

Study of VLE Phase Behavior and Correlating the Thermophysical Properties of Polymer Solutions Using a Local Composition-Based Model

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ABSTRACT: In this study, the recently proposed model by Pazuki et al., based on the local composition concept (LCC), has been used in correlating the vapor–liquid phase behavior of polymer solutions. Similar to the LCC models available in the literature, the proposed model has two combinatorial and residual terms to account for both entropic as well as enthalpic effects in solution. The Flory-Huggins model has been considered as the combinatorial part of the proposed model, while the equation proposed by Pazuki et al. was considered as the residual term. The proposed model has been used in correlating the vapor–liquid phase behavior for a large number of polymer–solvent mixtures at different conditions. The results obtained from the proposed model have been compared with those obtained from the UNIQUAC-FV model. The results showed that the pro-

posed model can accurately correlate the VLE data for polymer solutions studied in this work. Also, the proposed model has been used to obtain the thermophysical properties such as density, viscosity, and excess enthalpy for these polymer solutions. The results in connection with the thermophysical properties obtained from the proposed model have been compared with those obtained from the Poly-NRTL and the Poly-Wilson models. The results showed that the proposed model can accurately correlate the properties of polymer solutions at various conditions. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1356–1364, 2009

Key words: polymer solution; local composition models; thermophysical properties; local composition model; area surface fraction

INTRODUCTION

Aqueous two-phase systems (ATPS) containing two different types of polymer molecules have been extensively used in biotechnology and polymer processing. Recently, smart polymers such as polyethylene glycol (PEG) have been used in separation and purification of biomolecules such as amino acids and proteins. ATPS are suitable systems for partitioning of biomolecules in two immiscible phases.^{1,2} Therefore, determining the thermodynamic properties and study of the phase behavior of polymer solutions are indispensable in modeling and simulation of biomolecules extraction.

The excess Gibbs free energy is the most important property to be used for correlation and prediction of the VLE and LLE phase behavior for polymer solutions. The Flory-Huggins model is cornerstone to study the phase behavior of polymer solutions.³ According to the m-fluid theory Chen developed the NRTL model and proposed a segment-based thermodynamic model to study the

polymer–solvent systems.⁴ Also, Wu et al. calculated Helmholtz energy of polymer solutions and presented a modified local composition model similar to the NRTL model.⁵ Oishi and Prausnitz proposed a modified UNIFAC model for polymer solutions.⁶ Based on the nonrandom factor (NRF), Zafarani-Moattar and Sadeghi presented the Poly-NRTL-NRF model in correlating the VLE phase behavior of polymer solution.⁷ Radfarnia et al. studied VLE and LLE phase behavior of polymer solutions using modified quasi-chemical model and the UNIQUAC-NRF-FV model.^{8,9}

In this research, the model proposed by Pazuki et al. to study the phase behavior of amino acids and simple peptides in aqueous solutions¹⁰ has been extended for polymer solutions, Gibbs free energy of polymer solution, and activity coefficients of polymer and solvent. Vapor–liquid equilibrium of polymer solutions has been correlated using the proposed model and the results have been compared with those of the UNIQUAC-FV model. Also, thermophysical properties of polymer solutions such as density, viscosity, and excess enthalpy of polymer solutions have been correlated using the proposed model, the Poly-NRTL¹¹ and the Poly-Wilson¹² models and the results have been compared.

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DEVELOPED THERMODYNAMIC LOCAL COMPOSITION-BASED MODEL

Gibbs energy of polymer solutions has been considered as sum of the two terms, i.e., combinatorial and residual terms. Therefore, the excess Gibbs free energy can be written as follows:

$$\frac{g^{\text{ex}}}{RT} = \left(\frac{g^{\text{ex}}}{RT}\right)^{\text{comb.}} + \left(\frac{g^{\text{ex}}}{RT}\right)^{\text{res.}} \quad (1)$$

Thus, the activity coefficients of polymer and solvent can be obtained as:

$$\ln \gamma_i = (\ln \gamma_i)^{\text{comb.}} + (\ln \gamma_i)^{\text{res.}} \quad (2)$$

As mentioned earlier, the Flory-Huggins model has been considered as combinatorial part of the proposed model. Thus, the excess Gibbs free energy and activity coefficient of component i can be obtained from the below equations:

$$\left(\frac{g^{\text{ex}}}{RT}\right)^{\text{comb.}} = x_1 \ln \frac{\phi_1}{x_1} + x_2 \ln \frac{\phi_2}{x_2} \quad (3)$$

$$\ln \gamma_1^{\text{comb.}} = \ln \frac{\phi_1}{x_1} + 1 - \frac{\phi_1}{x_1} \quad (4)$$

where in the above equations ϕ_i is volume fraction of component i defined as:

$$\phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad (5)$$

In eq. (5) r is the number of segments per molecule. While in the Poly-Wilson and the Poly-NRTL activity coefficient models the reference states were considered to be hypothetical pure liquid for each components and these models were developed based on the local mole fraction concept (LMFC), the new model was proposed based on the local area fraction concept. The nonrandom case was considered to be the reference state for mixtures as well. Having chosen this kind of reference state makes the results of the model more accurate than those with the above hypothetical reference state.

The model proposed by Pazuki et al.¹⁰ was used as the residual term of the model to obtain the excess Gibbs free energy and activity coefficient of component i in solution. The local area fraction for polymer solution is defined as below:

$$\frac{\theta_{ij}}{\theta_{jj}} = \frac{\theta_i}{\theta_j} H_{ij} \quad (6)$$

where:

$$H_{ij} = \exp\left(-\frac{E_{ij}}{10 \times RT}\right) \quad (7)$$

Also, in the eq. (6) θ_i is the volume fraction of component i written as:

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \quad (8)$$

According to the m-fluid theory with two cells and with considering indexes (1) and (2) for solvent and polymer, respectively, the enthalpy of each cell has been obtained as follows:

$$h_1 = \theta_{11} h_{11} + \theta_{21} h_{21} \quad (9)$$

$$h_2 = \theta_{12} h_{12} + \theta_{22} h_{22} \quad (10)$$

where in the above equations h_i is enthalpy of cell i , and h_{ij} is difference enthalpy between species i and j . In this model the nonrandom mixture is considered as reference state.¹⁰

$$h_1^{\text{ref}} = \theta_1 h_{11} + \theta_2 h_{21} \quad (11)$$

$$h_2^{\text{ref}} = \theta_1 h_{12} + \theta_2 h_{22} \quad (12)$$

The excess enthalpy for each cell can be obtained as follows:

$$h_1^{\text{ex}} = h_1 - h_1^{\text{ref}} = (\theta_{21} - \theta_2)(h_{21} - h_{11}) \quad (13)$$

$$h_2^{\text{ex}} = h_2 - h_2^{\text{ref}} = (\theta_{12} - \theta_1)(h_{12} - h_{22}) \quad (14)$$

The excess enthalpy of solution can be given as:

$$h^{\text{ex}} = x_1 h_1^{\text{ex}} + x_2 h_2^{\text{ex}} \quad (15)$$

Combining eqs. (13) and (14) the excess enthalpy of solution can be obtained as follows:

$$h^{\text{ex}} = x_1(\theta_{21} - \theta_2)(h_{21} - h_{11}) + x_2(\theta_{12} - \theta_1)(h_{12} - h_{22}) \quad (16)$$

Using eq. (6) the local area fractions for solvent (1) and polymer (2) can be given as below:

$$\theta_{12} = \frac{\theta_1 H_{12}}{\theta_1 H_{12} + \theta_2} \quad (17)$$

$$\theta_{21} = \frac{\theta_2 H_{21}}{\theta_1 + \theta_2 H_{21}} \quad (18)$$

The excess enthalpy of solution using eqs. (17) and (18) can be presented as:

$$h^{\text{ex}} = \frac{x_1 \theta_2 H_{21} E_{21}}{\theta_1 + \theta_2 H_{21}} + \frac{x_2 \theta_1 H_{12} E_{12}}{\theta_1 H_{12} + \theta_2} - (x_1 \theta_2 E_{21} + x_2 \theta_1 E_{12}) \quad (19)$$

To obtain the excess Gibbs free energy the following relation is used:¹⁰

$$\frac{g^{\text{ex}}}{RT} = \int_0^{1/T} \frac{h^{\text{ex}}}{R} d\left(\frac{1}{T}\right) \quad (20)$$

Thus, the excess Gibbs free energy can take the following form:

$$\frac{g^{\text{ex}}}{RT} = -10 \times \left[x_1 \ln(\theta_1 + \theta_2 H_{21}) + x_2 \ln(\theta_1 H_{12} + \theta_2) + x_1 \theta_2 \ln H_{21} + x_2 \theta_1 \ln H_{12} \right] \quad (21)$$

The activity coefficients of solvent and polymer can be presented by the following equations:

$$\ln \gamma_1^{\text{res.}} = -10 \times \left[\ln(\theta_1 + \theta_2 H_{21}) + \theta_2 \left(\frac{H_{21}}{\theta_1 + \theta_2 H_{21}} - \frac{H_{12}}{\theta_1 H_{12} + \theta_2} \right) + \theta_2^2 (\ln H_{12} H_{21}) \right] \quad (22)$$

$$\ln \gamma_2^{\text{res.}} = -10 \times \left[\ln(\theta_1 H_{12} + \theta_2) + \theta_1 \left(\frac{H_{12}}{\theta_1 H_{12} + \theta_2} - \frac{H_{21}}{\theta_1 + \theta_2 H_{21}} \right) + \theta_1^2 (\ln H_{12} H_{21}) \right] \quad (23)$$

It should be noted that the excess Gibbs free energy as well as the activity coefficients in a multicomponent system can be written as:

$$\frac{g^{\text{ex, res.}}}{RT} = -10 \times \sum_i \theta_i \left[\ln \left(\sum_j \theta_j H_{ji} \right) - \sum_j \theta_j \ln H_{ji} \right] \quad (24)$$

$$\ln \gamma_i^{\text{res.}} = 10 \times \left[-\ln \left(\sum_j \theta_j H_{ji} \right) + 1 + \sum_j \frac{\theta_j H_{ij}}{\sum_k \theta_k H_{kj}} + \sum_j \theta_j \left(\sum_k \theta_k \ln \frac{H_{kj}}{H_{ij} H_{ji}} \right) \right] \quad (25)$$

RESULTS AND DISCUSSION

The proposed model has been used in correlating the VLE phase behavior of polymer solutions. The binary energy parameters E_{ij} and E_{ji} are assumed to be linearly dependent on temperature according to the following relations:

$$E_{ij} = E_{ij}^I + E_{ij}^{II}(T - T_0) \quad (26)$$

$$E_{ji} = E_{ji}^I + E_{ji}^{II}(T - T_0) \quad (27)$$

where in the above equation T_0 is 298.15 K. Parameters E_{ij}^I , E_{ij}^{II} , E_{ji}^I , and E_{ji}^{II} can be obtained by minimizing the following objective function:

$$\Omega_{\text{VLE}} = \sum_i \left(a_i^{\text{expt.}} - a_i^{\text{calc.}} \right)^2 \quad (28)$$

where in eq. (28) a_i is activity of solvent and superscript "expt." and "calc." refer to the experimental and calculated results, respectively.

The average absolute deviation (AAD) of the VLE experimental data for polymer–solvent systems using the proposed model and the UNIQUAC-FV model were reported in Table I. The results showed that the proposed model can more accurately correlate the VLE data of polymer solutions than the UNIQUAC-FV model. The regressed parameters for the proposed model obtained from VLE experimental data were reported in Table I. As seen from Table II, the proposed model can be accurately used to study the phase behavior of PEG + water and DEX + water systems to be employed in separation and purification of biomolecules.

Figures 1 and 2 compare the results obtained from the proposed model for PEG4000 + water and PIB + benzene systems at various temperatures with the corresponding experimental data. As can be seen from these figures, the results of the proposed model favorably are in good agreement with the experimental data.

Also Figure 3 shows the variation of the activity of water in PEG400 + PEG20000 + water, PEG1000 + PEG10000 + water, and PEG6000 + PEG20000 + water ternary systems with the weight fraction of polymer. This figure indicates that the proposed model can accurately correlate the VLE phase behavior of aqueous polymer–polymer systems.

The proposed model has been applied in correlating the excess enthalpy, viscosity, and density of polymer solutions. The relation between density and excess volume of polymer solution can be expressed as:

$$d = \frac{\sum_i x_i M_i}{\sum_i x_i V_i + V^{\text{ex}}} \quad (29)$$

where in eq. (29) d is the density of solution, M_i and V_i are molecular mass and molar volume of component i , respectively. According to the fundamental thermodynamic relation, the excess volume of solution can be obtained using the excess Gibbs free energy at constant temperature as follow:

$$V^{\text{ex}} = \left(\frac{\partial g^{\text{ex}}}{\partial P} \right)_{T,n} \quad (30)$$

TABLE I
Results of Binary VLE Correlation Using the UNIQUAC-FV and the Proposed Model

System	n	T/K	M_n	M_w	M_v	AAD% (UNIQUAC-FV)	AAD% (new model)	Ref.
PEG/water	16	308.15–338.15	296			2.83	0.04	13
PEG/water	32	308.15–338.15	430			0.86	0.02	13
PEG/water	16	308.15–338.15	4,237			0.79	0.03	13
PEG/water	29	308.15–338.15	5,989			0.24	0.02	13
PEG/benzene	20	297.75–307.75	335			0.85	0.02	14
PEG/benzene	18	297.75–307.75	1,460			0.33	0.08	14
PEG/benzene	20	297.75–307.75	4,150			0.16	0.01	14
PEG/2-propanol	20	298.15	296			5.7	0.14	15
PEG/2-propanol	13	298.15	995			2.2	0.20	15
DEX/water	13	293.15–333.15	23,600			0.12	0.00	14
DEX/water	23	293.15–333.15	46,300			0.11	0.03	14
DEX/water	47	293.15–333.15	64,800			0.12	0.06	14
DEX/water	30	293.15–333.15	101,000			0.10	0.05	14
PIB/benzene	6	283.15–313.15			40,000	0.55	0.30	16
PIB/benzene	29	298.15–338.15	45,000			1.7	1.68	16
PIB/benzene	71	298.15–338.15		50,000		3.2	2.82	16
PIB/benzene	12	338.15		100,000		3.6	3.6	16
PIB/pentane	22	298.15–328.15	1,170			1.5	1.37	16
PIB/pentane	10	295.15	2,700			0.6	0.47	16
PIB/pentane	21	298.15–328.15	2,250,000			0.5	0.26	16
PIB/cyclohexane	33	298.15–338.15		50,000		1.8	2.4	16
PIB/cyclohexane	30	298.15–338.15	100,000			1.3	1.1	16
PIB/hexane	24	298.15–338.15		50,000		3.6	2.42	16
PS/benzene	16	288.15–303.15			900,000	1.1	2.02	16
PS/cyclohexane	28	313.15–353.15	218,000			0.60	0.8	14
PS/toluene	26	313.15–353.15	218,000			1.8	1.7	14
Overall	625					1.40	0.83	

TABLE II
The Values of the Parameters Introduced into Using the Solvent Data in Polymer Solutions the Proposed Model to Activity Data of Solvent in Polymer Solution

System	n	T/K	M_n	M_w	M_v	E_{ij}^I	E_{ij}^{II}	E_{ji}^I	E_{ji}^{II}
PEG/water	16	308.15–338.15	296			79.251	-2.678	442.883	7.872
PEG/water	32	308.15–338.15	430			112.948	-3.261	504.738	6.497
PEG/water	16	308.15–338.15	4,237			122.936	-1.109	523.526	8.120
PEG/water	29	308.15–338.15	5,989			122.935	-1.154	523.523	8.032
PEG/benzene	20	297.75–307.75	335			689.800	117.211	1412.847	-69.431
PEG/benzene	18	297.75–307.75	1,460			224.645	128.250	570.561	-59.271
PEG/benzene	20	297.75–307.75	4,150			156.371	221.100	399.140	-102.166
PEG/2-propanol	20	298.15	296			206.391	-563.214	679.304	124.630
PEG/2-propanol	13	298.15	995			265.067	-2.268	785.544	8.622
DEX/water	13	293.15–333.15	23,600			200.277	-4.733	664.200	5.597
DEX/water	23	293.15–333.15	46,300			222.936	-15.789	709.494	11.304
DEX/water	47	293.15–333.15	64,800			235.284	-4.912	732.852	5.616
DEX/water	30	293.15–333.15	101,000			230.044	-2.706	728.841	4.482
PIB/benzene	6	283.15–313.15			40,000	-27.471	407.715	18.691	-279.663
PIB/benzene	29	298.15–338.15	45,000			-1338.12	-211.252	1712.244	109.024
PIB/benzene	71	298.15–338.15		50,000		-1314.34	-92.684	1767.035	46.656
PIB/benzene	12	338.15		100,000		-1309.81	87.940	1764.767	-44.140
PIB/pentane	22	298.15–328.15	1,170			-1428.26	76.072	1551.033	-40.292
PIB/pentane	10	295.15	2,700			-1430.73	76.072	1546.681	-40.292
PIB/pentane	21	298.15–328.15	2,250,000			-1428.11	78.351	1551.327	-35.786
PIB/cyclohexane	33	298.15–338.15		50,000		239.668	-299.28	540.257	154.810
PIB/cyclohexane	30	298.15–338.15	100,000			181.341	-150.967	407.467	79.543
PIB/hexane	24	298.15–338.15		50,000		329.730	121.981	674.350	-57.864
PS/benzene	16	288.15–303.15			900,000	236.817	-6.275	473.218	2.984
PS/cyclohexane	28	313.15–353.15	218,000			-13481.6	4.781	8434.166	-2.747
PS/toluene	26	313.15–353.15	218,000			233.281	-181.536	476.552	97.005

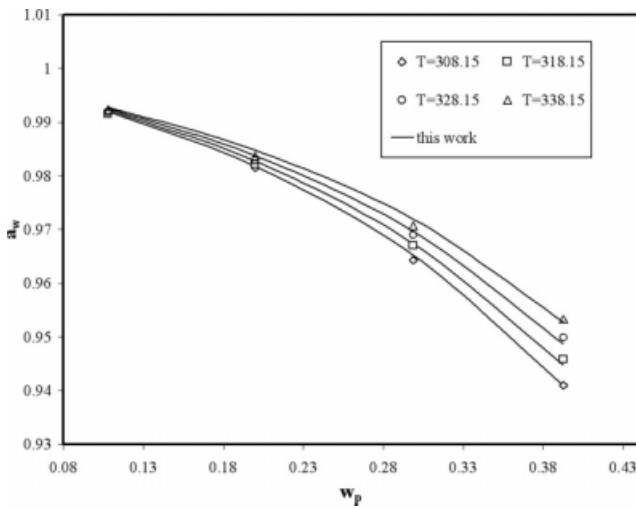


Figure 1 Plot of the activity of solvent against weight fraction of polymer for some PEG 4000 + water solution at various temperatures using the new model.

Based on eqs. (30) and (24) the excess molar volume for multicomponent systems is given by:

$$V^{\text{ex}} = \sum_i x_i \left(\frac{\sum_j \theta_j H_{ji} E_{ji}^v}{\sum_k \theta_k H_{ki}} - \sum_j \theta_j E_{ji}^v \right) \quad (31)$$

where in eq. (31) $E_{ij}^v = \frac{dE_{ij}}{dP}$. E_{ij}^v is adjustable parameter to be regressed by correlating the experimental density obtained from fitting the experimental density of polymer solution and the results of the proposed model. The regressed parameters of the proposed model are obtained by minimizing the following objective function:

$$\Omega_d = \sum_i \left(d_i^{\text{expt.}} - d_i^{\text{calc.}} \right)^2 \quad (32)$$

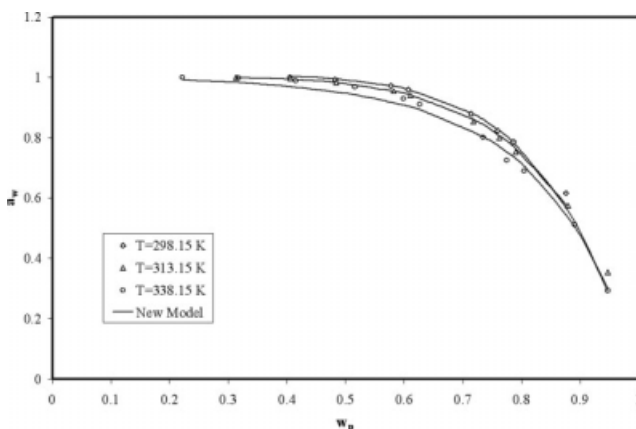


Figure 2 Plot of the activity of solvent against weight fraction of polymer for some PIB + benzene solution at various temperatures using the new model.

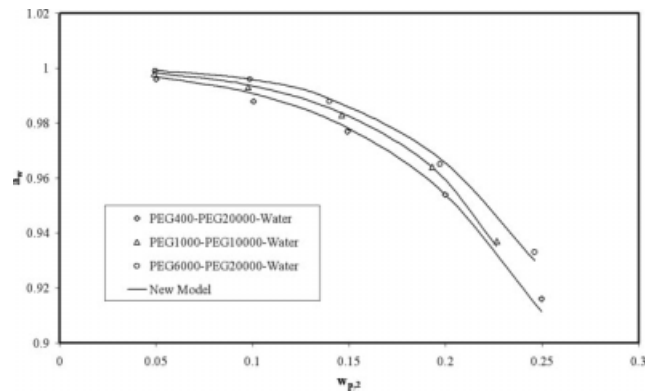


Figure 3 Plot of the activity of solvent against weight fraction of polymer for some polymer (1) + polymer (2) + water (3) ternary systems (Experimental data are obtained from Ref. 17).

The values of the parameters E_{ij} and E_{ji} which were used to correlate the experimental data for polymer solutions were directly obtained from the study of VLE phase behavior of polymer solutions. The adjustable parameters E_{ij}^v , E_{ji}^v , and the AAD% for various polymer solutions were reported in Table III. Also, the AAD% of the proposed model has been compared with the Poly-NRTL¹¹ and the Poly-Wilson¹² models.

The activity coefficient of each species for the Poly-Wilson model is obtained as:

$$\ln \gamma_i^{\text{res.}} = -10 \times \sum_i r_i \left[\ln \left(\sum_j X_j H_{ji} \right) + \sum_j X_j \left(\frac{H_{ij} - \sum_k X_k H_{kj}}{\sum_k X_k H_{kj}} \right) \right] \quad (33)$$

Also, the activity coefficient of each species for the Poly-NRTL model is obtained as below:

$$\ln \gamma_i^{\text{res.}} = \sum_i r_i \left[\frac{\sum_{j=1}^n X_j \tau_{ji} G_{ji}}{\sum_{k=1}^n X_k G_{ki}} + \sum_{j=1}^n \frac{X_j G_{ji}}{\sum_{k=1}^n X_k G_{ki}} \left(\tau_{ij} - \frac{\sum_{m=1}^n X_m \tau_{mi} G_{mi}}{\sum_{k=1}^n X_k G_{ki}} \right) \right] \quad (34)$$

where in the above equations:

$$X_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad (35)$$

The AAD% shows that the proposed model has better accuracy than the other models for correlation the experimental density of polymers solutions.

TABLE III
The Values of the Parameters and the AAD% for the Proposed, the Poly-Wilson, and the Poly-NRTL Models Obtained Using the Density Data of Polymer Solutions

System	M_n	T/K	n	E_{12}^v	E_{21}^v	AAD% (new model)	AAD% (Poly-Wilson)	AAD% (Poly-NRTL)	Ref.
PEG + water	300	298.15	10	-8935.51	50.280	0.37	2.36	1.13	18
PEG + water	400	298.15	10	-8936.39	29.807	0.17	2.62	1.40	18
PEG + water	600	298.15	10	-8996.3	-9.686	0.08	2.34	1.08	18
PEG + water	900	298.15	10	-24885.9	54.875	0.47	3.44	2.02	18
PEG + water	1,000	298.15	10	-15718.6	-3.448	0.09	2.65	1.21	18
PEG + water	1,500	298.15	10	145,600	-246.806	1.62	18.16	16.00	18
PEG + water	2,000	298.15	10	-35462.3	7.546	0.21	3.08	1.61	18
PEG + water	3,000	298.15	10	-61967.2	21.354	0.21	3.08	1.65	18
PEG + water	4,000	298.15	10	-61967.2	0.964	0.05	2.64	1.15	18
PEG + water	6,000	298.15	10	-61967.2	-36.953	0.40	3.08	1.51	18
PEG + water	10,000	298.15	10	-61967.2	-71.896	0.44	3.00	1.32	18
PEG + water	12,000	298.15	10	-61967.2	-50.49	0.49	2.68	1.19	18
PEG + water	15,000	298.15	10	-61967.2	-49.907	0.45	2.45	1.00	18
PEG + water	20,000	298.15	10	-61967.2	-43.216	0.46	2.22	0.90	18
PEG + water	35,000	298.15	10	-61967.2	-59.871	0.65	2.43	1.07	18
Overall			150			0.41	3.74	2.82	

The experimental density of polymer solutions and the results of the proposed model for PEG 400 + water system at various temperatures are compared in Figure 4.

The excess volume of PEG 400 + water system in wide range of temperature (300.15–328.15 K) is shown in Figure 5. Figure 5 compares the results for the excess volume of PEG 400 + water system at different temperatures with the corresponding experimental data. As observed from this figure, the results obtained from the proposed model are in good agreement with the experimental data.

The proposed model has been developed in the correlation of the viscosity of polymer solutions.

According to the Eyring theory, viscosity of solution can be obtained as:²⁰

$$\ln(\eta V) = \sum_i x_i \ln(\eta_i V_i) + \frac{g^{\text{ex},*}}{RT} \quad (36)$$

where in the above equation η and V are viscosity and molar volume of mixture and η_i and V_i are viscosity and molar volume of component i and $g^{\text{ex},*}$ is activation excess Gibbs free energy of solution. Molar volume and activation excess Gibbs free energy of solution are given as:

$$V = \sum_i x_i V_i \quad (37)$$

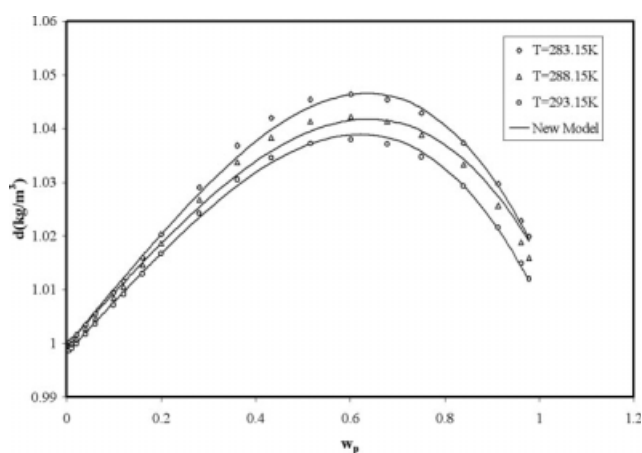


Figure 4 Plot of the density of polymer solution against weight fraction of polymer for a number of PEG 400 + water system (Experiential data are obtained from Ref. 19).

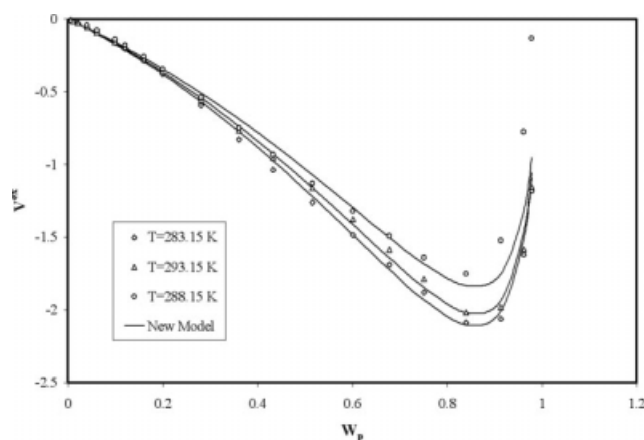


Figure 5 Plot of the excess molar volume of polymer solution against weight fraction of polymer for a number of PEG 400 + water system.

TABLE IV
The Values of the Parameters and the AAD% for the Proposed, the Poly-Wilson, and the Poly-NRTL Models Obtained Using the Viscosity Data of Polymer Solutions

System	M_n	T/K	n	E_{12}^{η}	E_{21}^{η}	AAD% (new model)	AAD% (Poly-Wilson)	AAD% (Poly-NRTL)	Ref.
PEG + 1,2-dimethoxyethane	192	298.15	14	-27756.9	36793.57	4.46	8.38	5.50	22
PEG + 1,2-dimethoxyethane	408	298.15	14	-40198	55000.96	5.55	13.51	6.39	22
PEG + 1,2-dimethoxymethane	192	298.15	14	-28576.3	36353.88	2.73	6.41	4.34	22
PEG + 1,2-dimethoxymethane	408	298.15	14	-44914.8	64182.29	9.59	8.90	5.06	22
PEG + 1,3-dioxolane	192	303.15	14	-27636.7	33668.07	0.49	2.27	1.16	23
PEG + 1,3-dioxolane	408	303.15	14	-43091.6	56941.02	4.60	3.35	1.43	23
PEG + 1,4-dioxane	192	303.15	14	-27322	34070.51	1.54	2.32	1.99	23
PEG + 1,4-dioxane	408	303.15	14	-39225.6	50392.24	3.43	3.55	1.97	23
PEG + oxolane	192	303.15	14	-28857.8	36211.74	0.39	3.35	3.05	23
PEG + oxolane	408	303.15	14	-44902	62656.15	6.51	5.47	3.31	23
PEG + oxane	192	303.15	14	-36240.1	51667.97	3.25	3.70	4.13	23
PEG + methyl acetate	400	298.15	11	-43375.3	59139.43	5.33	4.63	0.99	24
PEG + methyl acetate	400	303.15	11	-43547.3	59036.08	4.92	3.82	1.33	24
PEG + methyl acetate	400	308.15	11	-43619.6	59007.36	5.01	6.26	2.17	24
PVP + water	4,088	298.15	27	-82707.7	109437.4	1.91	3.17	16.97	21
PVP + water	4,088	308.15	27	-80687.5	104302.3	1.31	1.58	16.31	21
PVP + water	4,088	318.15	27	-81020.5	104153.2	1.50	2.48	15.22	21
PVP + water	4,088	328.15	27	-81328.1	104016	0.77	2.94	14.71	21
PEG + water	300	298.15	10	-3660.96	-3603.02	2.68	8.22	7.43	18
PEG + water	400	298.15	10	-4132.59	-4102.41	2.35	3.33	2.53	18
PEG + water	600	298.15	10	-5000.8	-5039.79	4.40	5.43	5.21	18
PEG + water	900	298.15	10	-5574.7	-5663.61	2.17	5.30	5.81	18
PEG + water	1,000	298.15	10	-5899.09	-6021.18	1.35	2.96	3.20	18
PEG + water	1,500	298.15	10	-6706.61	-6920.84	0.81	2.83	3.06	18
PEG + water	2,000	298.15	10	-7534.2	-7862.09	0.24	1.75	1.66	18
PEG + water	3,000	298.15	10	-8975.61	-9537.46	0.37	4.46	4.26	18
PEG + water	4,000	298.15	10	-10386.6	-11244.1	0.80	8.90	8.876	18
PEG + water	6,000	298.15	10	-12253.2	-13609.7	0.75	10.09	10.01	18
Overall			395			2.82	4.97	5.64	

$$\frac{\delta^{\text{ex}}}{RT} = -10 \times \left\{ \sum_i \theta_i \left[\ln \left(\sum_j \theta_j H_{ji}^{\eta} \right) - \sum_j \theta_j \ln H_{ji}^{\eta} \right] \right\} \quad (38)$$

$$H_{ij}^{\eta} = \exp \left(-\frac{E_{ij}^{\eta}}{10RT} \right) \quad (39)$$

In eq. (36) E_{ij}^{η} is an adjustable parameter for the proposed model obtained from the experimental data of viscosity for polymer solutions.

The adjustable parameters of the proposed model are obtained from minimization of the following objective function:

$$\Omega_{\eta} = \sum_i \left(\eta_i^{\text{expt.}} - \eta_i^{\text{calc.}} \right)^2 \quad (40)$$

For PVP + water and PEG + water systems, the viscosity of pure polymer are not available in the literature. In this case, the viscosity was considered as an adjustable parameter. The below correlation has been reported to give the viscosity of pure PVP at wide range of temperature:²¹

$$\eta_{\text{PVP}} = 1.5252 \times 10^{-5} \exp \left(\frac{7144.6}{T/K} \right) \quad (41)$$

Also, the following equation has been proposed for the prediction of the viscosity of pure PEG with molecular weight of polymer:¹⁸

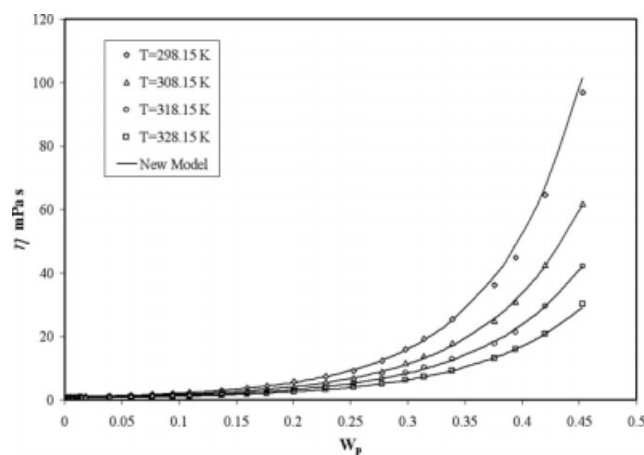


Figure 6 Plot of the viscosity of polymer solution against weight fraction of polymer for a number PVP + water system.

TABLE V
The Values of the Parameters and the AAD% for the Proposed, the Poly-Wilson, and the Poly-NRTL Models
Obtained Using the Excess Enthalpy Data of Polymer Solutions

System	n	T/K	M_n	E_{12}^h	E_{21}^h	AAD% (new model)	AAD% (Poly-Wilson)	AAD% (Poly-NRTL)	Ref.
PEG + 3-phenylpropyl alcohol	19	308.15	192	-2271.143	9752.591	21.73	18.93	18.37	25
PEG + 3-phenylpropyl alcohol	19	308.15	274	-2363.883	10547.087	11.73	21.76	19.28	25
PEG + 3-phenylpropyl alcohol	19	308.15	365	-1619.984	12980.663	5.64	23.34	19.86	25
PEG + 3-phenylpropyl alcohol	20	308.15	554	-1280.562	15599.550	10.15	23.08	19.98	25
PEG + 2-phenylpropyl alcohol	19	308.15	192	-6836.881	7181.948	12.40	11.90	11.98	26
PEG + 2-phenylpropyl alcohol	19	308.15	274	-7024.240	8395.717	11.34	10.74	10.84	26
PEG + 2-phenylpropyl alcohol	19	308.15	365	-7418.591	8555.870	7.74	9.72	8.08	26
PEG + 2-phenylpropyl alcohol	19	308.15	554	-7194.403	9767.971	8.87	11.81	10.11	26
PEG + dimethyl sulfoxide	19	308.15	192	-8284.137	12727.220	7.79	7.74	7.52	27
PEG + dimethyl sulfoxide	20	308.15	274	-7749.418	14804.583	13.28	10.96	11.89	27
PEG + dimethyl sulfoxide	20	308.15	365	-7088.088	15810.303	16.03	13.08	13.55	27
PEG + dimethyl sulfoxide	20	308.15	554	-6392.881	15802.180	18.70	18.03	13.79	27
Overall	232					12.12	15.09	13.77	

$$\eta_{\text{PEG}} = 6.5727 \times 10^{-3} (M_P/g \text{ mol}^{-1})^{3.1542} \quad (42)$$

In the above equation M_P is the number-average polymer molecular weight.

The adjustable parameters and the AAD% of the proposed model, the Poly-Wilson¹¹ and the Poly-NRTL¹² models were reported in the Table IV. The results indicate that the proposed model can correlate the viscosity of polymer solutions with better accuracy than the Wilson and NRTL models to correlate the viscosity of polymer solutions.

Also, the comparison between the experimental viscosity and the results of the proposed model for PVP + water was shown in Figure 6. As shown superior results can be achieved using the proposed model at various temperatures.

To obtain the excess enthalpy of polymer solutions the following equation can be used:

$$h^{\text{ex}} = \sum_i x_i \left(\frac{\sum_j \theta_j H_{ji} E_{ji}^h}{\sum_k \theta_k H_{ki}} - \sum_j \theta_j E_{ji}^h \right) \quad (43)$$

E_{ij}^h is considered as an adjustable parameter and can be obtained by minimizing the following objective function:

$$\Omega_h = \sum_i (h_i^{\text{expt.}} - h_i^{\text{calc.}})^2 \quad (44)$$

The binary interaction parameters of the developed model and the AAD% of the proposed model, the Poly-Wilson¹¹ and the Poly-NRTL¹² were reported in Table V. The results show that the proposed model can accurately correlate the excess enthalpy of polymer solutions than those obtained from the Poly-Wilson and Poly-NRTL models.

Figure 7 shows the comparison between the experimental excess enthalpy of polymer solution and the results of the proposed model for the system of PEG200 + dimethyl sulfoxide and PEG300 + dimethyl sulfoxide systems. As seen good agreement between results of the model and those of the experimental data can be achieved.

CONCLUSIONS

A local composition-based model has been used in correlating the vapor-liquid phase behavior of polymer solutions. In this equation, the Flory-Huggins model has been considered as the combinatorial term and the equation proposed by Pazuki et al. was considered as the residual term. The proposed model has been used in correlating the vapor-liquid phase behavior for a large number of polymer-solvent mixtures at different conditions.

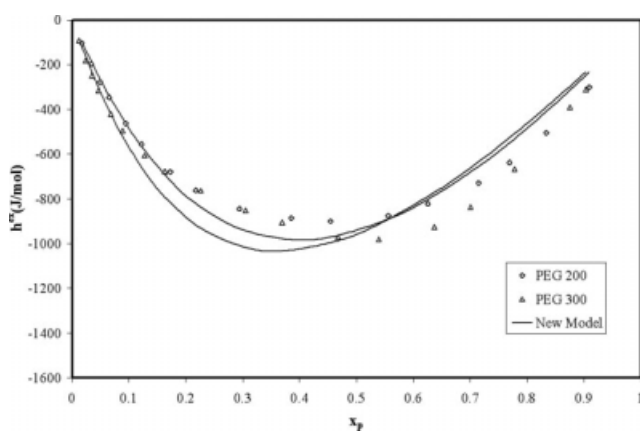


Figure 7 Plot of the excess molar enthalpy of polymer solution against mole fraction of polymer for PEG200 + dimethyl sulfoxide and PEG300 + dimethyl sulfoxide systems.

The results obtained from the proposed model have been compared with those obtained from the UNIQUAC-FV model. The results showed that the proposed model can accurately correlate the VLE data for polymer solutions studied in this work. Also, the proposed model has been used to obtain the thermophysical properties such as density, viscosity, and excess enthalpy for these polymer solutions. The results in connection with the thermophysical properties obtained from the proposed model have been compared with those obtained from the Poly-NRTL and the Poly-Wilson models. The results showed that the proposed model can accurately correlate the properties of polymer solutions at various conditions.

References

1. Albertsson, P. A. *Partition of Cell Particles and Macromolecules*, 3rd ed.; Wiley: New York, 1986.
2. Zaslavsky, B. Y. *Aqueous Two-Phase Partitioning. Physical Chemistry and Bioanalytical Applications*; Marcel Dekker: New York, 1995.
3. Flory, P. J. *J Chem Phys* 1941, 9, 660.
4. Chen, C. C. *Fluid Phase Equilib* 1993, 83, 301.
5. Oishi, T.; Prausnitz, J. M. *Ind Eng Chem Process Des Dev* 1978, 17, 333.
6. Wu, Y.-T.; Zhu, Z.-Q.; Lin, D.-Q.; Mei, L.-H. *Fluid Phase Equilib* 1996, 121, 125.
7. Zafarani-Moattar, M. T.; Sadeghi, R. *Fluid Phase Equilib* 2002, 202, 413.
8. Radfarnia, H. R.; Ghotbi, C.; Taghikhani, V.; Kontogeorgis, G. M. *Fluid Phase Equilib* 2005, 234, 94.
9. Radfarnia, H. R.; Ghotbi, C.; Taghikhani, V.; Kontogeorgis, G. M. *J Chem Thermodyn* 2006, 38, 923.
10. Pazuki, G. R.; Taghikhani, V.; Vossoughi, M. *Fluid Phase Equilib* 2007, 255, 160.
11. Orbey, H.; Chen, C. C.; Bokis, C. P. *Fluid Phase Equilib* 1998, 145, 169.
12. Sadeghi, R. *J Chem Thermodyn* 2005, 37, 55.
13. Eliassi, A.; Modarress, H.; Mansoori, G. A. *J Chem Eng Data* 1999, 44, 52.
14. Wohlfarth, C. *Vapor-Liquid Equilibrium Data of Binary Polymer Solutions*; Institut fur Physikalische Chemie, Elsevier: Germany, 1994.
15. Zafarani-Moattar, M. T.; Yeghaneh, N. *J Chem Eng Data* 2002, 47, 72.
16. Hao, W.; Elbro, H. S.; Alessi, P. *Polymer Solution Data Collection, Part 1: Vapor-Liquid Equilibrium, Vol. XIV*; DECHEMA: Frankfurt/Main, 1992.
17. Ninni, L.; Camargo, M. S.; Meirelles, A. J. A. *Thermochem Acta* 1999, 328, 169.
18. Kirincic, S.; Klofutar, C. *Fluid Phase Equilib* 1999, 155, 311.
19. Eliassi, A.; Modarress, H.; Mansoori, G. A. *J Chem Eng Data* 1998, 43, 719.
20. Novak, L. T.; Chen, C. C.; Song, Y. *Ind Eng Chem Res* 2004, 43, 5231.
21. Sadeghi, R.; Zafarani-Moattar, M. T. *J Chem Thermodyn* 2004, 36, 665.
22. Comelli, F.; Ottani, S.; Francesconi, R. R.; Castellari, C. *J Chem Eng Data* 2002, 47, 1226.
23. Ottani, S.; Vitalini, D.; Comelli, F.; Castellari, C. *J Chem Eng Data* 2002, 47, 1197.
24. Sadeghi, R. *Fluid Phase Equilib* 2005, 231, 53.
25. Castellari, C.; Francesconi, R.; Comelli, F. *Thermochim Acta* 2004, 424, 69.
26. Castellari, C.; Francesconi, R.; Comelli, F. *J Chem Eng Data* 2004, 49, 1032.
27. Comelli, F.; Ottani, S.; Francesconi, R.; Castellari, C. *J Chem Eng Data* 2003, 48, 995.