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New local composition model for polymer solutions

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Abstract

A new segment-based local composition model is presented for the excess Gibbs energy of polymer solutions. The excess Gibbs energy of a polymer solution is expressed as a sum of contributions of a combinatorial and a residual excess Gibbs energy term. The truncated Freed correction to Flory–Huggins expression as first correction for the configurational entropy of mixing is used as a combinatorial contribution to the excess Gibbs energy. A new expression based on the local composition concept, which is the NRF-Wilson model, is developed to account for the contribution of the residual excess Gibbs energy. The main difference between this model and the segment-based NRTL model available in the literature is in the nature of the short-range energy parameter and their references states. The utility of the model is demonstrated with the successful representation of the vapor–liquid equilibria, density and viscosity of several polymer solutions. The results show that, the model is valid for the whole range of polymer concentration, from dilute solution up to saturation. The results are compared with those obtained from the segment-based NRTL and segment-based Wilson models. The model presented in this work produces better results.

Keywords: Excess Gibbs energy; NRF-Wilson; Vapor–liquid equilibria

1. Introduction

An understanding of the thermodynamics of the polymer solutions is important in practical applications such as polymerization, devolatilization, and the incorporation of plasticizers and other additives. Diffusion phenomena in polymer melts and solutions are strongly affected by non-ideal solution behavior, since the chemical potential rather than the concentration provides the driving force for diffusion. Proper design and engineering of many polymer processes depend greatly upon accurate modeling of thermodynamic and transport properties such as solvent activity, density and viscosity.

There are two categories of models available for description of thermodynamic properties of polymer solutions. The excess Gibbs energy (G^{ex}) models, and the equation of state (EOS) models. Principal G^{ex} models for phase equilibrium calculations of polymer solution are those of Flory [1] and Huggins [2], who developed an expression based on lattice theory to describe the nonidealities of polymer solutions and of Edmond and Ogston [3], who modeled nonidealities with a truncated osmotic virial expansion based on McMillan–Mayer theory [4]. Local composition models such as UNIQUAC (universal quasi chemical) [5], UNIFAC (UNIQUAC functional group activity coefficient) [6], NRTL (nonrandom two-liquid) [7], NRF (nonrandom factor) [8] and Wilson [9] have also been used to describe the thermodynamics of polymer solutions. Among these local composition models, only the UNIQUAC model [5] can be used for the modeling of the phase equilibrium of polymer solutions (which involve molecules with very different structure) without further modification, because the UNIQUAC model accounts for molecular size and shape through the volume and surface area parameters. Recently, Pedrosa et al. [10] developed a segment-based UNIQUAC model that uses a combination of combinatorial term (represented by the entropic free volume, *p*-free volume and Freed Flory–Huggins equation) and the segment-based UNIQUAC model for residual term. The UNIFAC model [6] was extended to polymer solutions by Oishi and Prausnitz [11]. Two different versions of the NRTL model [7] have been used for polymer solutions. Chen [12] developed a segment-based local composition model for multisolvent, single polymer solutions, which uses a combination of the Flory–Huggins expression for the entropy of mixing molecules of different sizes and the NRTL equation for weak local physical interactions between solvent and segments of polymer chains. The Chen-NRTL model extensively has been used for the correlation of thermodynamic properties of polymer solutions

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Nomenclature

a	activity
b	empirical constant in Eqs. (31) and (32)
c	empirical constant in Eqs. (31) and (32)
C	coordination number in the Wilson model
d	density
E	dummy energy parameter
g	molar Gibbs energy
G	Gibbs energy
h	molar enthalpy
H	enthalpy parameter
M	number-average molar mass
n	number of moles
NP	number of points
P	pressure
r	number of segment
R	universal gas constant
T	absolute temperature
V	molar volume
x	mole fraction
X	effective mole fraction

Greek symbols

α	nonrandomness factor
β	dummy parameter
γ	activity coefficient
ϕ	segment fraction
η	viscosity

Superscripts

*	activation property
cal	calculated
Comb.	combinatorial
exp	experimental
E	excess
Res.	Residual
ref	reference state
η	parameter in the viscosity model
ν	pressure derivatives of activity coefficient parameters

Subscripts

i,j,k	any species, solvents or segments
I,J,K	any species, solvents or polymers
s	segment
w	solvent
p	polymer

[10,12–16]. Wu et al. [17] also developed the modified NRTL model for the representation of the Helmholtz energy of polymer solutions. They used a slightly different version of the NRTL equation; and for the entropic contribution, the truncated Freed [18] correction to the Flory–Huggins expression as first correction was used. Similar to the NRTL model, two different versions of the Wilson model [9] have also been used for polymer solutions. Xu et al. [19] developed the modified Wilson model for the representation of the excess Gibbs energy of single solvent, single polymer solutions and then applied it for the calculation of vapor–liquid equilibrium of aqueous polymer solutions. This model represents a synergistic combination of the excess entropy for mixing molecules of different sizes and the temperature dependent residual contribution, which combines the attractive interactions between solvent molecules and the segments with the contribution of the excess heat capacity. In our previous work [20], the Wilson model was extended in a different manner with reference [19] for the representation of the excess Gibbs energy of multicomponent polymer solutions. This model uses a combination of the Flory–Huggins expression for the entropy of mixing molecules of different sizes and the modified Wilson equation for weak local physical interactions between solvent and segments of polymer chains. The segment-based Wilson model extensively has been used for the correlation of thermodynamic properties of polymer solutions [15,20,21]. The segment-based NRF model has also been used for the correlation of thermodynamic properties of polymer solutions [10,14,22,23].

In this study, a new segment-based local composition model, which is a combination of the segment-based NRF model [14], and the segment-based Wilson model [20] namely NRF-Wilson model has been extended for the representation of the excess Gibbs energy of polymer solutions. To obtain the necessary expression for excess Gibbs energy for polymer solution, we considered two contributions. The truncated Freed correction to Flory–Huggins expression as first correction for the configurational entropy of mixing [18] is used as a combinatorial contribution to the excess Gibbs energy. The NRF-Wilson model is used to account for the contribution of the residual excess Gibbs energy. The main difference between this model and the segment-based NRTL model available in the literature is in the nature of the short-range energy parameter and their references states. In this model the short-range energy parameter between species in a local cell has an enthalpic nature but in the NRTL model has Gibbs energy nature. The references states for the segment-based NRTL model are pure liquids for solvents and a hypothetical segment aggregate state for segments but the references states for the model represented in this work are the random case for all the species. The utility of the model is demonstrated with the successful representation of the vapor–liquid equilibria, density and viscosity of several polymer solutions. The results show that, the model is valid for the whole range of polymer concentration, from dilute solution up to saturation. The results are compared with those obtained from the segment-based NRTL [12] and segment-based Wilson [20] models. The model presented in this work produces better results.

2. Theory

The excess Gibbs energy of a polymer solution may be expressed as the sum of the combinatorial contribution, $G^{\mathrm{E,comb.}}$, and the residual contribution, $G^{\mathrm{E,Res.}}$:

$$G^E = G^{E,\mathrm{Comb.}} + G^{E,\mathrm{Res.}} \tag{1}$$

Therefore, the activity coefficient of component I (polymers or solvents) in a polymer solution can also be considered as the sum of two contributions:

$$\ln \gamma_I = \ln \gamma_I^{\mathrm{Comb.}} + \ln \gamma_I^{\mathrm{Res.}} \tag{2}$$

In this work, the Freed correction to Flory–Huggins expression [18] was used for the combinatorial contribution and the NRF-Wilson model was used for the residual contribution to the excess Gibbs energy.

2.1. Combinatorial contributions to the excess Gibbs energy

Following Wu et al. [24], we used the following modified Flory–Huggins equation for the combinatorial contribution of multicomponent polymer solutions:

$$\frac{G^{E,\mathrm{Comb.}}}{RT} = \sum_I n_I \ln\left(\frac{\phi_I}{x_I}\right) + 0.5\sum_I\sum_J \beta_{IJ} r_I n_I \phi_J \tag{3}$$

$$\beta_{IJ} = \alpha\left(\frac{1}{r_I} - \frac{1}{r_J}\right)^2 \tag{4}$$

where the first term on the right hand side of Eq. (3) accounts for the contribution for the excess entropy associated with random mixing, and is the same as the expression in Flory–Huggins theory. The second term is the correction to the Flory–Huggins theory, and may be understood as the local composition effect from the chained segments in a polymer. From appropriate differentiation of the Eq. (3), one obtains activity coefficient of a component I in the system as

$$\ln \gamma_I^{\mathrm{Comb.}} = \ln\left(\frac{\phi_I}{x_I}\right) + 1 - \frac{\phi_I}{x_I} + r_I\left[\sum_J \beta_{JI}\phi_J(1-\phi_I) - 0.5\sum_{J\neq I}\sum_{K\neq I}\beta_{JK}\phi_J\phi_K\right] \tag{5}$$

where

$$\phi_I = \frac{r_I n_I}{\sum_J r_J n_J} \tag{6}$$

$$r_I = \sum_i r_{i,I} \tag{7}$$

In these relations, n_I and x_I are the number of moles and the mole fraction of the component I, respectively. $r_{i,I}$ is the number of the segment i in the component I. α is the nonrandom factor.

2.2. Residual contributions to the excess Gibbs energy

Following Chen [12], for the modification of the NRF-Wilson model to polymer solutions, the local composition concept is applied to the individual segments and solvent molecules, not the polymer chain. This approach reflects the vision that each segment should exert unique local physical interaction characteristics with its immediate neighboring solvent species or segments. This unique physical interaction of the segments determines the most favorable local environment around a segment. Advantage of the segment-based models over classical models for correlation of polymer solution experimental data is that, unlike the classical models, they can cover a wide range of polymer molar masses with a series of interaction parameters, which provides a predictive capability.

In a polymer solution the short-range forces originate from the solvent–solvent, segment–segment and solvent–segment interactions. To consider these interactions and similar to the approach of Chen [12], we assume the existence of two types of local cells. In a local cell the effective local mole fractions of species j and i in the immediate neighborhood of a central species i, respectively denoted by X_{ji} and X_{ii}, can be related to the effective global mole fractions of species j and i, respectively, denoted by X_j and X_i, through

$$\frac{X_{ji}}{X_{ii}} = \left(\frac{X_j}{X_i}\right)H_{ji} \tag{8}$$

where

$$X_i = \frac{\sum_I x_I r_{i,I}}{\sum_J \sum_j x_J r_{j,J}} \tag{9}$$

In a major departure from the NRTL model, the parameter H_{ji} in Eq. (8) is related to the local cell enthalpies by

$$H_{ji} = \exp\left(-\alpha\frac{E_{ji}}{RT}\right) \tag{10}$$

$$E_{ji} = h_{ji} - h_{ii} \tag{11}$$

The effective local mole fractions are related through the following relation:

$$\sum_j X_{ji} = 1 \quad \text{(cells with a central species } i\text{)} \tag{12}$$

Using these equations the effective local mole fractions can be expressed in terms of the effective mole fractions as

$$X_{ji} = \frac{X_j H_{ji}}{\sum_k X_k H_{ki}} \tag{13}$$

For a multicomponent polymer solution, the local composition contributions to the excess enthalpy can be expressed as:

$$H^{E,\mathrm{Res.}} = \sum_I\sum_i n_I r_{i,I} h_i^E \tag{14}$$

where h_i^E is the molar contribution of cells with a central species i to the excess enthalpy of the whole solution and can be defined with respect to a reference state as:

$$h_i^E = h_i - h_i^{\text{ref}} \tag{15}$$

The molar enthalpy of cells with a central species i, h_i, can be related to the effective local mole fractions as

$$h_i = \sum_j X_{ji} h_{ji} \tag{16}$$

Another major difference between the NRTL model and the NRF-Wilson model is in their reference states. The references states for the segment-based NRTL model are pure liquids for solvents and a hypothetical segment aggregate state for segments [12]. But the reference states for the NRF-Wilson model are the random case for all the species.

$$h_i^{\text{ref}} = \sum_j X_j h_{ji} \tag{17}$$

Combining Eqs. (13)–(17) the following expression for the excess enthalpy of multicomponent polymer solutions is obtained:

$$H^{E,\text{Res.}} = \sum_I \sum_i n_I r_{i,I} \left(\frac{\sum_j X_j H_{ji} E_{ji}}{\sum_k X_k H_{ki}} - \sum_j X_j E_{ji} \right) \tag{18}$$

The excess Gibbs energy can then be obtained by combining Eq. (18) and the following exact thermodynamic relation:

$$\frac{G^{E,\text{Res.}}}{RT} = \frac{1}{R} \int_0^{\frac{1}{T}} H^E \,\mathrm{d}\left(\frac{1}{T}\right) \tag{19}$$

The expression for the excess Gibbs energy is obtained as

$$\frac{G^{E,\text{Res.}}}{RT} = -\frac{1}{\alpha} \sum_I \sum_i n_I r_{i,I} \left[\ln \sum_j X_j H_{ji} - \sum_j X_j \ln H_{ji} \right] \tag{20}$$

As can be seen from Eq. (20), it has been assumed that the model parameters E_{ji} are independent of temperature. Eqs. (20) and (3) may be combined with Eq. (1) to give the complete NRF-Wilson model for excess Gibbs energy. Combining obtained equation and the following exact thermodynamic relation for molar excess Gibbs energy, g^E,

$$\mathrm{d}\left(\frac{g^E}{RT}\right) = \frac{V^E}{RT}\mathrm{d}P - \frac{h^E}{RT^2}\mathrm{d}T = \sum_I \ln \gamma_I \mathrm{d}x_I \tag{21}$$

We have

$$\begin{aligned} \ln \gamma_I = {} & -\frac{1}{\alpha} \sum_i r_{i,I} \left[\ln\left(\sum_j X_j H_{ji}\right) \right. \\ & + \sum_j X_j \left(\frac{H_{ij} - \sum_k X_k H_{kj}}{\sum_k X_k H_{kj}} \right) \\ & \left. + \sum_j X_j \left(\sum_k X_k \ln H_{kj} - \ln H_{ij} - \ln H_{ji} \right) \right] \\ & + \ln\left(\frac{\phi_I}{x_I}\right) + 1 - \frac{\phi_I}{x_I} + r_I \left[\sum_J \beta_{JI} \phi_J (1 - \phi_I) \right. \\ & \left. - 0.5 \sum_{J \neq I} \sum_{K \neq I} \beta_{JK} \phi_J \phi_K \right] \end{aligned} \tag{22}$$

$$V^E = \sum_I \sum_i x_I r_{i,I} \left(\frac{\sum_j X_j H_{ji} E_{ji}^v}{\sum_k X_k H_{ki}} - \sum_j X_j E_{ji}^v \right) \tag{23}$$

where, E_{ji}^v is pressure derivatives of activity coefficient parameters, $((E_{ji}/(P)_{T,X}$ and V is the molar volume. As can be seen from the Eq. (23), the Flory–Huggins equation has not been appeared in the relation for excess molar volume. This is because the combinatorial term is independent of pressure. In the above relations the species I and J can be solvent or polymer molecules and species i, j and k can be solvent molecules or segments. As can be seen from Eqs. (22) and (23), for the correlation of activity coefficients, the model requires two binary interaction parameters, E_{ij} and E_{ji}, and for the correlation of excess molar volume (or density) the model requires four binary interaction parameters, E_{ij}, E_{ji}, E_{ij}^v and E_{ji}^v for each of the solvent–solvent interaction pairs, the solvent–segment interaction pairs, and the segment–segment interaction pairs. In this work, the parameters E_{ij} and E_{ji} have been obtained from fitting the experimental solvent activity data to the NRF-Wilson model and then the parameters E_{ij}^v and E_{ji}^v have been obtained from fitting the model equation to the density data. The segment-based NRF-Wilson local composition model has some semi empirical basis, and the model parameters carry plausible physical significance resulting from the local composition concept. As can be seen from Eq. (15), the negative value of E_{ji} indicates that j–i interaction to be stronger than i–i interaction and the positive value of E_{ji} indicates that i–i interaction is stronger than j–i interaction.

The absolute rate theory approach of Eyring provides the following expression for the viscosity of a liquid mixture [13,23]:

$$\ln(\eta V) = \sum_i x_i \ln(\eta_i V_i) + \frac{g^{E*}}{RT} \tag{24}$$

where η and V are viscosity and molar volume of mixture, respectively, η_i and V_i are viscosity and molar volume of component i, respectively and g^{E*} is the molar excess Gibbs energy of activation for flow.

Extension of the concepts of classical thermodynamics to the viscous flow behavior of liquid mixtures can be made by

Table 1
Regressed energy parameters for the new model, and a comparison with results obtained with the segment-based NRTL model [12] and segment-based Wilson model [20] to solvent activity data of some polymer solutions

System	T (K)	M_p (g mol^{-1})	NP	E_{ws} (J mol$^{-1}\times 10^{-3}$)	E_{sw} (J mol$^{-1}\times 10^{-3}$)	AAD$^a\times10^2$ (new model)	AAD$\times10^2$ (NRTL)	AAD$\times10^2$ (Wilson)	Ref.
PDMS (s)+n-hexane (w)	303.15	26,000	12	−1.7365	−1.4286	0.74	0.98	0.98	[28]
PDMS (s)+n-pentane (w)	303.15	31,300	6	−1.4240	2.5260	1.22	1.29	1.27	[28]
PEG (s)+H_2O (w)	298.15	200	12	0.5250	1.9670	0.95	2.38	2.36	[25]
PEG (s)+H_2O (w)	298.15	400	12	0.5250	1.9670	1.92	1.11	1.06	[25]
PEG (s)+H_2O (w)	298.15	600	12	0.5250	1.9670	2.57	1.65	1.63	[25]
PEG (s)+H_2O (w)	298.15	1000	8	0.5250	1.9670	0.19	0.50	0.48	[25]
PEG (s)+H_2O (w)	298.15	1450	10	0.5250	1.9670	0.34	0.55	0.53	[25]
PEG (s)+H_2O (w)	298.15	3350	8	0.5250	1.9670	0.14	0.55	0.54	[25]
PEG (s)+H_2O (w)	298.15	3800	13	0.5250	1.9670	0.14	0.83	0.81	[29,30]
PEG (s)+H_2O (w)	298.15	6000	8	0.5250	1.9670	0.17	0.69	0.68	[25]
PEG (s)+H_2O (w)	298.15	8000	8	0.5250	1.9670	0.15	0.61	0.60	[25]
PEG (s)+H_2O (w)	298.15	10,000	8	0.5250	1.9670	0.18	0.59	0.57	[25]
PEG (s)+H_2O (w)	298.15	20,000	8	0.5250	1.9670	0.17	0.70	0.69	[25]
PEGMA (s)+1-butanol (w)	298.15	361	17	−7.2900	−4.2760	0.27	0.58	0.59	[31]
PS (s)+chloroform (w)	298.15	290,000	11	−3.7100	−2.6450	1.44	3.42	3.43	[32]
PPG (s)+1-butanol (w)	298.15	976	24	−4.2850	4.2260	0.34	0.44	0.44	[33]
PPG (s)+H_2O (w)	298.15	404	9	−10.0000	−4.5090	0.27	0.039	0.039	[34]
PVP (s)+1-butanol (w)	298.15	13,750	17	−9.7050	10.7850	1.20	1.23	1.17	[35]
PVP (s)+H_2O (w)	298.15	4088	15	−0.4220	−0.1050	0.37	0.30	0.30	[26]

AAD=(1/NP)Σ($|a_{w,exp}-a_{w,cal}|$)/$a_{w,exp}$.

assuming equivalence between the Gibbs energy of activation for flow and the equilibrium Gibbs energy of mixing. Taking this direct relationship between the thermodynamics and the transport property, the NRF-Wilson model for excess Gibbs energy developed in this work, is used to account for the viscosity deviation from ideal behavior [13,23].

A segment-based model should be more physically realistic for large molecules when diffusion and flow are viewed to occur by a sequence of individual segment jumps into vacancies rather than large molecule jumps into large vacancies. Following Novak et al. [13], by application of the segment concept to the Eyring rate-based model and using the segment-based polymer NRF-Wilson model for describing deviations from ideality we have:

$$\ln(\eta V)=\sum_i X_i\ln(\eta_i\bar{V}_i)+\frac{g^{E*}}{RT}\tag{25}$$

$$V=\sum_i X_i\bar{V}_i\tag{26}$$

$$\eta_i=\frac{\sum_I r_{i,I}\eta_I}{\left(\sum_I r_{i,I}\right)}\tag{27}$$

$$\bar{V}_i=\frac{\sum_I r_{i,I}V_{i,I}}{\left(\sum_I r_{i,I}\right)}\tag{28}$$

$$\frac{g^{E*}}{RT}=-\frac{1}{\alpha}\sum_i X_i\left[\ln\left(\sum_j X_j\exp\left(-\alpha\frac{E^{\eta}_{ji}}{RT}\right)\right)-\sum_j X_j\left(-\alpha\frac{E^{\eta}_{ji}}{RT}\right)\right]\tag{29}$$

where g^{E*} is the molar excess Gibbs energy of activation for flow in the lattice notation. $V_{i,I}$ is the molar volume of the segment i in the component I. The excess term in the Eyring–NRF-Wilson viscosity model, like the NRF-Wilson excess Gibbs energy expression, has some semiempirical basis and the model parameters (E^{η}_{ji}) carry plausible physical significance resulting from the local composition concept. The segment version of the NRF-Wilson model assumes that the liquid has a lattice structure that can be described as cells with central species (segments or solvents) that are surrounded by various species (segments or solvents) in the mixture. The distribution of the species around these central species is determined by enthalpies of interaction for the activated state. The use of a local composition model to model the excess term is a reasonable approach because intermolecular friction and

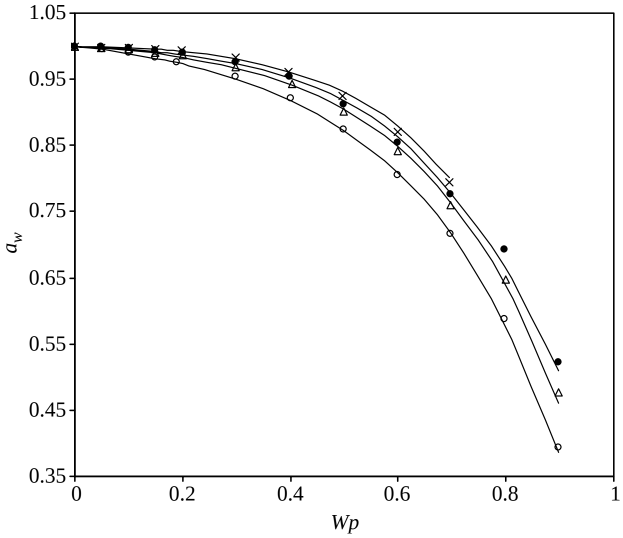

Fig. 1. Plot of the experimental water activity against the water activity calculated for the model for some PEG+H_2O systems at 298.15 K: ○, PEG200; △, PEG400; ●, PEG600; ×, PEG1450; and —, calculated.

Table 2
Regressed energy parameters for the new model, and a comparison with results obtained with the segment-based NRTL density model [36] and segment-based Wilson density model [36] to density data of some polymer solutions

System	T (K)	M_p(g mol^{-1})	NP	E_{ws} (J mol^{-1}× 10^{-3})	E_{sw} (J mol^{-1}× 10^{-3})	E^v_{ws} (cm^3 mol^{-1})	E^v_{sw}(cm^3 mol^{-1})	AAD×10^5 (new model)	AAD×10^5 (NRTL)	AAD×10^5 (Wilson)	Ref.
PEG (s)+H_2O (w)	298.15	300	10	0.525	1.967	1.030	4.96×10^{-3}	153.46	150.28	148.58	[37]
PEG (s)+H_2O (w)	298.15	400	10	0.525	1.967	1.030	4.96×10^{-3}	123.76	119.20	118.29	[37]
PEG (s)+H_2O (w)	298.15	600	10	0.525	1.967	1.030	4.96×10^{-3}	63.30	59.62	58.33	[37]
PEG (s)+H_2O (w)	298.15	900	10	0.525	1.967	1.030	4.96×10^{-3}	63.56	56.52	56.24	[37]
PEG (s)+H_2O (w)	298.15	1000	10	0.525	1.967	1.030	4.96×10^{-3}	42.29	38.10	36.61	[37]
PEG (s)+H_2O (w)	298.15	1500	10	0.525	1.967	1.030	4.96×10^{-3}	28.24	19.82	20.01	[37]
PEG (s)+H_2O (w)	298.15	2000	10	0.525	1.967	1.030	4.96×10^{-3}	12.17	13.00	11.78	[37]
PEG (s)+H_2O (w)	298.15	3000	10	0.525	1.967	1.030	4.96×10^{-3}	7.86	12.48	9.95	[37]
PEG (s)+H_2O (w)	298.15	4000	10	0.525	1.967	1.030	4.96×10^{-3}	18.01	23.54	23.01	[37]
PEG (s)+H_2O (w)	298.15	6000	10	0.525	1.967	1.030	4.96×10^{-3}	29.56	36.03	36.18	[37]
PEG (s)+H_2O (w)	298.15	10,000	10	0.525	1.967	1.030	4.96×10^{-3}	62.21	67.84	68.92	[37]
PEG (s)+H_2O (w)	298.15	12,000	10	0.525	1.967	1.030	4.96×10^{-3}	68.93	73.81	74.90	[37]
PEG (s)+H_2O (w)	298.15	15,000	10	0.525	1.967	1.030	4.96×10^{-3}	54.89	58.76	60.30	[37]
PEG (s)+H_2O (w)	298.15	20,000	10	0.525	1.967	1.030	4.96×10^{-3}	50.03	53.27	54.90	[37]
PEG (s)+H_2O (w)	298.15	35,000	10	0.525	1.967	1.030	4.96×10^{-3}	63.58	67.85	68.97	[37]
PPG (s)+1-Butanol (w)	298.15	1025	23	−4.285	4.226	−1.2896	2.2321	2.26	2.53	7.40	[16]
PVP (s)+H_2O (w)	298.15	4088	23	−0.422	−0.105	−4.4622	1.3660	5.43	5.52	16.5	[26]
PVP (s)+H_2O (w)	308.15	4088	23	−0.422	−0.105	−4.4622	1.3660	3.91	4.21	14.12	[26]
PVP (s)+H_2O (w)	318.15	4088	23	−0.422	−0.105	−4.4622	1.3660	4.30	4.50	15.04	[26]
PVP (s)+H_2O (w)	328.15	4088	23	−0.422	−0.105	−4.4622	1.3660	6.24	6.37	18.34	[26]

viscosity should be affected by nearest neighbors. Parameters E_{ji}^{η} are the composition and temperature-independent parameters referred to here as the segment-based NRF-Wilson binary parameters for the activated state. In fact, the NRF-Wilson term in the segment-based viscosity model refers to an energy barrier associated with a segment jump, whereas the Wilson activity coefficient model refers to molecular interactions in the liquid phase. Parameters of the NRF-Wilson activity coefficient model are obtained by fitting phase equilibrium data, whereas the parameters of the NRF-Wilson viscosity model are obtained by fitting viscosity data. Also, following Novak et al. [13], only the residual contribution of the new model has been used for g^{E*}.

3. Results and discussion

The applicability of the new model developed in this paper has been tested using experimental solvent activity, density and viscosity data of a variety of polymer solutions. The results have been compared with those obtained from the segment-based NRTL [12] and segment-based Wilson [20] models. The model developed in this study correlates the experimental data with comparable and in most cases with better accuracy than the other two models. A value of $r=1$ was used for solvents and for polymers the value of r is ratio of the molar volume of polymer to that of solvent. We found that a better quality of fitting with the new model developed in this work is obtained with $\alpha=0.5$ for all of tested systems. Therefore this value was used in this work. As stated by Chen [12], the nonrandomness factor (α), in the range of 0.2–0.3, has no significance impact on the behavior of the segment-based polymer NRTL model. In this work, it has been fixed at 0.25. In the segment-based polymer Wilson [20] model the value of C has been fixed at 10. The same procedure has been used with all three models.

3.1. Solvent activity

Eq. (22) for solvent has been used for the correlation of solvent activity data of several polymer solutions. In the case of polyethylene glycol (PEG) + H_2O system [25], the model parameters, E_{sw} and E_{ws}, between the segments of polymer and water have been calculated from the experimental water activity data of several aqueous PEG solutions at different PEG molar masses at 298.15 K. It was found that the calculated parameters are independent of the polymer molecular weights and can also give a very good representation of the vapor–liquid equilibrium of other PEG aqueous solutions with the deviations being practically within the experimental accuracy. Therefore, the same parameters are used for all PEGs with different chain lengths. The evaluated parameters along with the corresponding deviation for the systems studied are listed in Table 1. As can be seen from Table 1, the model parameters are independent of polymer molar mass. On the basis of the deviation obtained, given in Table 1, we conclude that the proposed model represents the experimental solvent activity data of polymer solutions, with good accuracy. Also in Table 1, the results are compared with those obtained from the segment-based polymer NRTL [12] and segment-based polymer Wilson [20] models. Comparison between experimental and correlated water activity data is shown in Fig. 1 for PEG + H_2O systems at 298.15 K.

3.2. Density

The relationship between the density and the excess molar volume of a solution is established by the following equation:

$$d=\frac{\sum_I x_I M_I}{\sum_I x_I V_I + V^E} \tag{30}$$

where, d is the density of solution, M_I and V_I are molar mass and molar volume of pure component I. The published density data was fitted, as $1/d$ against concentration and temperature, using Eqs. (23) and (30). The model parameters E_{ij} were calculated from the experimental solvent activity data and then the model parameters E_{ij}^{v} were calculated from the density data of polymer solutions. The evaluated parameters along with the corresponding deviation for the systems studied are listed in Table 2. As can be seen from Table 2, the model parameters are independent of polymer molar mass and temperature. On the basis of the deviation obtained, given in Table 2, we conclude that the proposed model represents the experimental density data of polymer solutions, with good accuracy. Also in Table 2, the results are compared with those obtained from the segment-based NRTL and segment-based Wilson density models [36]. To see more of the reliability of the present model, the experimental and calculated density data has been shown in Fig. 2 for polyvinyl pyrrolidone (PVP) + H_2O [26] system at different temperatures.

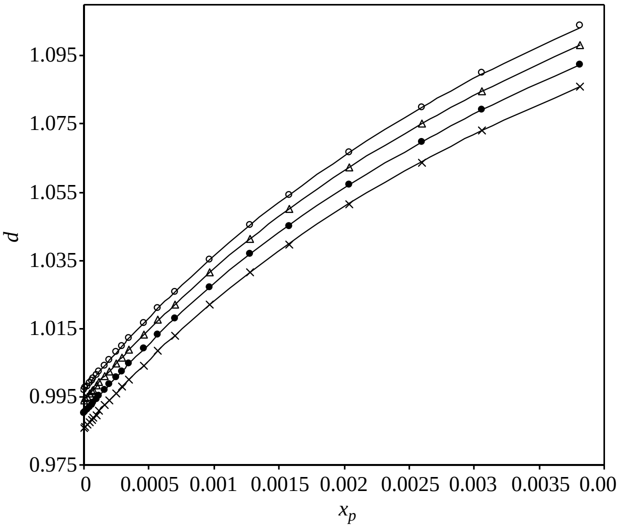

Fig. 2. Plot of the experimental density against the density calculated for the model for some PVP + H_2O systems at different temperatures: ○, $T=298.15$ K; △, $T=308.15$ K; ●, $T=318.15$ K; ×, $T=328.15$ K; and —, calculated.

Table 3
Regressed energy parameters for the new model, and a comparison with results obtained with the segment-based Eyring-NRTL [13] and segment-based Eyring–Wilson [21] models to viscosity data of several polymer solutions

System	T (K)	M_p (g mol^{-1})	NP	E^{η}_{ws} (J mol^{-1}×10^{-3})	E^{η}_{sw} (J mol^{-1}×10^{-3})	AAD×10^2 (new model)	AAD×10^2 (NRTL)	AAD×10^2 (Wilson)	Ref.
PVP (s)+H_2O (w)	298.15	4088	23	0.0216	10.5025	1.41	16.97	3.17	[26]
PVP (s)+H_2O (w)	308.15	4088	23	0.0216	10.5025	1.22	16.31	1.58	[26]
PVP (s)+H_2O (w)	318.15	4088	23	0.0216	10.5025	1.55	15.22	2.48	[26]
PVP (s)+H_2O (w)	328.15	4088	23	0.0216	10.5025	0.95	14.71	2.94	[26]
PEG (s)+H_2O (w)	298.15	300	10	−32.7865	27.2122	5.65	7.43	8.22	[27]
PEG (s)+H_2O (w)	298.15	400	10	−32.7865	27.2122	1.10	2.53	3.33	[27]
PEG (s)+H_2O (w)	298.15	600	10	−32.7865	27.2122	4.43	5.21	5.43	[27]
PEG (s)+H_2O (w)	298.15	900	10	−32.7865	27.2122	6.38	5.81	5.30	[27]
PEG (s)+H_2O (w)	298.15	1000	10	−32.7865	27.2122	3.95	3.20	2.96	[27]
PEG (s)+H_2O (w)	298.15	1500	10	−32.7865	27.2122	3.85	3.06	2.83	[27]
PEG (s)+H_2O (w)	298.15	2000	10	−32.7865	27.2122	1.31	1.66	1.75	[27]
PEG (s)+H_2O (w)	298.15	3000	10	−32.7865	27.2122	3.44	4.26	4.46	[27]
PEG (s)+H_2O (w)	298.15	4000	10	−32.7865	27.2122	7.95	8.76	8.90	[27]
PEG (s)+H_2O (w)	298.15	6000	10	−32.7865	27.2122	9.31	10.01	10.09	[27]
PEG (s)+1,3-dioxolane (w)	303.15	192	14	−5.4302	8.0424	0.94	1.16	2.27	[38]
PEG (s)+1,3-dioxolane (w)	303.15	408	14	−5.4302	8.0424	1.08	1.43	3.35	[38]
PEG (s)+1,4-dioxane (w)	303.15	192	14	-6.1935×10^{-7}	3.0017	1.37	1.99	2.32	[38]
PEG (s)+1,4-dioxane (w)	303.15	408	14	-6.1935×10^{-7}	3.0017	1.66	1.97	3.55	[38]
PEG (s)+oxane (w)	303.15	192	14	−8.2187	11.5904	3.44	4.13	3.70	[38]
PEG (s)+oxane (w)	303.15	408	14	−8.2187	11.5904	3.26	4.28	5.25	[38]
PEG (s)+oxolane (w)	303.15	192	14	−4.9055	7.0912	1.31	3.05	3.35	[38]
PEG (s)+oxolane (w)	303.15	408	14	−4.9055	7.0912	1.23	3.31	5.47	[38]
PEG (s)+1,2-dimethoxyethane (w)	298.15	192	14	−5.8540	6.9640	2.05	5.50	8.38	[39]
PEG (s)+1,2-dimethoxyethane (w)	298.15	408	14	−5.8540	6.9640	1.97	6.39	13.51	[39]
PEG (s)+dimethoxymethane (w)	298.15	192	14	−5.5819	7.2848	1.62	4.34	6.41	[39]
PEG (s)+dimethoxymethane (w)	298.15	408	14	−5.5819	7.2848	1.48	5.06	8.90	[39]
PEG (s)+methyl acetate (w)	298.15	400	11	−5.6709	5.5474	0.96	0.99	4.63	[40]
PEG (s)+methyl acetate (w)	303.15	400	11	−5.6709	5.5474	1.24	1.33	3.82	[40]
PEG (s)+methyl acetate (w)	308.15	400	11	−5.6709	5.5474	1.89	2.17	6.26	[40]

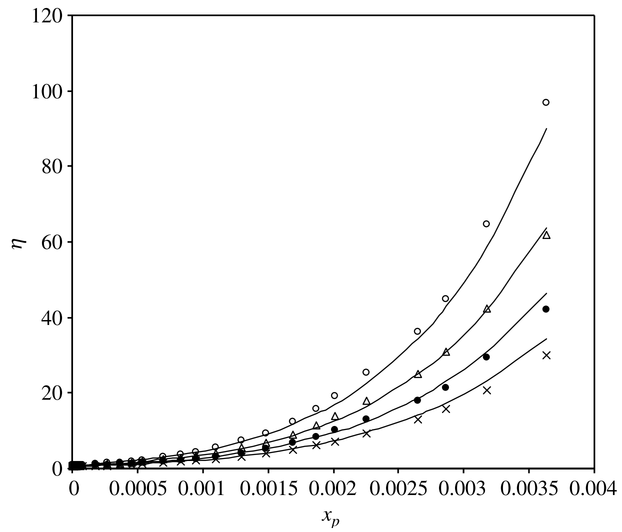

Fig. 3. Plot of the experimental viscosity against the viscosity calculated for the model for some PVP+H_2O systems at different temperatures: ○, $T=298.15$ K; △, $T=308.15$ K; ●, $T=318.15$ K; ×, $T=328.15$ K; and —, calculated.

3.3. Viscosity

The proposed model has also been used for correlating experimental viscosity data for a variety of polymer solutions. In the case of PVP+H_2O [26] and PEG+H_2O [27] systems, the pure polymer viscosity was not available. In these cases, the polymer viscosity was treated as an adjustable parameter. In the case of PVP+H_2O systems at different temperatures, the following relation was used to describe the temperature dependence of the pure polymer viscosity:

$$\eta_p/\text{mPa s} = b \exp\left(\frac{c}{T/K}\right) \quad (31)$$

This equation was substituted as η_I in the Eq. (27) and by fitting the model equation to the experimental viscosity data of PVP+H_2O system [26] at different temperatures the parameters b and c were calculated to be 1.5252×10^{-5} and 7.1446×10^3, respectively. Also, in the case of PEG+H_2O systems at different polymer molar masses, the following Mark–Houwink type relation was used to account for the polymer molar mass dependence of the pure polymer viscosity:

$$\eta_p/\text{mPa s} = b(M_p/\text{g mol}^{-1})^c \quad (32)$$

where M_p is the number-average polymer molar mass. Similarly this equation was substituted as η_I in the Eq. (27) and by fitting the model equation to the experimental viscosity data of PEG+H_2O system [27] at different polymer molar masses the parameters b and c were calculated to be 6.5727×10^{-3} and 3.1542, respectively. The evaluated parameters along with the corresponding deviation for the systems studied are listed in Table 3. As can be seen from Table 3, the model parameters are independent of polymer molar mass and temperature. On the basis of the deviation obtained, given in Table 3, we conclude that the proposed model represents the experimental viscosity data of polymer solutions, with good accuracy. Also in Table 3, the results are compared with those obtained from the segment-based Eyring-NRTL [13] and segment-based Eyring–Wilson [21] models. As can be seen from the Table 3, the model developed in this study correlates the experimental viscosity data with comparable and in most cases with better accuracy than the other two models. To show the reliability of the proposed model, comparison between experimental and correlated viscosity data are shown in Fig. 3 for PVP+H_2O [26] system.

As can be seen from the Tables 1–3, the model developed in this study correlates the experimental thermodynamic and transport properties of polymer solutions with comparable and in the most cases with better accuracy than the other two models. It has been shown that [8,41] for the local composition models, when the random case is considered for the reference state of the components, the model becomes more flexible than the case in which pure component is considered for the reference state of components.

4. Conclusion

A new segment-based local composition model, which is a polymer NRF-Wilson model, has been presented for evaluating the thermodynamic properties of polymer solutions, and appears to be reliable both for correlating and predicting the vapor–liquid equilibria, density and viscosity of homologous polymer solutions at different polymer molar masses and temperatures. The results are compared with those obtained from the segment-based NRTL and segment-based Wilson models. The model presented in this work produces better results.

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