Hamid R. Radfarnia, Grozdana Bogdanić[1],Vahid Taghikhnai, Cyrus Ghotbi
Department of Chemical and Petroleum Engineering,
Sharif University of Technology,Tehran, Iran
[1]INA-Industrija nafte d.d., Research and Development Sector, Zagreb

The *UNIQUAC-NRF* Segmental Interaction Model for Vapor-Liquid Equilibrium Calculations for Polymer Solutions

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Summary

This paper presents a new segment-based thermodynamic model containing the combinatorial and energetic contributions to the excess Gibbs energy for correlating/predicting of the vapor-liquid equilibrium (VLE) of polymer solutions. The model is derived from the *UNIQUAC-NRF* model, recently proposed by Haghtalab and Asadollahi, following the idea to associate the nonideality of polymer-solvent mixture with polymer segment-solvent interaction parameters. Segment activity coefficients are calculated by means of the *UNIQUAC-NRF* model. At the present state of development, 16 binary segmental interaction parameters have been estimated. The capability of the model is demonstrated with successful representation of VLE correlation/prediction for 40 polymer-solvent systems. The model is capable of correlating predicting the VLE of polymer solutions with satisfactory accuracy and can provide a thermodynamic framework for calculating the VLE of polymer solutions using weakly temperature-dependent *UNIQUAC-NRF* parameters.

KEYWORDS
polymer solutions
segmental interaction *UNIQUAC-NRF* model
vapor-liquid equilibrium calculation

KLJUČNE RIJEČI
polimerne otopine
računanje fazne ravnoteže kapljevina-para
segmentni interakcijski *UNIQUAC-NRF* model

Segmentni interakcijski *UNIQUAC-NRF* model za računanje fazne ravnoteže kapljevina-para polimernih otopina

Sažetak

Prikazan je novi segmentni interakcijski model za koreliranje i predviđanje fazne ravnoteže kapljevina-para (VLE) polimernih otopina. Izraz za Gibbsovu energiju miješanja *UNIQUAC-NRF* modela sastoji se od kombinatornoga i rezidualnoga (energetskoga) doprinosa. Model je izveden iz Haghtalab-Asadollahijeva *UNIQUAC-NRF* modela i omogućuje izračunavanje aktivnosti otapala, tretirajući neidealnu polimernu otopinu kao smjesu segmenata polimer-otapalo. Segmentni interakcijski parametri računani su primjenom *UNIQUAC-NRF* modela. Model je u fazi testiranja i do sada je određeno 16 binarnih segmentnih interakcijskih *UNIQUAC-NRF* parametara. Mogućnosti modela za koreliranje, odnosno predviđanje fazne ravnoteža kapljevina-para prikazane su sumiranjem rezultata računanja aktivnosti velikog broja polimernih otopina (40 sustava polimer-otapalo). Vidljivo je da postoji vrlo dobro slaganje računanja fazne ravnoteže kapljevina-para s eksperimentalnim podacima i model se s termodinamičkoga stajališta može smatrati okosnicom za računanje ravnoteže kapljevina-para polimernih otopina.

Introduction

Just as for mixtures of low-molar-mass components, there are also two different approaches to predicting the vapor-liquid equilibrium (VLE) in mixtures which contain polymers: activity-coefficient (g^E-models) and equation-of-state (EoS) approach. The last decade has seen a dramatic development in the application of group-contribution activity-coefficient models for polymers in areas such as estimation of solubility limits in LLE and SLE, selective dissolution, gas solubility's, applications related to techniques for tailoring or modifying polymers to desired physical properties, applications related to biotechnology, and many others. Group-contribution methods available today can handle supercritical compounds, very asymmetric systems, and even systems containing polymers.

In principle, VLE calculations may be provided using any model for Gibbs energy. Recently, Haghtalab and Asadollahi[1] presented a new g^E-model, dubbed *UNIQUAC-NRF*, for studying the phase behavior of aqueous two-phase polymer-polymer systems of polyethylene glycol and dextrane. Their g^E-model is based on assumptions similar to those of the *NRTL-NRF* model[2,3] derived by Hagtalab and Vera, and on the local composition expression of *UNIQUAC*, using random state as a reference state.

This paper describes a new segment-based thermodynamic model containing combinatorial and energetic contributions to Gibbs excess energy for correlating/predicting VLE derived from the *UNIQUAC-NRF* model, following the idea to associate the nonideality of polymer-solvent mixture with polymer segment-solvent interaction parameters, as done earlier by ten Brinke et al.[4], Chen[5], and Bogdanić and Vidal[6], rather than with functional group interaction parameters. The groups are defined as segments or monomer-repeating units of polymers or copolymers, or as the solvent molecule. While this reduces the flexibility of the model, it is an acceptable price to pay for a fair predictive power.

Description of the segmental interaction model

The model is derived from the *UNIQUAC-NRF* model proposed by Haghtalab and Asadollahi[1]. The general equation for the activity coefficient is given by the expression:

$$\ln \gamma_i = \ln \gamma_i^{comb} + \ln \gamma_i^{resid} \tag{1}$$

where

$$\ln \gamma_i^{comb} = \ln\left(\frac{\phi_i}{x_i}\right) + \frac{z}{2} q_i \ln\left(\frac{\theta_i}{\phi_i}\right) + l_i - \left(\frac{\phi_i}{x_i}\right)\sum_{j=1}^{n} x_j l_j \tag{2}$$

and

$$\ln \gamma_i^{resid} = q_i \left[l + \ln \Gamma_{ii} - \sum_{j=1}^{n} \theta_j \Gamma_{ij} + q_i (1-\theta_i) \sum_{\substack{j=1 \\ j\neq i}}^{n} \theta_j \ln\left(\frac{\Gamma_{ij}\,\Gamma_{ji}}{\Gamma_{ii}\,\Gamma_{jj}}\right) \right. \tag{3}$$

$$\left. - \frac{1}{2} \sum_{\substack{k=1 \\ k\neq i}}^{n} \sum_{\substack{l=1 \\ l\neq k,i}}^{n} \theta_k \theta_l \ln\left(\frac{\Gamma_{kl}\,\Gamma_{lk}}{\Gamma_{kk}\,\Gamma_{ll}}\right) \right]$$

where θ_i and ϕ_i are surface area and volume fractions, while r_i and q_i are the volume and surface parameters of the component i:

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \tag{4}$$

$$\phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \tag{5}$$

Γ_{ij} is the nonrandomness parameter

$$\Gamma_{ij} = \frac{\tau_{ij}}{\sum_k \theta_k \tau_{kj}} \tag{6}$$

where τ_{ij} is the interaction parameter of i-j pairs, respectively.

For the calculation of the residual term, $\ln \gamma_i^{resid}$, the mixture is considered as a solution of segments, and the molar fraction of each segment is calculated as:

$$X_k = \frac{\sum_i^{ncomp} x_i \upsilon_k^{(i)}}{\sum_j^{ncomp} \sum_m^{nseg} x_j \upsilon_m^{(j)}} \tag{7}$$

where x_i and x_j are the mole fractions of the respective components i and j. The summations are extended to the total number of components, ncomp, and to the total number of segments, nseg. $\upsilon_k^{(i)}$ and $\upsilon_m^{(i)}$ are the numbers of segments k in the component i, and of segments m in the component j. Their values are equal to the number of repeating units for a homopolymer, and to one for the solvent. For a copolymer, the value of $\upsilon_k^{(i)}$ is obtained from the molar mass of the copolymer, M_i, from the molar fraction, $X_k^{(i)}$ of each copolymer segment k, which characterizes the copolymer composition, and from the molar mass of each segment M_k

$$\upsilon_k^{(i)} = \frac{M_i}{\sum_m^{nseg} X_m^{(i)} M_m} X_k^{(i)} \tag{8}$$

From the molar fractions X_k, the activity coefficients of the segments Γ_k in the mixture are calculated by applying a model of nonideality. We have used the residual term of the *UNIQUAC-NRF* model[1], and for a binary mixture the expression of $\ln \Gamma_k$ is:

$$\ln \Gamma_k = Q_k \left[1 + \ln \Gamma_{kk} - \sum_{j=1}^{n} \Theta_j \Gamma_{kj} + (1-Q_k) \sum_{\substack{j=1 \\ j\neq k}}^{n} \Theta_j \ln\left(\frac{\Gamma_{kj}\,\Gamma_{jk}}{\Gamma_{kk}\,\Gamma_{jj}}\right) \right. \tag{9}$$

$$\left. - \frac{1}{2} \sum_{\substack{m=1 \\ m\neq k}}^{n} \sum_{\substack{n=1 \\ n\neq m,k}}^{n} \Theta_k \Theta_l \ln\left(\frac{\Gamma_{mn}\,\Gamma_{nm}}{\Gamma_{mm}\,\Gamma_{nn}}\right) \right]$$

In this expression Q_k represents the surface parameters of the segments, derived from the van der Waals area[7], and Θn and Θ_m their surface fractions

$$\Theta_m = \frac{X_m Q_m}{\sum_n^{nseg} X_n Q_n} \tag{10}$$

The nonrandomness paremeter, Γ_{nm}, was calculated using the following relation:

$$\Gamma_{nm} = \frac{\tau_{nm}}{\sum_n \Theta_n \tau_{nm}} \tag{11}$$

The values of τ_{nm} are derived from the interaction parameters between segments, a_{nm}, by the relation:

$$\tau_{nm} = \exp\left(-\frac{a_{nm}}{RT}\right) \tag{12}$$

In the present paper, the segmental interaction parameters are assumed to have a linear temperature dependency, which is expressed as:

$$a_{nm} = a_{n,m,1} + a_{n,m,2}\,(T - T_0) \tag{13}$$

where m and n denote segments in the *UNIQUAC-NRF* table, and T_0 is a reference temperature equal to 298.15 K.

The activity coefficients of segments $\Gamma_k^{(i)}$ in pure components must also be evaluated. For a solvent or a homopolymer, they are equal to one and for copolymer they are calculated using Eq. (9), where the surface fractions will be obtained from the mole fractions of the segments in the pure copolymer, $X_k^{(i)}$.

Finally, the activity coefficients of the components, solvent, homopolymer or copolymer, are obtained by the relation:

$$\ln \gamma_i^{resid} = \sum_k \upsilon_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \tag{14}$$

It should be underlined that the term $\ln \Gamma_k^{(i)}$ in Eq. (14) takes into account the internal repulsion effect in copolymers[4].

Estimation of the segmental interaction parameters and parameter table

The procedure requires the van der Waals volumes and the molecular surface parameters of the segments for the application of the segmental *UNIQUAC-NRF* model. The van der Waals volumes and molecular surface parameters are calculated using additive group contributions[7,8].

The *UNIQUAC-NRF* segmental interaction parameters were estimated from the experimental VLE data. The objective function for the parameter estimation may be defined in many ways. We tried different functions and decided to estimate parameters that will minimize the following expression:

$$OF = \sum_j \sum_i \left(\frac{\gamma_{ji}^{exp} - \gamma_{ij}^{cal}}{\gamma_{ji}^{exp}} \right)^2 \qquad (15)$$

where γ_{ji}^{exp} and γ_{ij}^{cal} are the calculated and experimental activity coefficients, i is summed over the number of measured variables in a data point, and j is summed over the total number of data points. The optimization algorithm used in the parameter estimation program is the Nelder and Mead simplex method[9].

The obtained segmental interaction parameters are presented in Table 1, together with references to data used in parameter estimations.

Results and discussion

This section presents an evaluation of the capability of segmental interaction model to correlate and predict the VLE of polymer-solvent mixtures. The results of calculations for more than 40 polymer-solvent systems are presented.

Table 2 includes references to experimental data for 16 binary polymer-solvent systems selected for the estimation of the *UNIQUAC-NRF* segmental interaction parameters To illustrate the capability of the model to correlate VLE, the results of calculations are summarized in the same Table (the absolute mean percent deviations between experimental and calculated activity coefficients of solvents) and shown in Figure 1, which compare correlated phase equilibrium with experimental data for binary polymer-solvent mixture of PDMS/heptane system.

Table 2 shows that the experimental data are fitted within 6 % errors in solvent activity coefficients.

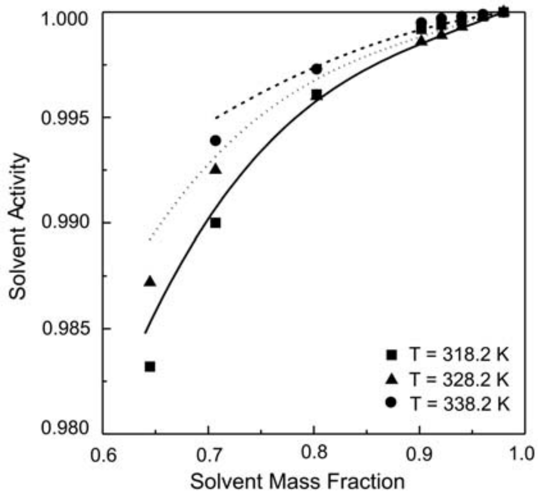

FIGURE 1. Activity of water in PEG (M_n=5 989 g/mol) as predicted by the *UNIQUAC-NRF* segmental interaction model at 318.2 K (——),■ exp. data[11]; 328.2 K (------), ▲ Exp. data[11] and 338.2 K (----), • exp. data[11]

TABLE 1. Binary, temperature-dependent segmental interaction parameters of the *UNIQUAC-NRF* segmental interaction VLE model

Segment (1)	Segment (2)	$a_{12,1}$ (J mol^{-1})	$a_{12,2}$ (J mol^{-1})	$a_{21,1}$ (J mol^{-1})	$a_{21,2}$ (J mol^{-1})	Systems included in the data base	Ref.
EG	water	-239.08	0.65	-30.72	0.04	PEG/water	11
EG	benzene	-209.06	2.79	-479.03	7.14	PEG/benzene	13
EG	2-propanol	4.77	-0.46	-2.02	0.04	PEG/2-propanol	10
DEX	water	625.26	1.34	2.39	-0.96	DEX/water	12
DMS	2-butanone	-4.19	0.84	-10.05	2.01	PDMS/2-butanone	13
DMS	HMDS	-171.64	-1.26	-161.77	-0.38	PDMS/HMDS	13
DMS	heptane	6.19	-0.79	-3.83	0.86	PDMS/heptane	13
DMS	octane	10.69	-0.78	6.11	-1.14	PDMS/octane	13
IB	benzene	-384.07	1.93	-892.83	3.06	PIB/benzene	13
S	cyclohexane	6.10	-2.10	-196.05	0.08	PS/cyclohexane	13
S	toluene	32.75	-1.36	59.40	-2.41	PS/toluene	13
S	benzene	-11.29	0.93	-32.27	0.04	PS/benzene	13
S	CHCl3	21.61	-0.66	-11.77	0.54	PS/CHCl3	13
S	2-butanone	-23.42	1.00	3.83	-0.16	PS/2-butanone	13
PG	methanol	281.59	1.09	-809.94	-2.88	PPG/methanol	13
VAL	water	-122.96	2.54	22.99	-4.60	PVAL/water	13

TABLE 2. Results of vapor-liquid equilibrium correlation by the UNIQUAC-NRF segmental model

System	$M_n \cdot 10^{-3}$ (g/mol)	$M_w \cdot 10^{-3}$ (g/mol)	$M_v \cdot 10^{-3}$ (g/mol)	Temp. range (K)	No. of data points	Δ (%)[a]	Ref.
PEG/water	0.296	-	-	308.15 - 338.15	16	0.03	11
PEG/benzene	5.7	-	-	318.15 - 343.15	14	13.88	13
PEG/2-propanol	0.995	-	-	298.15	13	5.95	10
DEX/water	46.3	-	-	293.15 - 333.15	23	0.01	12
PDMS/2-butanone	16.0	-	-	303.15	3	11.20	13
PDMS/HMDS	1.54	-	-	298.15	11	3.00	13
PDMS/heptane	1.54	-	-	298.15 - 313.15	38	13.92	13
PDMS/octane	4.17	-	-	298.15 - 313.15	27	15.53	13
PIB/benzene	-	-	40	283.15 - 313.15	6	0.24	13
PS/cyclohexane	49.0	-	-	290.55 - 303.55	42	0.03	13
PS/toluene	49.0	-	-	298.15 - 338.15	27	0.67	13
PS/benzene	63.0	-	-	288.15 - 333.15	31	16.50	13
PS/CHCL3	90.0	-	-	298.15 - 323.15	6	6.53	13
PS/2-butanone	97.2	-	-	283.15 - 323.15	12	2.01	13
PPG/methanol	3.35	-	-	248.15 - 298.15	16	1.76	13
PVAL/water	67.0	-	-	303.15	5	6.72	13
Overall deviation						6.03	

[a]Absolute mean percent deviations

The VLE prediction for 24 polymer-solvent systems by presented model is shown below. Table 3 and Figures 2 and 3 summarize the results of the calculations. Figures 2 and 3 compare the predicted VLE with experimental data for PDMS/hexane and PEG/water systems.

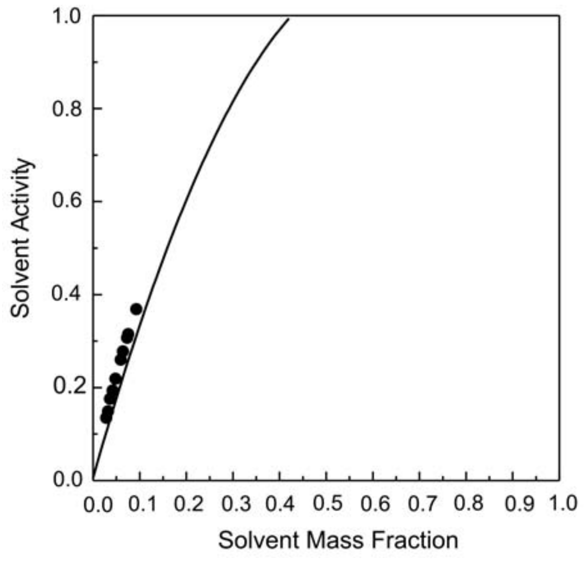

FIGURE 2. Activity of heptane in PDMS (M_n=140 000 g/mol) as predicted (——) by the *UNIQUAC-NRF* segmental interaction model at 308.2 K. • Exp. data[13]

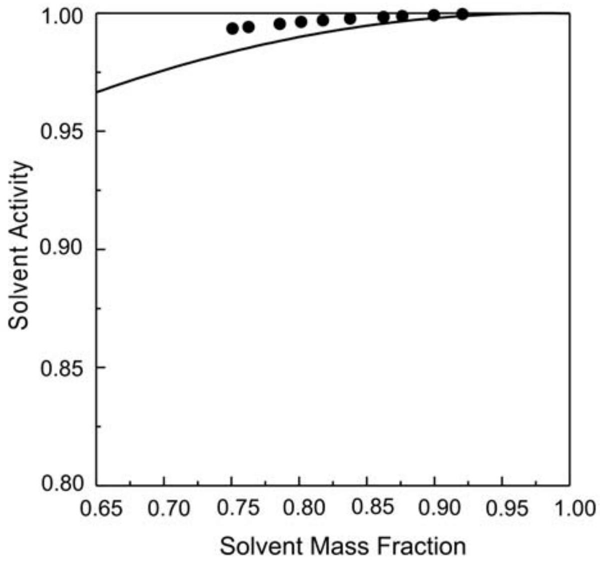

FIGURE 3. Activity of heptane in PDMS (M_n=1 540 g/mol) as correlated (——) by the UNIQUAC-NRF segmental interaction model at 313.2 K. • Exp. data[13]

The results show that the model for the VLE correlation/prediction of nonpolar, moderately polar and polar systems with strong specific interactions, is applicable. It is clear (Table 3) that the proposed model provides a fairly good prediction of the VLE of polymer solutions.

TABLE 3. Results of predicting the vapor-liquid equilibrium data by the *UNIQUAC-NRF* segmental model

System	$M_n \cdot 10^{-3}$ (g/mol)	$M_w \cdot 10^{-3}$ (g/mol)	$M_v \cdot 10^{-3}$ (g/mol)	Temp. range (K)	No. of data points	Δ (%)[a]	Ref.
PEG/water	0.430	-	-	308.15 - 338.15	32	0.06	11
	423.7	-	-	308.15 - 338.15	16	0.15	11
	5.989	-	-	308.15 - 338.15	29	0.06	11
PEG/benzene	0.335	-	-	297.75 - 307.75	20	0.47	12
	146.0	-	-	297.75 - 307.75	18	0.47	12
	415.0	-	-	297.75 - 307.75	20	0.01	12
PEG/2-propanol	296.0	-	-	298.15	20	4.07	12
DEX/water	23.6	-	-	293.15 - 333.15	13	0.05	10
	6 4.8	-	-	293.15 - 333.15	47	0.04	12
	101.0	-	-	293.15 - 333.15	30	0.05	12
PDMS/2-butanone	4.6	-	-	303.15	3	11.69	12
	220.0	-	-	303.15	3	11.00	13
PDMS/HMDS	0.958	-	-	298.15	9	5.14	13
	4.17	-	-	298.15	11	2.13	13
PDMS/heptane	140.0	-	-	308.15 - 323.15	17	0.44	13
PDMS/octane	140.0	-	-	293.15 - 323.15	33	0.59	13
PS/cyclohexane	154.0	-	-	298.15 - 308.15	30	0.03	13
PS/toluene	154.0	-	-	298.15 - 338.15	24	5.83	13
	900.0	-	-	298.15	5	9.33	13
	290.0	-	-	298.15 - 353.15	18	33.55	13
PS/benzene	20.0	-	-	293.15	14	21.49	13
	900.0	-	-	288.15 - 333.15	30	21.42	13
PS/CHCl3	290.0	-	-	298.15 - 323.15	23	6.4	13
PS/2-butanone	10.3	-	-	321.65	9	21.11	13
PPG/methanol	1.955	-	-	248.15 - 298.15	16	3.01	13
	0.150	-	-	248.15 - 298.15	16	2.54	13
PVAL/water	14.7	-	-	303.15	5	8.20	13
Overal deviation						5.51	

[a] Absolute mean percent deviations

Conclusion

The results of our studies on the VLE correlation and prediction of a large amount of polymer-solvent systems presented in Table 2 and 3 clearly show that there is a remarkable agreement between the VLE phase behavior obtained experimentally and the one calculated using the segmental interaction model. Interaction parameters listed in Table 1 are sufficiently quantitative to be of predictive value for polymer-solvent systems studied in this work.

List of symbols

Variables

a_{ij}	interaction parameter between segments i and j
M_i	molar mass of the component i
r_i	volume parameter of component i
R	gas constant, 8314 J $kmol^{-1}$ K^{-1}
q_i	surface parameter of component i
Q_n	surface area of the segment n
T	temperature

T_0	reference temperature (298.15 K)
x_i	mole fraction of component i
X_k	mole fraction of segment k

Greek letters

Δ	absolute mean deviation
ϕ_i	volume fraction of component i
γ_i	activity coefficient of component i
γ_i^{comb}	combinatorial contribution to the activity coefficient
γ_i^{resid}	residual contribution to the activity coefficient
Γ_{ij}	nonrandomness factor
θ_i	surface fraction of component i
Θ_n	surface fraction of the segment n
τ_{nm}	interaction parameters between segments n and m

Superscripts

cal	calculated
comb	combinatorial
exp	experimental
resid	residual

Subscripts

i	component i
j	component j
m	segment of the type m
n	segment of the type n

List of abbreviations

HDMS	hexamethyl disiloxane
ncomp	total number of components
nexp	number of experimental data
nseg	total number of segments
OF	objective function Šsee Eq. (15)Ć
P	poly
VLE	vapor-liquid equilibrium

Polymer segments

DEX	dextran
DMS	dimethylsiloxane
EG	ethylen glycole
IB	isobutylene
S	polystyrene
VAL	vinyl alcohol

Polymers

DEX	dextran
PDMS	poly(dimethylsiloxane)
PEG	poly(ethylen glycol)
PIB	polyisobutylene
PS	polystyrene
PVAL	poly(vinyl alcohol)

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CORRESPONDENCE

Dr. sc. Grozdana Bogdanić
INA - Industrija nafte d.d., Research and Development Sector
Lovinčićeva bb, POB 555
HR-10 002 Zagreb, Croatia / Hrvatska
Tel.: +385-1-23-81-645, Fax: +385-1-24-52-794
E-mail: grozdana.bogdanic@ina.hr