

A new modified Wilson equation for the calculation of vapor–liquid equilibrium of aqueous polymer solutions

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Abstract

A local composition model based on the lattice theory and two-fluid theory, considering the excess heat capacity, which is a modified Wilson equation, is developed for the excess Gibbs energy of aqueous polymer solutions. The 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. The results of the extrapolation with respect to molecular weight of phase equilibrium in aqueous polymer solutions with this model are very satisfactory, with only two adjustable parameters.

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1. Introduction

Water soluble polymers have a variety of industrial applications, and are especially used for the separation and purification of biomolecules in aqueous two-phase systems (ATPS). Mixtures of poly(ethylene glycol) (PEG)+dextran (DX)+water form a two phase liquid–liquid system to separate biomolecules, cell organelles and viruses [1–3]. Recently, ATPS are combined with temperature induced phase separation, offering an effective solution to the problems of polymer removal and recycling. Recently, a random copolymer of ethylene oxide and propylene oxide (EOPO) named UCON is widely used to separate proteins, nucleic acids, enzymes, and other biomolecules [4–6] for being economic favorable. For the thermodynamic modeling of these separation methods, water is a special and key component and closely related with

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other two phase forming components. Therefore, water activity has been chosen as the objective in this research. Because experimental phase equilibrium data are often missing, the availability of fast and reliable predictive methods is a practical necessity for the design and optimization of most industrial processes.

Many G^E models have been developed in the past several decades [7–10]. The thermodynamic properties of aqueous polymer solutions cannot be correlated by simple lattice models such as the Flory–Huggins (F–H) theory, for the strong orientation—dependent interaction forces, such as hydrogen bonds. Heil and Prausnitz [11] first introduced an equation for the excess Gibbs energy based on a non random distribution of molecules into polymer solutions, which considered as the forerunner of recent practical successful relations for G^E . The only weakness of the Heil–Prausnitz treatment is the use of the Wilson relation for the entropic contribution, which is a poor substitute for the corresponding Flory–Huggins term. A correlative G^E model [12], which used a combination of the F–H type expression for entropic and NRTL theory for the local composition contribution, suggests that the model parameters are independent of temperature, chain length and polymer concentration. Since the NRTL equation is one of the preferred models for evaluating the enthalpic departures from ideality, Vetere [13] developed a predictive method based on the NRTL equation for the solvent activity prediction of low molecular weight compounds. The results appeared to be reliable both for correlation and prediction of vapor–liquid equilibrium (VLE) of a wide class of polymeric mixtures. For the description of systems with strong, local interactions, there are several successful models [14,15]. Recently, Wu et al. [16], based on these ideas, introduced the two-fluid theory, proposing a modified NRTL model for evaluating the thermodynamic properties of polymer solutions. This model appears to be accurate both for correlation and prediction of the VLE of homologous polymer solutions.

In molecular modeling, it is very common to focus directly on the entropic and enthalpic contributions to the Gibbs free energy and Helmholtz free energy, without specifically considering the excess heat capacity. In this work, a new G^E model considering the excess heat capacity is developed. The polymer solution systems of interest are aqueous solutions of PEG and EOPO, because both PEG and EOPO are popular components in ATPS.

2. Model development

The model development is shown to start with the excess Gibbs energy G^E . Choosing T , P and composition as natural independent variables, the following excess properties are used:

$$G^E = H^E - TS^E \quad (1)$$

$$c_P^E = \left(\frac{\partial H^E}{\partial T} \right)_{P,x} \quad (2)$$

$$c_P^E = T \left(\frac{\partial S^E}{\partial T} \right)_{P,x} \quad (3)$$

where c_P^E is known as a function of temperature and composition, which provides an important link between the excess enthalpy and the excess entropy. Combining Eqs. (2) and (3), after integrating, an expression for S^E can be obtained:

$$S^E = C + \int \frac{1}{T} \left(\frac{\partial H^E}{\partial T} \right)_{P,x} dT \quad (4)$$

where C is a temperature independent contribution, which can be intuitively understood as the size/shape contribution to the excess entropy. If we suppose $C = S_c^E = \lim_{T \rightarrow \infty} S^E$, one gets:

$$S^E = S_c^E + \int_{\infty}^T \frac{1}{T} \left(\frac{\partial H^E}{\partial T} \right)_{P,x} dT \quad (5)$$

Here, S_c^E is the combinatorial excess entropy. Substitution of Eq. (5) into Eq. (1) gives the excess Gibbs energy:

$$\frac{G^E}{RT} = -\frac{S_c^E}{R} + \frac{H^E}{RT} - \frac{1}{R} \int_{\infty}^T \frac{1}{T} \left(\frac{\partial H^E}{\partial T} \right)_{P,x} dT \quad (6)$$

The first-term is called combinatorial contribution, independent of temperature, and accounts for the size/shape contribution; the last two terms both depending on temperature are called the residual contribution.

2.1. Combinatorial contribution

For the calculation of G_c^E , the Guggenheim's athermal entropy of mixing [17] is used here. Due to the athermal assumption and lattice model, $H^E = 0$ and $V^E = 0$, it gives $G_c^E = A^E$. Here, we define $X_i = \theta_i$, i.e. the effective mole fraction of segment is equal to the surface/area fraction. The resulting expression is:

$$\frac{G_c^E}{RT} = n_1 \ln \frac{X_1}{x_1} + n_2 \ln \frac{X_2}{x_2} + \frac{z}{2} q_1 n_1 \ln \frac{X_1}{\Phi_1} + \frac{z}{2} q_2 n_2 \ln \frac{X_2}{\Phi_2}$$

or

$$\frac{G_c^E}{N_r kT} = \frac{\Phi_1}{r_1} \ln \frac{X_1}{x_1} + \frac{\Phi_2}{r_2} \ln \frac{X_2}{x_2} + \frac{z}{2} q_1 \frac{\Phi_1}{r_1} \ln \frac{X_1}{\Phi_1} + \frac{z}{2} q_2 \frac{\Phi_2}{r_2} \ln \frac{X_2}{\Phi_2} \quad (7)$$

where $N_r = N_1 r_1 + N_2 r_2$, $\Phi_1 = N_1 r_1 / N_r$, $\Phi_2 = 1 - \Phi_1$, $N_q = N_1 q_1 + N_2 q_2$, $X_1 = N_1 q_1 / N_q$, $X_2 = 1 - X_1$, n_1 , n_2 and N_1 , N_2 are the mole numbers and molecule numbers of solvent and polymer, r_1 and r_2 the numbers of segments per molecule of solvent and polymer, Φ_1 and Φ_2 the volume fractions of solvent and polymer. q_i is the effective segment number and is expressed as usual:

$$q_i = \frac{r_i(z-2) + 2}{z} = r_i \left[\frac{1 - 2(1 - 1/r_i)}{z} \right] \quad (8)$$

When $z = \infty$, $q = r$, $\theta = \Phi$ ($X = \Phi$), Eq. (7) reduces to the Flory–Huggins equation.

2.2. Residual contribution

For the calculation of the residual contribution G_R^E , H^E is the critical variable, which is in this work assumed to be identical to the excess energy of mixing ΔE . The reference states for the equation of ΔE are pure liquid for the solvent and a hypothetical segment aggregation state for the polymer segments, as stated by Wu et al. [16]. After replacing the local mole fractions with the effective local mole fractions, equations [18] derived from Guggenheim's quasi-chemical theory can be written:

$$\frac{X_{21}}{X_{11}} = \frac{X_2}{X_1} \exp \left[\frac{-(\varepsilon_{21} - \varepsilon_{11})}{RT} \right], \quad \frac{X_{12}}{X_{22}} = \frac{X_1}{X_2} \exp \left[\frac{-(\varepsilon_{12} - \varepsilon_{22})}{RT} \right] \quad (9)$$

Following the derivation of the local composition equations, the energy of mixing is given [16]:

$$H^E = \Delta E = \frac{z}{2} n_q [X_1 X_{21} (\varepsilon_{21} - \varepsilon_{11}) + X_2 X_{12} (\varepsilon_{12} - \varepsilon_{22})] \quad (10)$$

We define the structural factor of the solution $2/z$ as the non-random factor α (the typical choice of non-random factor is 0.3 [7]). Substituting (9) into (10),

$$\frac{H^E}{RT} = n_q X_1 X_2 \left(\frac{\tau_{21} G_{21}}{X_1 + X_2 G_{21}} + \frac{\tau_{12} G_{12}}{X_2 + X_1 G_{12}} \right) \quad (11)$$

where $G_{21} = \exp(-\alpha\tau_{21})$, $G_{12} = \exp(-\alpha\tau_{12})$, $\tau_{21} = (1/\alpha)((\varepsilon_{21} - \varepsilon_{11})/RT)$, $\tau_{12} = (1/\alpha)((\varepsilon_{12} - \varepsilon_{22})/RT)$.

Then, the residual contribution is obtained after integration and rearrangement:

$$\frac{G_R^E}{RT} = -\frac{n_q}{\alpha} [X_1 \ln(X_1 + X_2 G_{21}) + X_2 \ln(X_2 + X_1 G_{12})] \quad (12)$$

or

$$\frac{G_R^E}{kT} = -\frac{N_q}{\alpha} [X_1 \ln(X_1 + X_2 G_{21}) + X_2 \ln(X_2 + X_1 G_{12})]$$

Combining the above two contribution terms, the expression for the activity of water is written:

$$\begin{aligned} \ln a_1 = & \ln X_1 + X_2 \left(1 - \frac{q_1}{q_2} \right) + \frac{q_1}{\alpha} \left(\ln \frac{X_1}{\Phi_1} + \left(\frac{r_1 q_2}{r_2 q_1} - 1 \right) \Phi_2 \right) \\ & + \frac{q_1}{\alpha} \left[-\ln(X_1 + X_2 G_{21}) + X_2 \left(\frac{G_{21}}{X_1 + X_2 G_{21}} - \frac{G_{12}}{X_2 + X_1 G_{12}} \right) \right] \end{aligned} \quad (13)$$

It is very easy to extend to multicomponent mixtures (see Appendix A). According to the definition of α , q_i is rewritten as

$$q_i = r_i \left[1 - \alpha \left(1 - \frac{1}{r_i} \right) \right] \quad (8a)$$

For systems with oriented interactions, the following expressions, according to the suggestion of Wu et al. [16], are used here

$$\tau_{ji} = a_{ji}^{(1)} \left(\frac{T_0}{T} \right) + a_{ji}^{(2)} \left(\frac{T_0}{T} \right)^2 \quad (14a)$$

$$\tau_{ij} = a_{ij}^{(1)} \left(\frac{T_0}{T} \right) + a_{ij}^{(2)} \left(\frac{T_0}{T} \right)^2 \quad (14b)$$

where $a^{(1)}$ and $a^{(2)}$ are adjustable model parameters and assumed to be temperature and composition independent. If the temperature range is not wide, we can fix $a_{ji}^{(2)} = a_{ij}^{(2)}$, as stated by Wu et al. [16].

3. Results and discussion

In order to evaluate the capabilities of the new model proposed in this work, we use the experimental VLE data of PEG and EOPO solutions published in literature (listed in Table 1). M is set to be the number

Table 1
Water activities of aqueous PEG solutions ($\alpha = 0.3$)

Polymer	\overline{M}_n	r_2	Temperature (K)	Polymer concentration ^a	N^b	Model parameters ^c			Deviation (%)		Note	References
						$a_{21}^{(1)}$	$a_{12}^{(1)}$	$a_{21}^{(2)} = a_{12}^{(2)}$	Eq. (13) ^c	Wu ^c		
PGE150	150	8	297.6, 332.6	0.28–0.90	34	3.5458 (3.2931)	−1.1236 (−2.0107)	−0.7213 (0.0)	1.1 (1.8)	2.2 (3.7)	Extrapolation	[19]
PGE200	200	10	293.1, 298.1, 313.1, 333.1	0.14–0.90	48				0.7 (1.8)	1.3 (3.2)	Correlation	[20,21]
PGE300	300	14	303.1, 323.1, 338.1	0.29–0.90	15				1.46 (2.0)	1.4 (3.5)	Extrapolation	[22]
	296	14	308.1, 318.1, 328.1, 338.1	0.10–0.39	16				0.08 (0.24)	0.4 (0.6) ^d	Extrapolation	[23]
PGE400	430	21	308.1, 318.1, 328.1, 338.1	0.01–0.32	32				0.03 (0.08)	0.17 (0.24) ^d	Extrapolation	[23]
PGE600	600	27	293.1, 313.1, 333.1	0.23–0.90	30				1.4 (2.3)	2.9 (3.4)	Extrapolation	[21]
PGE1000	1000	45	298.1	0.15–0.38	16				0.06 (0.09)	0.07 (0.16)	Extrapolation	[24,25]
PGE1500	1500	67	293.1, 313.1, 333.1	0.34–0.99	20	4.8313 (4.6259)	−2.0605 (−2.2849)	−0.2461 (0.0)	1.6 (2.1)	1.3 (4.10)	Extrapolation	[21]
PGE3000	3000	131	328.1, 338.1	0.49–0.99	14				1.5 (1.5)	1.8 (2.5)	Correlation	[22]
PGE4000	3750	171	298.1	0.15–0.38	5				0.26 (0.26)	0.1 (0.25)	Extrapolation	[25]
	4237	194	308.1, 318.1, 328.1, 338.1	0.04–0.39	16				1.7 (1.7)	1.4 (1.5) ^d	Extrapolation	[23]
PGE5000	5000	227	333.1, 338.1	0.49–0.99	16				1.8 (1.9)	1.8 (2.3)	Correlation	[22]
PGE6000	5989	273	308.1, 318.1, 328.1, 338.1	0.03–0.36	25				0.11 (0.11)	0.24 (0.25) ^d	Extrapolation	[23]
	6230	283	293.1, 333.1	0.11–0.67	35				0.36 (0.4)	0.6 (0.7) ^d	Extrapolation	[9]
	6750	307	313.1, 333.1	0.32–0.99	18				5.5 (5.5)	5.8 (5.5) ^d	Extrapolation	[21]
PGE8000	6400	291	298.1	0.18–0.37	12				0.11 (0.17)	0.13 (0.21)	Extrapolation	[24]
PGE5000	39005	1771	293.1, 333.1	0.11–0.68	25				0.32 (0.38)	0.53 (0.58) ^d	Extrapolation	[9]

^a Weight fraction.

^b N is the number of experimental data points; deviation (%) = $(1/N) \sum [|a_{\text{exp}} - a_{\text{cal}}|/a_{\text{exp}}] \times 100\%$.

^c The values in brackets are results without oriented interactions.

^d The modified NRTL model using parameters given in literature [16].

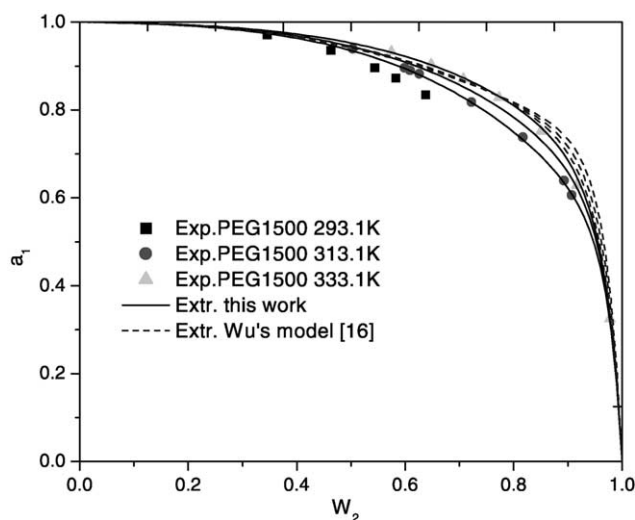


Fig. 1. Water activity in PEG 1500—water solutions without oriented interactions. The experimental data are from Herskowitz [21].

average molecular weight (M_n) for polymer. Since the van der waals volume of a repeated unit in PEG molecule is very close to the double of a water molecule, V_2 is approximated as $(2n_p + 1)V_1$, where n_p is the polymerization degree of a PEG molecule and can be calculated from M_n . Similarly, for EOPO, V_2 is approximated as $(5n_p + 1)V_1$. Then for polymer, $r_2 = V_2/V_1$ and for water $r_1 = 1$. Therefore, there are only two or three adjustable parameters (without oriented interactions, $a_{ji}^{(2)} = a_{ij}^{(2)} = 0$; otherwise, $a_{ji}^{(2)} = a_{ij}^{(2)} \neq 0$). Parameters are calculated by minimizing the sum of squares:

$$SSQ = \sum_{j=1}^N (a_1^{\text{exp.}} - a_1^{\text{calc.}})_j^2 \quad (15)$$

The extrapolation results of VLE data (activities) for PEG and EOPO with different molecular weights are given in Tables 1 and 2, and for some systems, the results are also shown in Figs. 1–4. In order to compare the results with those from the modified NRTL model, the same procedure that Wu et al. [16] used is followed for PEG aqueous solutions. We first correlated the parameters for PEG 200, and the extrapolation for PEG with molecular weights less than 1000 is very good. Then, the parameters were readjusted to the experimental data of both PEG 3000 and PEG 5000 solutions, to extrapolate those for molecular weight higher than 1500. Agreement between the calculated and experimental values of solvent activity is satisfactory, except for one set of PEG 6000 data. This is probably due to the fact that no number average molecular weight is given and M_n is simply set to be 6750, according to the molecular weight range 6000–7500.

From Table 1 and Figs. 1 and 2, it can be observed that the activity deviation obtained with the proposed model is smaller than that with the modified NRTL model [16], no matter with or without oriented interactions. For PEG with molecular weight higher than 3000, the water activity deviation is almost the same with two and three parameters, which means that the oriented interaction plays a very small role for high molecular weight, and just two parameters are enough for the pure correlations of

Table 2
Results of the correlation and extrapolation of water activity at 298.15 K for EOPO solutions

Polymer	\overline{M}_n	r_2	Polymer concentration ^a	N^b	Model parameters ^c			Deviation (%)	Note	Reference
					$a_{21}^{(1)}$	$a_{12}^{(1)}$	$a_{21}^{(2)} = a_{12}^{(2)}$			
EOPO800	780	39	04–0.54	13	3.4086 (1.4683)	−1.3062 (−0.9554)	−0.3617 (0.0)	0.04 (0.1)	Correlation	[26]
EOPO2000	2340	116	0.07–0.61	9				0.2 (0.3)	Extrapolation	[26]
EOPO4000	3640	179	0.09–0.66	13				0.3 (0.4)	Extrapolation	[26]

^a Weight fraction.

^b N is the number of experimental data points; deviation (%) = $(1/N) \sum [|a_{\text{exp.}} - a_{\text{cal.}}|/a_{\text{exp.}}] \times 100\%$.

^c The values in brackets are results without oriented interactions.

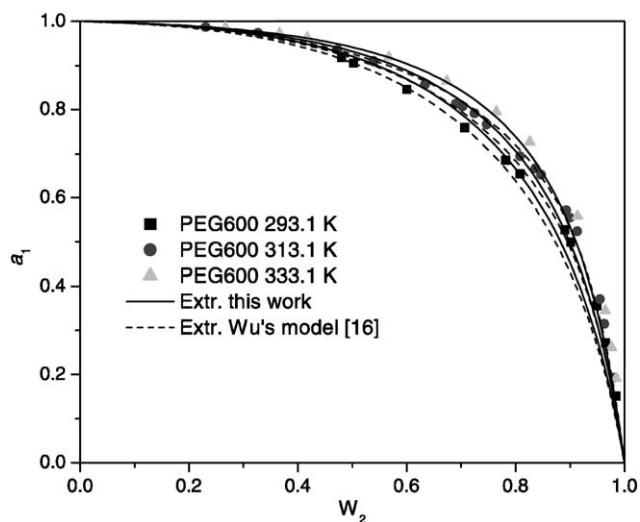


Fig. 2. Water activity in PEG600—water solutions with oriented interactions. The experimental data are from Herskowitz [21].

the phase behavior of PEG aqueous systems as shown in Fig. 3. The correlative and extrapolative results for PEG systems using only two parameters are reliable with the deviation values not larger than 2.3 except that of PEG 6750, including PEG systems with molecular weight smaller than 1000 with strong end groups, as shown in Table 1. The most important reason is that, in this new model, considered the excess heat capacity, the expression of the residual contribution for the excess Gibbs energy consists of two temperature-dependent terms, which are combined together and represented with a modified Wilson

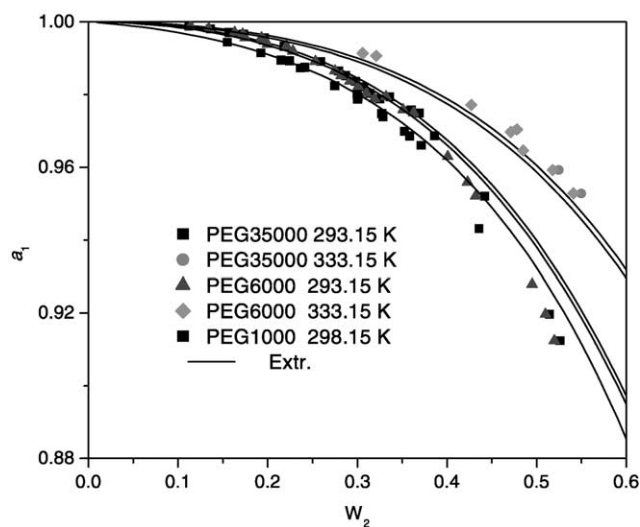


Fig. 3. Water activity in PEG—water solutions with two parameters. The data for PEG 1000 are from Ochs et al. [24] and Lin et al. [25], those for PEG 6000 and PEG 35000 are from Großmann [9].

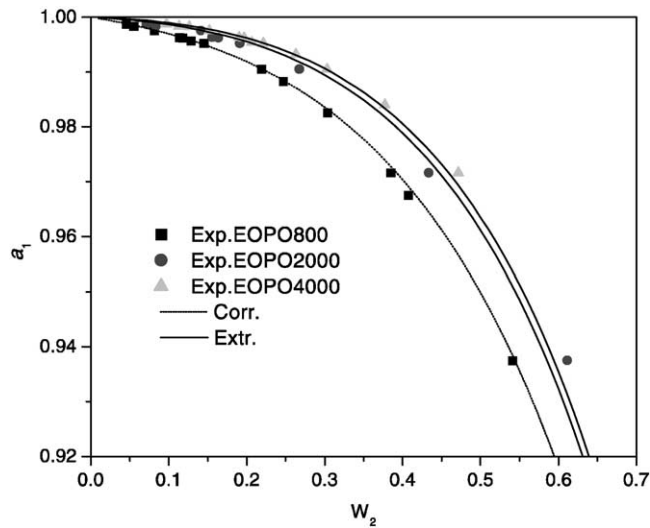


Fig. 4. Water activity in EOPO—water solutions. The experimental data are from Li et al. [26].

equation. No reports are available considering the heat capacity in the residual contribution for polymer systems in the literature. Therefore, the heat capacity must play an important role for lower molecular weight PEG aqueous systems with strong oriented interactions.

In general, the model developed in this work provides an accurate way of correlating and extrapolating the water activity of polymer solutions with its own advantages. As shown in Table 2 and Fig. 4, the extrapolation results for EOPO 2000 and EOPO 4000 aqueous solutions using the adjustable parameters correlated from EOPO 800 solution are very satisfactory. It is known that EOPO is the new polymer of great interest for ATPS in recent years.

4. Conclusions

A new modified Wilson equation based on the local composition model and the two-fluid theory is developed for the representation of thermodynamic properties for aqueous PEG and EOPO solutions. It is reliable both for correlating and extrapolating the VLE behavior of homologous aqueous polymer solutions. After considering the heat capacity, the oriented interaction seems not so strong for polymers with high molecular weight. Only two adjustable parameters are enough to extrapolate the activity of water in aqueous polymer systems including those with strong oriented interaction.

List of symbols

a	interaction parameter defined in Eq. (14), or activity
A^E	excess Helmholtz energy of a mixture
c_p^E	excess heat capacity/heat capacity change of mixing
Corr.	correlation
Extr.	extrapolation

$G, G^E(G^{E'})$	binary parameter, excess (partial) Gibbs free energy
H^E	excess enthalpy
M, M_n	molecular weight, number-average molecular weight
n	mole number of segment–segment pairs
N	number of molecules (segment–segment pairs), or experimental data points
P	pressure
q	effective segment number of polymer
r	number of segments per molecule
S^E	excess entropy
SSQ	sum of squares
T	absolute temperature
T_0	reference temperature, 298.15 K
V^E	excess volume
x	mole fraction of polymer solutions
X	effective mole fraction of segments
z	coordination number in the lattice theory

Greek letters

α	non-random factor in the Wilson model
∂	partial derivative
ε	interaction energy between segment–segment pairs
Φ	volume fraction
θ	surface/area fraction
τ	binary interaction parameter
∞	infinity

Subscripts

c	combinatorial factor
i, j	any species or segments
ii, ij, jj	segment-segment pairs
R	residual contribution
1, 2	solvent and polymer, respectively

Superscripts

E	notation of excess quality
(1), (2)	notation for distinguishment

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Appendix A

For multicomponent aqueous solutions, the activity coefficient of specie i is expressed according to Eq. (A.1) equation. Since it has a very similar form to describe the residual contribution, that is why it is regarded as a modified Wilson model. In addition, like NRTL models, it can also go back to the Flory–Huggins equation when $1/\alpha = 0$.

$$\ln a_i = \ln X_i + \sum_{k=1}^m X_k \left(1 - \frac{q_i}{q_k} \right) + \frac{q_i}{\alpha} \ln \frac{X_i}{\Phi_i} + \frac{q_i}{\alpha} \sum_{k=1}^m \left(\frac{q_k r_i}{q_i r_k} - 1 \right) \Phi_k + \frac{q_i}{\alpha} \left[-\ln \left(\sum_{k=1}^m X_k G_{ki} \right) + 1 - \frac{\sum_{k=1}^m X_k G_{ik}}{\sum_{j=1}^m X_j G_{jk}} \right] \quad (\text{A.1})$$

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