\tau_{12}\tau_{21})\right], \tag{24}$$

$$(\ln\gamma_1)^R_{\text{N-Wilson-NRF}} = Z\left[\ln\Gamma_{11} + x_2(\Gamma_{21} - \Gamma_{12}) + x_2^2\ln(\tau_{12}\tau_{21})\right], \tag{25}$$

where Eq. (25) is used for binary non-athemal mixtures (non-polymeric systems).

3. Application of S-Wilson-NRF model to binary polymer solutions

In this work, we apply the S-Wilson-NRF model for VLE calculation of the binary polymer solutions. For the combinatorial and the residual terms, the Flory-Huggins equation and the new S-Wilson-NRF function are used, respectively, so that for consistency of these two terms, the parameter of volume for solvent molecule is assumed to be unity ($r_1 = 1$). Thus, using Eqs. (22) and (23) the closed form of the molar excess Gibbs and the activity coefficient functions for a binary polymer solution can be written as:

$$\left(\frac{g^E}{RT}\right) = x_1\ln\frac{\phi_1}{x_1} + x_2\ln\frac{\phi_2}{x_2} + Z\left[x_1\ln\Gamma_{11} + x_2\ln\Gamma_{22} + \frac{x_1x_2}{x_1 + x_2r_2}\ln(\tau_{12}\tau_{21}^{r_2})\right], \tag{26}$$

$$\ln\gamma_1 = \ln\left(\frac{\phi_1}{x_1}\right) + \left(1 - \frac{1}{r_2}\right)\phi_2 + Z\left[\ln\Gamma_{11} + \phi_2\left(\Gamma_{21} - \frac{1}{r_2}\Gamma_{12} + \frac{1}{r_2} - 1\right) + x_2\phi_2\ln(\tau_{12}\tau_{21}^{r_2})\right], \tag{27}$$

where Eq. (27) presents the activity coefficient function for a solvent in a binary polymer solution. Therefore, the activity of solvent is expressed as:

$$a_1 = \gamma_1 x_1. \tag{28}$$

4. Results and discussion

The Segmental-Wilson-NRF model provides a logical framework for extension of the Wilson local composition model for VLE calculation of polymeric systems. In this work, the activity of solvent is calculated for the 24 binary polymeric solutions at different conditions. As mentioned earlier, the S-Wilson-NRF model is based on interactions among segments of a polymer chain and solvent molecules. Influence of a number of segments has been considered as a variable in the new model. Thus, in this work for all polymer systems with the same solvent and various molar mass of polymer, activity of solvent is correlated using only one single pair parameters.

For coordination number, i.e. Z, a value of 10 is used and the segment numbers of the polymers, r_2, are given by Wolfarth [18] that is calculated using Eq. (4). To take the temperature effect into account, a simple temperature dependent correlation for the adjustable parameters is used as:

$$\lambda_{12} = \frac{a_{12}}{T}, \tag{29}$$

$$\lambda_{21} = \frac{a_{21}}{T}, \tag{30}$$

where the parameters a_{12} and a_{21} are coefficients of the adjustable parameters and are calculated by optimization the activity data of solvent for a single or several binary polymer solutions at the whole range of temperatures and molar masses of polymers using the objective function:

$$\text{AAD\%} = \frac{1}{N} \sum_{1}^{N} \left| \frac{a_1^{\text{exp}} - a_1^{\text{cal}}}{a_1^{\text{exp}}} \right| \times 100. \tag{31}$$

Here, N is the number of data points, a_1^{cal} is calculated solvent activity, and a_1^{exp} is the experimental solvent activity data that are obtained using the data compilation of Wolfarth [18]. Table 1 shows the specifications of the binary polymer systems which are used in this work. As one can see, in the new model, effect of temperature is inserted in Eqs. (29) and (30).

Using the same sources of data, the Flory-Huggins χ model [19] and the two other local composition functions such as segmental-NRTL-NRF [8] and segmental-NRTL [15] are used for optimization of the activity data, so that the parameters of these models are regressed using the same approach. The combinatorial Flory-Huggins function is applied for the four models, but using the different residual terms. The activity coefficient equations of the models are given in the Appendix. Table 2 presents the parameters of the S-Wilson-NRF model and the Absolute Average Deviation (AAD%) of the solvent activity for the different polymer solutions using the four models. As one can see, the results of the S-Wilson-NRF model are in very good agreement with the experiment. As shown in Table 2, the results of the S-Wilson-NRF and S-NRTL models are close and more accurate than the other models. Therefore, the S-Wilson-NRF model gives very good results as good as the S-NRTL model that both models are suitable for VLE calculation of polymer solutions. Figure 1 shows the experimental and the correlated activity of toluene versus weight fraction of polystyrene at the various molar masses and temperatures. Similarly, Figure 2 presents the change of activity of benzene against the weight fraction of

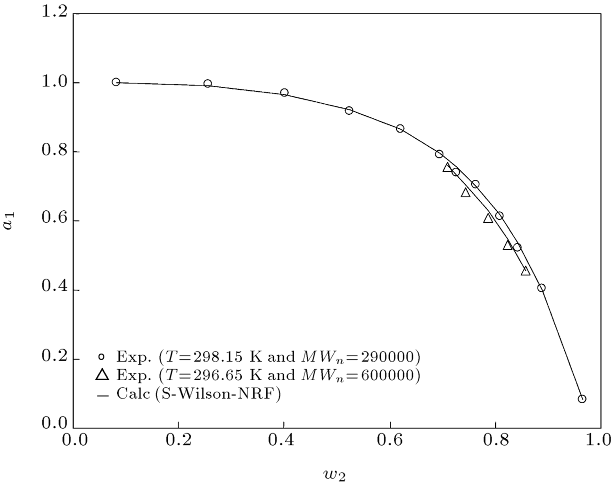

Figure 1. The activity of toluene in polystyrene against the weight fraction of polymer.

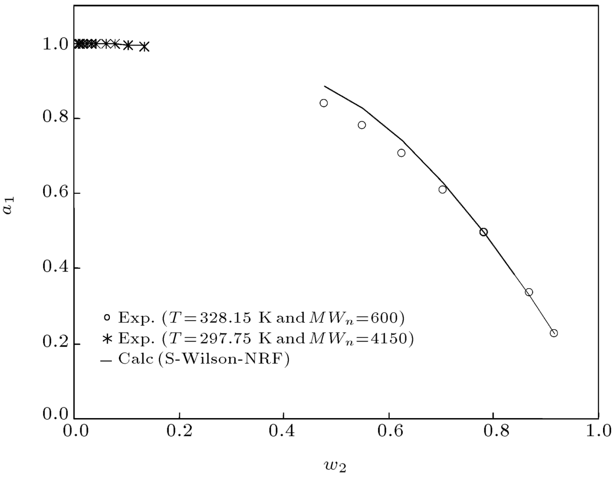

Figure 2. The activity of benzene in polyethylene glycol against the weight fraction of polymer.

Table 1. The specifications of the binary polymer solutions used in this work[a].

System	Solution	MW_n	r_2	T/K	N
1	Dextran/water	23600	1311	293.15, 313.15, 333.15	106
		46300	2572	293.15, 313.15, 333.15	
		64800	3600	293.15, 313.15, 333.15	
		101000	5611	293.15, 313.15, 333.15	
2	PEG/water	335	19	297.75, 307.75	279
		400	16	298.15	
		600	33	293.1, 313.10, 333.10	
		650	36	297.75, 307.75	
		1000	40	298.15	
		1460	81	297.75, 307.75	
		1500	83.3	293.15, 298.15, 313.10, 333.10	
		3790	211	298.15	
		4150	230	297.75, 307.75	
		5750	319.4	293.15, 313.10	
		6000	333	293.15, 298.15, 313.10, 333.10	
		8000	444	323.15, 333.15, 343.15	
		35000	1944	293.15	
3	PEG/benzene	335	4.3	297.75, 307.75	65
		600	6.5	328.15	
		1460	19	297.75, 307.75	
		4150	53	297.75, 307.75	
4	PEG/tetrachloromethane	395	2.6	303.15	27
		400	2.6	303.15	
		600	3.9	303.15	
5	PEG/ethylbenzene	3272	30.82	343.75	19
6	PIB/n-pentane	1170	12	298.15, 308.15, 318.2, 328.15	26
7	PIB/n-hexane	50000	580	298.15, 313.15, 338.15	23
8	PIB/cyclohexane	100000	973	298.15, 313.15, 338.15	26
		4700000	55846	296.65	
9	PIB/toluene	50000	543	298.15, 313.15, 338.15	14
10	PS/benzene	3600	38	303.15, 323.15, 343.15	128
		19200	200	303.15, 323.15, 343.15	
		103800	1081	303.15, 323.15, 343.15	
		218000	2791	313.2, 333.2	
11	PS/toluene	290000	2502	298.15	17
		600000	6510	296.65	
12	PS/cyclohexane	218000	2590	313.2, 333.2, 353.15	28
13	PS/propylacetat	290000	2011	298.15, 343.14	19
14	PS/dicholoromethane	600000	7060	296.65	6
15	PS/acetone	15700	191	298.15, 323.15	14
16	PS/m-xylene	53700	506	403.15, 423.15, 44815	22
17	PS/tetrachloromethane	600000	3903	296.65	4
18	PPG/water	400	22.2	303.15, 323.15	14
19	PPG/toluene	2660	28.9	323.15, 343.75	28
20	PPG/methanol	1120	27	263.15, 273.15, 288.15, 298.15	60
		1955	48	263.15, 273.15, 288.15, 298.15	
		3350	82	263.15, 273.15, 288.15, 298.15	
21	PVAc/benzane	50500	560	303.15	29
		158000	2023	313.15, 333.15	
22	PVAc/toluene	158000	1715	313.15, 333.15	20
23	PVAc/vinyl acetate	150000	1660	303.15	10
24	PVK/benzene	750	7	279.15, 288.15, 298.15, 308.15, 318.15, 328.15	265
		1400	13	279.15, 288.15, 298.15, 308.15, 318.15, 328.15	
		5600	55	279.15, 288.15, 298.15, 308.15, 318.15, 328.15	
		26000	250	279.15, 288.15, 298.15, 308.15, 318.15, 328.15	
		94000	900	279.15, 288.15, 298.15, 308.15, 318.15, 328.15	
		324000	3000	279.15, 288.15, 298.15, 308.15, 318.15, 328.15	
Overall					**1249**

[a]: All of data are given from Wohlfarth's book [18].

Table 2. The adjustable parameters of the S-Wilson-NRF model for the binary polymer solutions and comparison of the average absolute deviation (AAD%) of the activity of solvent for the S-Wilson-NRF, S-NRTL-NRF, S-NRTL and Flory-Huggins χ models with experiment [18].

System	**S-Wilson-NRF**		**AAD%^{a}**			
	a_{12}/K	**a_{21}/K**	**S-Wilson-NRF**	**S-NRTL-NRF**	**S-NRTL**	**F-H**
1	-451370	83.8	0.19	0.26	0.04	0.04
2	1386.3	-70.0	0.95	2.00	0.94	1.67
3	4543.1	-756.2	0.56	0.17	0.16	0.31
4	-2846.7	740.2	4.28	4.18	4.80	6.01
5	-9.75	2.46	0.36	0.31	0.32	0.33
6	-4036.3	272.5	1.11	5.35	0.90	1.71
7	-34199	63.5	1.64	3.94	2.56	3.22
8	-8114.1	11.1	1.25	1.12	1.22	1.23
9	63.5	-19.3	3.72	3.92	3.57	4.03
10	-118.0	4.5	4.45	4.59	4.48	4.51
11	-51462	36.2	1.14	2.50	3.49	6.65
12	-473848	182.2	1.39	22.93	1.30	1.39
13	-273317	150.1	0.87	7.82	1.47	3.17
14	2165024	-298.2	0.79	0.25	0.71	0.76
15	-45466	220.9	1.61	29.05	1.03	1.43
16	33123	-65.4	2.79	2.63	2.71	2.82
17	1563180	-487.3	0.15	0.07	0.11	1.91
18	-9692	289.7	5.82	37.50	2.88	9.39
19	12841	-543.2	2.19	1.77	1.54	1.55
20	10360	-1443.8	4.23	4.61	3.64	4.67
21	525.4	-0.3192	2.01	2.27	2.37	2.45
22	-111827	64. 8	2.52	9.22	1.57	2.19
23	48236	-15.2	1.19	1.67	2.21	2.90
24	-906.1	73.9	11.61	13.11	11.91	12.93
Overall			**3.94**	**6.01**	**3.95**	**4.62**

^{a}: $\mathrm{AAD\%} = (1/N)\sum_{1}^{N}\left|\left(a_1^{\mathrm{exp}} - a_1^{\mathrm{cal}}\right)/a_1^{\mathrm{exp}}\right| \times 100$.

polyethylene glycol at two different molar masses of the polymer and various temperatures. For comparison, Figure 3 shows the results for the solution of propylacetate and polystyrene at $MW_n = 290000$ and 298.15 K using the new S-Wilson-NRF, S-NRTL-NRF, S-NRTL and Flory-Huggins χ models. As one can see from these figures, the results of the present model demonstrate a very good agreement with the experiment. Also deviation of the correlated solvent activity from the experimental values against the weight fraction of polymers is shown by Figure 4. It presents that the deviation enhances as the weight fraction increases. Finally, the new model is used for correlation of the excess molar enthalpy (heat of mixing) of the binary polymer solutions. In this section, using Eq. (20), the excess molar enthalpies for the PEG/3-phenylpropyl alcohol, PEG/2-phenylethyl alcohol and PEG/dimethyl sulfoxide solutions are correlated at the four different

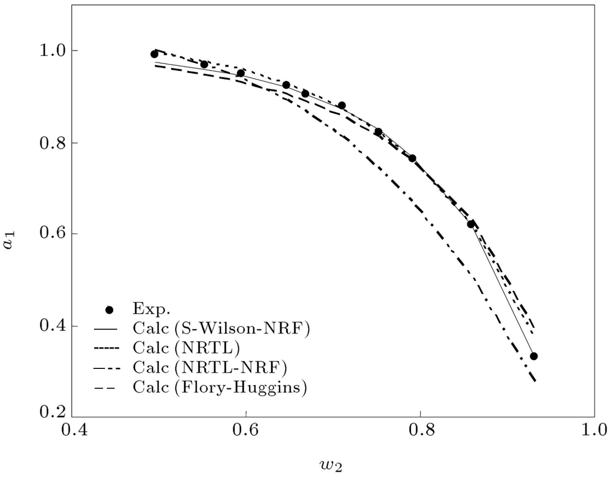

Figure 3. The activity of propylacetate in polystyrene against the weight fraction of polymer at $MW_n = 290000$ and $T = 298.15$ K.

Table 3. The adjustable parameters and the percent of average absolute deviation (AAD%) for correlation of the excess molar enthalpy (heat of mixing) data for the binary polymer systems using S-Wilson-NRF and extended S-Wilson models[a].

System					**First approach**			**Second approach**			**AAD%[b] (S-Wilson) [20]**	**Data ref.**
	MW_n	r_2^c	T/K	N	a_{12}/K[d]	a_{21}/K[d]	AAD%[b]	a_{12}/K[d]	a_{21}/K[d]	AAD%[b]		
PEG/3-phenylpropyl alcohol	192	1.4	308.15	17	-549.32	-542.71	13.22	-529.39	-537.33	18.42	18.93	[21]
	274	2.0	308.15	17				-517.63	-575.09	12.24	21.76	[21]
	365	2.7	308.15	17				-541.31	-568.84	5.88	23.34	[21]
	554	4.1	308.15	18				-650.99	-535.15	8.88	23.08	[21]
PEG/2-phenylethyl alcohol	192	1.6	308.15	17	-985.45	-812.38	13.17	-876.3	-796.52	9.22	11.90	[22]
	274	2.2	308.15	17				-1025.04	-806.14	7.03	10.74	[22]
	365	3.0	308.15	17				-1061.16	-818.61	5.99	9.72	[22]
	554	4.5	308.15	17				-1288.39	-778.85	9.06	11.81	[22]
PEG/dimethyl sulfoxide	192	2.5	308.15	17	-1791.2	-807.82	16.68	-1544.17	-931.13	2.52	7.74	[23]
	274	3.5	308.15	18				-1773.65	-870.27	5.32	10.96	[23]
	365	4.7	308.15	18				-1928.15	-797.76	8.66	13.08	[23]
	554	7.1	308.15	18				-2126.43	-698.62	10.89	18.03	[23]
Overall				**208**			**14.38**			**8.67**	**15.11**	

[a]: The extended S-Wilson models correlated a pair adjustable parameters for each molecular mass [20];

[b]: $\text{AAD\%} = (1/N) \sum_{1}^{N} \left| \left(h^{E,\exp} - h^{E,\text{cal}}\right) / h^{E,\exp} \right| \times 100$;

[c]: $r_2 = MW_n / MW_1$;

[d]: the values of parameters and the AAD% for the new model are obtained for the average molecular weight of polymer.

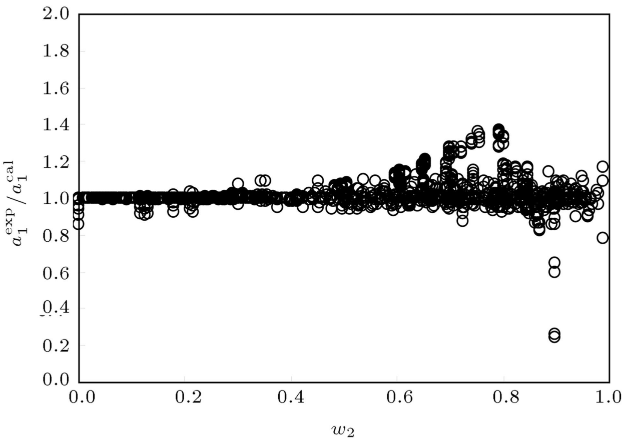

Figure 4. Comparison of the correlated values, using the present model, with the experiment for the activity of the solvents in different polymer solutions.

number-average molar masses of polymer and 308.15 K. The results of the present model are compared with those of the extended segmental Wilson model that is available in the work of Sadeghi [20].

It is noteworthy that the main approach in this work is that, for each solution with the different number-average molar masses, only single pair parameters are adjusted (first approach) unlike the work of Sadeghi [20] in which, for the same solutions with the different number-average molar masses, the multiple pair parameters were correlated. Therefore, for a fair comparison between S-Wilson-NRF and S-Wilson models, for each number-average molar mass of every solution, one pair of parameters is correlated similar to the work of Sadeghi [20] (second approach). Table 3 summarizes the results and the percent Absolute Average Deviations (AAD%) for correlation of the excess molar enthalpy of the three polymer systems as PEG/3-phenylpropyl alcohol [21], PEG/2-phenylethyl alcohol [22] and PEG/dimethyl sulfoxide [23]. Using the first approach the results demonstrate, although the new model possess better accuracy in an overall sense, for the two binary solutions namely PEG/2-phenylethyl alcohol and PEG/dimethyl sulfoxide, the S-Wilson model shows better accuracy. However, the potential of the present new model in correlation of the excess molar enthalpy of polymer solutions needs more investigation using only one pair of parameters for any solution with different number-average molar masses. Moreover, the results of the both models, using the second approach as a fair comparison, reveals that the accuracy of the S-Wilson-NRF is better than the S-Wilson model for all the three binary polymer systems at the similar conditions. Based on the first approach, Figure 5 shows the experimental and calculated excess molar enthalpy versus mole fraction of PEG for the various polyethylene glycol solutions at $MW_n = 274$ and 308.15 K. As one can see, the global fitting of the heat of mixing for the same polymer systems with various molar masses allows one to conclude that the

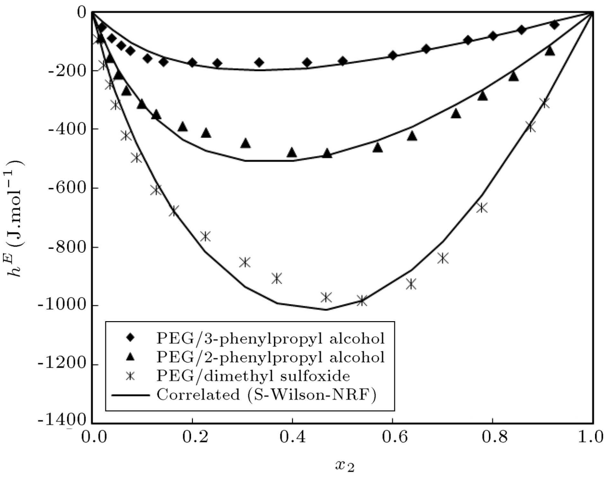

Figure 5. Excess molar enthalpy of polyethylene glycol solution against the mole fraction of polymer at $MW_n = 274$ and $T = 308.15$ K.

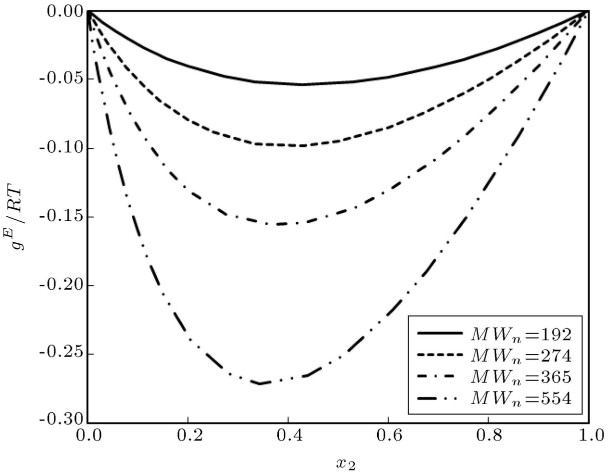

Figure 6. Calculated excess molar Gibbs free energy of 3-phenylpropyl alcohol (1) + PEG (2) binary solution by the S-Wilson-NRF model at different polymer molecular weight and $T = 308.15$ K.

present model demonstrates an acceptable accuracy in correlation of the excess molar enthalpy of the polymer solutions. Also Figures 6 and 7 demonstrate the calculated results of the S-Wilson-NRF model for excess molar Gibbs energy and excess molar entropy of the 3-phenylpropyl alcohol (1) + PEG (2) systems, respectively, at different molar masses of the polymer. In addition, Figure 7 shows that the excess molar entropy of the above binary solution enhances with increasing of the polymer molecular weight. One may note that using the S-Wilson-NRF model in lowest molecular weight of a given polymer, i.e. 192, with a small segment number, 1.4, the predicted excess molar entropy is negative, and for the higher molecular weight, i.e. 274, 365, 554, the excess molar entropy is positive. Finally, for comparison, Figure 8 shows, simultaneously, the excess molar energies for the 3-phenylpropyl alcohol (1) + PEG (2) system at molar masss 365 and 308.15 K.

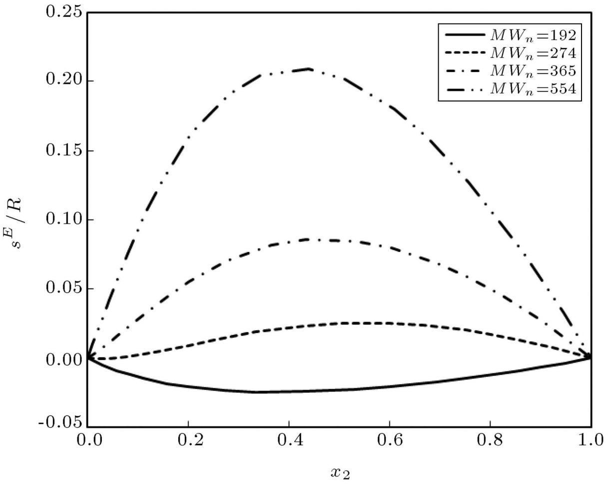

Figure 7. The effect of polymer molecular weight on excess molar entropy of 3-phenylpropyl alcohol (1) + PEG (2) binary system calculated by the S-Wilson-NRF model at different polymer molecular weight and $T = 308.15$ K.

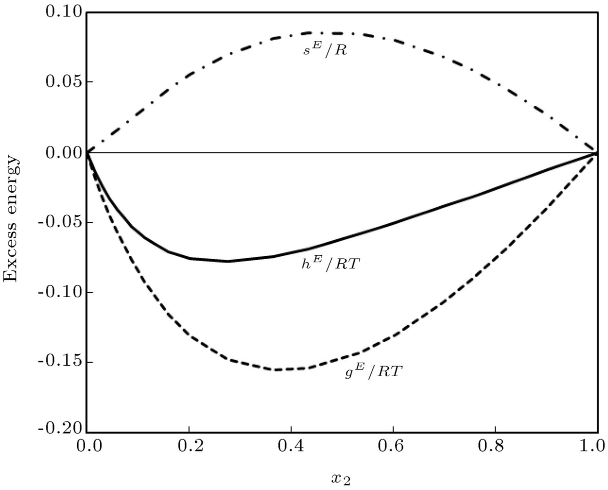

Figure 8. Calculated excess molar Gibbs energy, excess molar enthalpy and excess molar entropy of 3-phenylpropyl alcohol (1) + PEG (2) binary solution by the S-Wilson-NRF model at $MW_n = 365$ and $T = 308.15$ K.

5. Conclusion

The new local composition model, Segmental-Wilson-NRF, based on the volume fraction was developed and a new excess Gibbs energy function for description of the binary polymer-solvent systems was obtained. The new activity coefficient function consists of two parts, combinatorial and residual terms, so that in this work the combinatorial Flory-Huggins and the S-Wilson-NRF equations were used for these two terms, respectively. Using a two-energy parameter for a binary polymer solution with different molar masses, the activity of solvent for 24 binary polymer mixtures were correlated at various temperatures. The overall AAD% values of 3.89% were obtained for the all polymer solutions. Moreover, using the present model, the heat of mixing for several different polymer solutions was correlated. Comparisons of the results of the new model with the others demonstrated that the S-Wilson-NRF model is appropriate for calculation of the thermodynamic properties of polymer solutions.

Nomenclature

a	Activity
a_{12}, a_{21}	Adjustable parameters
AAD	Absolute Average Deviation
g	Molar Gibbs free energy
h	Molar enthalpy
MW_n	Number-average molar mass of polymer
N	Number of data points
PEG	Polyethylene glycol
PIB	Polyisobutylene
PPG	Polypropylene glycol
PS	Polystyrene
PVAc	Polyvinyl acetate
PVK	Poly(N-vinylcarbozol)
R	Universal gas constant
r	Segment numbers of polymer
T	Absolute temperature
w	Weight fraction
x	Mole fraction
Z	Coordination number

Greek letters

ϕ	Volume fraction
Γ	Non-random factor
γ	Activity coefficient
λ	Adjustable parameter

Subscripts

s	Solvent
i, j	Any compound
1	Solvent
2	Polymers

Superscripts

C	Combinatorial
cal	Calculated
exp	Experimental
E	Excess property
R	Residual
0	Reference state

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Appendix

Flory-Huggins model:

$$\ln\gamma_1=\ln\left[1-\left(1-\frac{1}{r}\right)\phi_2\right]+\left(1-\frac{1}{r}\right)\phi_2+\chi\phi_2^2.$$

S-NRTL model:

$$\ln\gamma_1=\ln\frac{\phi_1}{x_1}+\left(1-\frac{1}{r}\right)\phi_2+\phi_2^2\left[\tau_{12}\left(\frac{G_{21}}{\phi_1+\phi_2G_{21}}\right)^2+\frac{\tau_{12}G_{12}}{(\phi_2+\phi_1G_{12})^2}\right],$$

$$G_{ij}=\exp(-\alpha_{ij}\tau_{ij}).$$

S-NRTL-NRF model:

$$\ln\gamma_1=\ln\frac{\phi_1}{x_1}+\left(1-\frac{1}{r}\right)\phi_2+\phi_2^2\Bigg[\lambda_{21}(\Gamma_{21}-1)+\frac{1}{r}\lambda_{12}(\Gamma_{12}-1)+\phi_1\lambda_{21}\Gamma_{21}^2\left(1-\frac{1}{\tau_{21}}\right)+\frac{1}{r}\phi_1\lambda_{12}\Gamma_{12}^2\left(\frac{1}{\tau_{21}}-1\right)\Bigg],$$

$$\Gamma_{ij}=\frac{\tau_{ij}}{\phi_j+\phi_i\tau_{ij}},$$

$$\tau_{ij}=\exp\left(-\frac{\lambda_{ij}}{Z}\right).$$

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