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Study of phase behaviour for the aqueous two-phase polymer–polymer systems using the modified UNIQUAC-NRF model

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A modified form of the UNIQUAC-NRF activity coefficient model was used to study the phase behaviour of the aqueous two-phase systems (ATPSs) of polyethylene glycol (PEG) and dextran (DEX) with different molecular weights at various temperatures. In the proposed model, a ternary interaction parameter was added to the expression for the excess Gibbs free energy and, in turn, to the corresponding activity coefficient rendered by the UNIQUAC-NRF model. The combinatorial part of the new model takes the same form as that of the original UNIQUAC model and the residual part considers the nonrandomness and also the binary and the ternary interactions among the molecules in mixtures of PEG, DEX, and water. The results show that the new model can more accurately correlate the experimental data for the systems studied in this work than those obtained from the original UNIQUAC and the UNIQUAC-NRF activity coefficient models. In order to favourably compare the results the same minimisation procedure and the same experimental data were used for the models studied in this work. The results for the Root Mean Square Deviations (RMSD) produced by the three UNIQUAC-based models are also reported.

Keywords: aqueous two-phase system; UNIQUAC-NRF model; activity coefficient

1. Introduction

Polymer solutions are liquid mixtures with at least one component that consists of a much larger molecule, i.e., polymers, than those of the other components. Liquid–liquid extraction using the aqueous two-phase polymer solutions (ATPS) is carried out when two highly water-soluble polymers are dissolved in water. Polyethylene glycol (PEG) and dextran (DEX) are two conventional water-soluble polymers that are used for separation of biologically active materials. Existing water in the ATPS of PEG + DEX provides a suitable environment for bio-macromolecules. Thus, such systems are used for separation of proteins and enzymes in aqueous solutions. ATPS are increasingly used in biochemistry and cell biology for separation of macromolecules from cell organelles [1–3]. Albertson [1] introduced aqueous two-phase partitioning systems for

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separation and purification of the biological molecules such as proteins and enzymes. Study of the equilibrium data and thermodynamic representation of the phase diagram for the ATPS are a necessary step towards the design of the bio-molecule separation processes. The concept of the osmotic virial expansion and the lattice theory were mainly used to develop the thermodynamic models for strongly nonideal ATPS. Flory [4] and Huggins [5] developed an expression based on the lattice theory to describe the nonideality of phase behaviour for polymer solutions. Brooks [6] presented a lattice model for particle partitioning by extending the Flory–Huggins theory for polymer–solvent solutions to those of multi-component systems. Diamond and Hsu [7,8] presented two simple correlations in predicting the protein partitioning in ATPS of PEG + DEX. Edmond and Ogston [9] used the osmotic virial expansion to represent the properties of ATPS, and modeled nonideality of polymer solutions with a truncated osmotic virial expansion based on the McMillan–Mayer theory [10]. King *et al.* [11] applied the simple virial expansion truncated after the second virial coefficient term to predict the phase diagrams and to determine the bimolecular partitioning behaviour of polymer–polymer ATPS. However, the application of the virial expansion truncated after the second-order term is most appropriate for dilute polymer solutions [12]. Haynes *et al.* [13] also included a higher order virial coefficient terms to obtain a more accurate phase diagram.

Following the liquid-solution-theory approach of King *et al.* [11], Cabezas *et al.* [14] used the isothermal–isobaric virial expansion of Hill [15] to predict ternary phase equilibrium. The models based on the local composition concept have been also used to describe the phase behaviour of aqueous two-phase polymer–polymer systems. Kang and Sandler [16–19] have used the UNIQUAC model to study the ATPS of PEG + DEX systems incorporating the effect of polymer polydispersity and fractionation.

Wu *et al.* [20] also used a modified NRTL model to study the phase behaviour of polymer solutions. Nagata [21] showed that a good correlation for the ternary liquid–liquid equilibria for nonpolymer solutions with strongly nonideal phase behavior is possible using the extended UNIQUAC and Wilson models through the inclusion of ternary interaction parameters, attributed to the unlike three-body interactions in the mixture. The model was also extended to the quaternary mixtures. Nagata *et al.* [22] applied this new model to correlate experimental data for a number of nonpolymer liquid–liquid systems. Also, Nagata *et al.* [23,24] proposed a modified Wilson model considering a three-body interaction and used in the ternary and quaternary LLE systems. Grossmann *et al.* [25] presented an empirical model for ATPS containing PEG and DEX. They also included a ternary parameter in their model.

Recently, Haghtalab and Asadollahi [26] developed the UNIQUAC-NRF model and applied their model to a number of polymer solutions. In this model the same assumptions proposed by Haghtalab and Vera [27,28] for the NRTL-NRF model were used. The completely random mixture is considered as a reference state and the nonrandom factor, Γ , is used to show the deviation of the local composition from the bulk composition.

In this work, a new model, based on the UNIQUAC-NRF model, was proposed to study the liquid–liquid equilibria in aqueous polymer solutions. In the proposed model, a ternary interaction term was included to explain the three-body interactions between the molecules in the mixtures. The proposed model was used to study the phase behaviour of the ATPS of PEG + DEX at different temperatures and molecular weights.

2. Modelling

Recently, Haghtalab and Asadollahi [26] proposed the UNIQUAC-NRF model to study of the phase behaviour of aqueous two-phase polymer mixtures. According to the concept of local area fractions, the following relations can be expressed as:

$$\frac{\theta_{ij}}{\theta_{jj}} = \frac{\theta_i}{\theta_j} \tau_{ij}, \quad (1)$$

$$\theta_{ij} + \theta_{jj} = 1, \quad (2)$$

where θ_{ij} is local area fraction of molecule i surrounding central molecule j , and θ_i is bulk area fraction. In Equation (1), τ_{ij} is the interaction parameter for i - j pairs which is given by the following relation:

$$\tau_{ij} = \exp\left(-\frac{\Delta u_{ij}}{RT}\right). \quad (3)$$

It should be noted that Equation (2) is the relation for the local area balance around the central cell j . In the UNIQUAC-NRF model, local area fraction is related to the bulk area fraction by a nonrandom factor, Γ_{ij} as

$$\theta_{ij} = \theta_i \Gamma_{ij}, \quad (4)$$

where Γ_{ij} shows the deviation of local composition from bulk composition in mixture.

Using Equations (1) and (2), the nonrandom factor can be obtained as

$$\Gamma_{ij} = \frac{\tau_{ij}}{\sum_k \theta_k \tau_{kj}}. \quad (5)$$

Finally, the UNIQUAC-NRF model gives the excess Gibbs free energy as below [26]:

$$\begin{aligned} \left(\frac{g^E}{RT}\right)_{\text{UNIQUAC-NRF}} &= \sum_{i=1}^n x_i \ln\left(\frac{\phi_i}{x_i}\right) + \frac{z}{2} \sum_{i=1}^n q_i x_i \ln\left(\frac{\phi_i}{\theta_i}\right) \\ &+ \sum_{i=1}^n q_i x_i \left[\ln \Gamma_{ii} + \sum_{\substack{j=1 \\ j \neq i}}^n \theta_j \ln\left(\frac{\Gamma_{ji}}{\Gamma_{ii}}\right) \right]. \end{aligned} \quad (6)$$

The corresponding expression of the activity coefficient for component i in a solution is represented by the following equation

$$\begin{aligned} (\ln \gamma_i)_{\text{UNIQUAC-NRF}} &= \ln\left(\frac{\phi_i}{x_i}\right) + \frac{z}{2} q_i \ln\left(\frac{\theta_i}{\phi_i}\right) + l_i - \left(\frac{\phi_i}{x_i}\right) \sum_{j=1}^n (x_j l_j) \\ &+ q_i \left[1 + \ln \Gamma_{ii} - \sum_{j=1}^n \theta_j \Gamma_{ij} + (1 - \theta_i) \sum_{\substack{j=1 \\ j \neq i}}^n \theta_j \ln\left(\frac{\Gamma_{ij} \Gamma_{ji}}{\Gamma_{ii} \Gamma_{jj}}\right) \right. \\ &\left. - \frac{1}{2} \sum_{k=1}^n \sum_{\substack{l=1 \\ l \neq k, i}}^n \theta_k \theta_l \ln\left(\frac{\Gamma_{kl} \Gamma_{lk}}{\Gamma_{kk} \Gamma_{ll}}\right) \right]. \end{aligned} \quad (7)$$

To improve correlation of ternary LLE, the modified UNIQUAC-NRF was introduced using the same approach of Nagata for nonpolymer solutions [21–24]. The modified UNIQUAC-NRF model takes the three-body interaction effects between the polymer and solvent molecules into account. The existence of the three-body interactions can obviously affect the phase behavior of multi-component mixtures [21–24]. The effects are considered by introducing a ternary interaction parameter in the UNIQUAC-NRF model. For multi-component systems, the expression for the excess Gibbs free energy of the modified UNIQUAC-NRF model is presented as follows:

$$\left(\frac{g^E}{RT}\right)_{\text{ModifiedUNIQUAC-NRF}} = \sum_{i=1}^n x_i \ln\left(\frac{\phi_i}{x_i}\right) + \frac{z}{2} \sum_{i=1}^n q_i x_i \ln\left(\frac{\phi_i}{\theta_i}\right) + \sum_{i=1}^n q_i x_i \left[\ln \Gamma_{ii} + \sum_{\substack{j=1 \\ j \neq i}}^n \theta_j \ln\left(\frac{\Gamma_{ji}}{\Gamma_{ii}}\right) + \sum_{\substack{j=1 \\ j \neq i}}^n \sum_{\substack{k=1 \\ k \neq i \\ k > j}}^n \theta_j \theta_k \theta_i \ln \tau_{jki} \right]. \tag{8}$$

The first two terms in Equation (8) are attributed to the combinatorial part of the original UNIQUAC equation, i.e., the Guggenheim-Staverman term [29]. The third term is the residual part of the UNIQUAC-NRF model and the fourth term introduces the ternary interactions between molecules in mixture.

Since the molecular weight of polymers is much larger than that of solvent molecules, the mole fraction is an inconvenient unit of concentration for polymer–solvent solutions. Therefore, the weight fraction-based activity coefficient, Ω , is frequently used [17,30–32]. For component i in a mixture, the weight fraction-based activity coefficient takes the following form:

$$\begin{aligned} (\ln \Omega_i)_{\text{ModifiedUNIQUAC-NRF}} &= \ln\left(\frac{\phi'_i}{w_i}\right) + \frac{z}{2} M_i q'_i \ln\left(\frac{\theta'_i}{\phi'_i}\right) + M_i l'_i - \left(\frac{M_i \phi'_i}{w_i}\right) \sum_{j=1}^n (w_j l'_j) \\ &+ M_i q'_i \left[1 + \ln \Gamma'_{ii} - \sum_{j=1}^n \theta'_j \Gamma'_{ij} + (1 - \theta'_i) \sum_{\substack{j=1 \\ j \neq i}}^n \theta'_j \ln\left(\frac{\Gamma'_{ij} \Gamma'_{ji}}{\Gamma'_{ii} \Gamma'_{jj}}\right) - \frac{1}{2} \sum_{\substack{k=1 \\ k \neq i}}^n \sum_{\substack{l=1 \\ l \neq k, i}}^n \theta'_k \theta'_l \ln\left(\frac{\Gamma'_{kl} \Gamma'_{lk}}{\Gamma'_{kk} \Gamma'_{ll}}\right) \right] \\ &+ M_i q'_i \left[\left(\sum_{\substack{j=1 \\ j \neq i}}^n \sum_{\substack{k=1 \\ k \neq i \\ k > j}}^n \theta'_j \theta'_k \theta'_i \ln \tau_{jki} \right) + (1 - 3\theta'_i) \left(\sum_{\substack{j=1 \\ j \neq i}}^n \sum_{\substack{k=1 \\ k \neq i \\ k > j}}^n \theta'_j \theta'_k \right) \left(\sum_{\substack{l=1 \\ m=1 \\ m \neq l \\ p=1 \\ p \neq l \\ p > m}}^n \theta'_l \ln \tau_{mpl} \right) \right], \tag{9} \end{aligned}$$

where τ_{ij} and τ_{jki} are the binary and ternary interaction parameters, respectively; ϕ'_i and θ'_i are volume and surface area fraction of component i , respectively. Also, Γ' is the nonrandom factor and l'_i is the size parameter. These parameters can be given according to the following sets of relations:

$$\phi'_i = \frac{r'_i w_i}{\sum_j r'_j w_j}, \quad (10)$$

$$\theta'_i = \frac{q'_i w_i}{\sum_j q'_j w_j}, \quad (11)$$

$$\Gamma'_{ij} = \frac{\tau_{ij}}{\sum_k \theta'_k \tau_{kj}}, \quad (12)$$

$$l'_i = \frac{z}{2}(r'_i - q'_i) - \left(r'_i - \frac{1}{M_i}\right). \quad (13)$$

3. Results and discussion

The volume and surface parameters of Equation (9), i.e., r' and q' , are directly obtained from [17], as reported in Table 1. Using extensive experimental data for various ATPS of PEG + DEX systems [1,11,25,32,33], the binary as well as the ternary interaction parameters appearing in Equation (9) can be obtained by minimising the following objective function [17,26]

$$\text{O.F} = \sum_k^N \sum_i^3 \sum_j^2 \left(w_{ijk}^{\text{expt.}} - w_{ijk}^{\text{Calcd}} \right)^2, \quad (14)$$

where w_{ijk} is the weight fraction of component i in phase j for the k th experimental tie-line. The superscripts *expt.* and *Calcd* denote to the experimental and calculated values for weight fraction of components, respectively. Nelder and Mead Simplex Search method [34] was used for minimisation of the objective function. For a given set of parameters, phase equilibrium calculations are performed using the weight-based iso-activity criterion as follows [17,32]

$$(w_i \Omega_i)^I = (w_i \Omega_i)^{II}. \quad (15)$$

Table 1. Surface and volume parameters used in the UNIQUAC-based model [17].

Component	$r' \times 10^2$	$q' \times 10^2$
DEX	2.717	1.96
PEG	3.87	2.57
H ₂ O	5.11	7.78

For each tie-line, the values for w_i in lower phase are obtained iteratively using the experimental data for w_i in upper phase and applying the activity coefficient model [35–38]. Similarly, the values for w_i in upper phase can be calculated from the experimental w_i in lower phase. The RMSD of the results obtained from the UNIQUAC, the UNIQUAC-NRF and the modified UNIQUAC-NRF models for the ATPS systems containing PEG and DEX are presented and compared in Table 2. As seen from Table 2, for all cases, the modified UNIQUAC-NRF model can more accurately correlate the experimental data at different temperatures and molecular weights than those obtained from the UNIQUAC-NRF model. Also the modified UNIQUAC-NRF gives acceptable results in comparison to those of the UNIQUAC model. Good agreement between the results of the modified UNIQUAC-NRF model and the experimental data can be justified by inclusion of the three-body interactions between the molecules in the solutions.

The values for the binary interaction parameters for the original UNIQUAC and the UNIQUAC-NRF models were presented in Tables 3 and 4. It is worth stating that in order to unequivocally compare the results of the models studied in this work, the same minimisation procedure and the same experimental data were used for each specified model.

Table 5 gives the values for both the binary and the ternary interaction parameters, i.e., A_{ij} and τ_{ijk} for the modified UNIQUAC-NRF activity coefficient model. As expounded earlier, the ternary interaction parameters reflect the unlike three-body interactions between two polymer molecules and one solvent molecule in mixture. The values of the parameters reported in Table 5 can be directly used to study the phase behaviour of the ATPS for PEG + DEX + water at different conditions.

Figure 1 shows the comparison of the tie-lines obtained from UNIQUA-based models studied in the present work with those of the experimental data for the system of PEG 6000 + DEX 500 with number average molecular weight 179,347 at 283.15 K. Results obtained from the modified UNIQUAC-NRF model are slightly better than those obtained from the original UNIQUAC and the UNIQUAC-NRF models.

Figure 2 shows the phase diagram and binodal curves for the ATPS of PEG6000 + DEX at 293.15 K at different DEX molecular weight. As seen from Figure 2, good agreement between the results obtained from the modified UNIQUAC-NRF and the experimental data can be attained. This observation can confirm the superiority of the proposed model in this work.

Figure 3 gives the phase diagram for the ATPS of PEG + DEX17 at 293.15 K at various PEG molecular weights. A careful observation of Figure 3 reveals that the PEG molecular weight has a much stronger effect on the phase diagram and binodal curve than the DEX molecular weight.

4. Conclusions

In this work, a modified form of the UNIQUAC-NRF activity coefficient model was proposed and used to study the phase behaviour of ATPS of PEG and DEX. In the proposed UNIQUAC-based model a ternary interaction term was added to the expression for the excess Gibbs free energy and, in turn, to the corresponding expression for the activity coefficient given by the UNIQUAC-NRF model on the weight fraction scale. The combinatorial part of the new model is considered to be the same as the original UNIQUAC and the residual part takes the nonrandomness as well as the binary and the

Table 2. The percent of the root mean square deviation (RMSD) produced from correlation of the UNIQUAC-based models.

System	Temperature (k)	No. of tie-lines	PEG	DEX	Mn × 10 ⁻³	PEG Mn × 10 ⁻³	DEX	RMSD ^a %				Reference
								UNIQUAC (%)	UNIQUAC-NRF (%)	Modified UNIQUAC-NRF (%)	UNIQUAC-NRF (%)	
A	293.15	6	PEG 20000	D 17	15.0-20.0	23	3.56	3.39	3.04	[1]		
B	293.15	4	PEG 4000	D 17	3.0-3.7	23	0.34	1.19	0.24	[1]		
C	293.15	5	PEG 6000	D 24	6.0-7.5	40.5	3.87	3.2	3.08	[1]		
D	293.15	5	PEG 4000	D 48	3.0-3.7	180	2.58	1.02	0.76	[1]		
E	273.15	5	PEG 4000	D 48	3.0-3.7	180	4.57	4.07	3.74	[1]		
F	293.15	7	PEG 6000	D 17	6.0-7.5	23	1.41	1.73	1.70	[1]		
G	273.15	4	PEG 6000	D 17	6.0-7.5	23	1.25	2.14	1.88	[1]		
H	293.15	5	PEG 6000	D 68	6.0-7.5	280	2.68	3.24	2.31	[1]		
I	273.15	4	PEG 6000	D 68	6.0-7.5	280	3.7	3.81	3.26	[1]		
J	293.15	4	PEG 6000	D 37	6.0-7.5	83	1.2	1.26	0.73	[1]		
K	273.15	5	PEG 6000	D 37	6.0-7.5	83	2.82	3.85	3.04	[1]		
L	273.15	6	PEG 3000	D 500	3.14	101	3.31	1.86	1.50	[30]		
M	313.15	7	PEG 3000	D 500	3.14	101	2.18	2.47	1.72	[30]		
N	277.15	4	PEG 6000	D 500	6.23	179.347	2.67	2.41	2.34	[24]		
O	283.15	4	PEG 6000	D 500	6.23	179.347	2.18	2.89	1.48	[24]		
P	293.15	7	PEG 6000	D 500	6.23	179.347	6.67	6.28	5.92	[24]		
Q	313.15	4	PEG 6000	D 500	6.23	179.347	8.52	6.36	3.33	[24]		
R	277.15	4	PEG 35000	D 500	39.005	179.347	3.14	3.13	3.12	[24]		
S	293.15	8	PEG 35000	D 500	39.005	179.347	5.47	4.09	4.02	[24]		
T	298.15	8	PEG 8000	DT-500	8.92	167	4.70	7.88	6.04	[11]		
U	298.15	6	PEG 3350	DT-70	3.69	37	5.07	5.68	5.58	[11]		
V	281.15	4	PEG 6000	D 28700	6	28.7	3.74	3.61	3.22	[31]		
W	296.15	4	PEG 6000	D 28700	6	28.7	1.85	2.27	1.42	[31]		
X	311.15	4	PEG 6000	D 28700	6	28.7	2.09	2.47	1.83	[31]		
Average r.m.s.d							3.3	3.4	2.7			

Note: ^aRMSD = $1/N \sqrt{\sum_{k=1}^N \sum_{j=1}^2 \sum_{i=1}^3 (w_{ijk}^{\text{Calcd}} - w_{ijk}^{\text{exp}} / w_{ijk}^{\text{Calcd}} + w_{ijk}^{\text{exp}})^2}$, w_{ijk}^{Calcd} , w_{ijk}^{exp} and N are calculated, experimental and the number of components, respectively.

Table 3. Binary interaction parameters for the UNIQUAC model.^{a,b}

System	A_{12}	A_{21}	A_{13}	A_{31}	A_{23}	A_{32}
A	275.405	-184.442	-299.971	317.060	-383.341	478.607
B	360.887	-174.0428	-306.297	318.737	-357.536	380.969
C	538.787	-236.607	-307.059	333.203	-381.432	480.513
D	385.157	-208.727	-318.332	372.784	-385.311	518.653
E	336.072	-213.224	-309.521	382.369	-395.616	592.491
F	636.161	-281.565	-326.632	400.168	-427.888	626.181
G	674.091	-282.363	-312.543	385.941	-418.226	625.822
H	256.715	-183.144	-303.582	323.201	-390.697	517.939
I	208.214	-160.119	-322.402	408.409	-404.268	598.122
J	366.042	-205.429	-319.931	365.941	-392.005	513.728
K	374.791	-183.204	-294.302	329.435	-348.291	428.847
L	430.571	-230.631	-284.701	306.375	-373.016	508.288
M	415.325	-234.136	-343.675	401.680	-428.425	588.486
N	430.746	-237.109	-283.711	295.856	-376.103	503.319
O	331.876	-187.849	-292.066	307.721	-357.460	438.701
P	273.235	-181.293	-316.246	356.199	-391.380	515.790
Q	261.534	-163.868	-278.987	200.934	-355.912	342.212
R	292.293	-201.148	-267.075	238.158	-360.808	430.561
S	272.082	-198.837	-293.223	292.384	-388.937	494.764
T	228.961	-175.697	-337.358	404.243	-426.438	599.613
U	84.063	-69.267	-378.434	529.027	-456.455	711.832
V	439.772	-240.351	-286.858	318.021	-380.109	530.354
W	504.441	-266.467	-316.738	351.089	-421.803	584.938
X	475.941	-257.838	-331.168	372.029	-429.397	585.369

Notes: ^aSubscripts of 1, 2, and 3 refer to DEX, PEG, and H₂O, respectively.

^b $\tau_{ij} = \exp(-A_{ij}/T)$.

Table 4. Binary interaction parameters for the UNIQUAC-NRF model

System	A_{12}	A_{21}	A_{13}	A_{31}	A_{23}	A_{32}
A	-455.723	-368.193	-274.856	-268.234	-312.456	-237.856
B	-288.129	7.687	-280.439	-334.762	-292.951	-253.753
C	-107.064	-37.524	-268.256	-209.747	-305.734	-294.969
D	-755.211	-467.901	-279.744	-279.378	-328.994	-488.777
E	-872.899	-409.093	-254.221	-201.897	-323.824	-607.489
F	-688.491	-372.851	-305.089	-484.624	-321.217	-338.608
G	-733.569	-302.865	-273.771	-401.221	-299.360	-405.295
H	-427.263	-435.822	-263.742	-174.946	-314.304	-458.013
I	-652.052	-424.491	-245.376	-150.751	-305.659	-560.319
J	-704.649	-109.882	-284.078	-337.004	-321.769	-424.612
K	-506.816	-163.057	-252.641	146.182	-325.779	-587.338
L	-1083.184	-623.754	-271.378	-343.415	-336.329	-764.235
M	-525.679	-484.081	-300.781	-284.675	-336.429	-350.374
N	-465.471	-25.252	-248.539	-12.431	-297.903	-300.280
O	-357.210	-121.492	-248.539	-12.431	-297.903	-300.280
P	-463.707	-281.014	-266.269	-165.123	-309.5541	-308.996
Q	-312.127	-151.624	-284.877	94.487	-367.482	-588.611
R	-756.875	-423.381	-261.439	-217.695	-327.007	-495.259
S	-632.043	-453.181	-272.354	-220.446	-328.996	-427.239
T	-726.412	-414.396	-282.728	-266.307	-336.041	-443.737
U	-391.739	-97.876	-271.219	-175.108	-312.619	-257.938
V	-672.046	-457.207	-260.641	-289.545	-296.307	-423.477
W	-653.707	-504.517	-289.686	-331.888	-328.146	-388.198
X	-459.079	-374.779	-287.744	-286.302	-315.422	-249.599

Table 5. Binary and ternary interaction parameters for the modified UNIQUAC-NRF model.

System	A_{12}	A_{21}	A_{13}	A_{31}	A_{23}	A_{32}	τ_{231}	τ_{132}	τ_{123}
A	-502.889	-392.745	-272.005	-244.685	-317.565	-297.279	1.458	0.686	1.669
B	-731.506	-302.797	-297.333	-395.770	-334.584	-401.013	4.568	1.829	1.374
C	-823.098	-323.745	-308.080	-483.503	-337.422	-447.962	8.882	14.498	7.980
D	-685.658	-391.662	-275.671	-251.995	-322.069	-432.168	0.891	1.223	0.990
E	-957.916	-457.268	-257.357	-222.417	-332.418	-676.976	1.449	0.751	1.742
F	-760.066	-549.702	-311.226	-530.938	-325.678	-375.552	0.662	0.421	6.240
G	-884.709	-553.596	-288.433	-491.693	-316.359	-493.793	0.348	0.065	1.048
H	-340.713	-421.508	-263.244	-169.848	-317.104	-478.372	1.011	0.469	1.411
I	-557.904	-501.641	-247.104	-177.336	-318.788	-715.679	3.031	0.862	11.336
J	-873.346	-550.676	-291.983	-408.878	-329.576	-517.286	1.721	0.739	1.809
K	-880.084	-226.997	-261.075	196.033	-360.029	-942.354	0.534	0.874	1.576
L	-944.253	-539.295	-266.214	-310.234	-323.325	-642.854	1.361	4.968	8.837
M	-171.893	-41.134	-285.197	-167.614	-324.723	-258.934	1.429	0.734	1.467
N	-538.352	-147.754	-249.987	103.485	-314.833	-469.160	1.024	0.947	0.917
O	-528.453	-20.849	-253.455	-89.618	-309.361	-350.682	1.323	0.749	1.199
P	-479.394	-263.645	-267.695	-180.814	-309.231	-300.748	1.510	0.544	1.059
Q	-896.751	-279.979	-294.589	168.156	-407.916	-968.305	15.165	0.940	1.833
R	-767.422	413.224	-268.442	-284.877	-343.701	-689.927	1.853	1.489	1.381
S	-608.108	-437.334	-270.251	-201.110	-328.319	-423.332	1.547	0.957	2.028
T	41.848	39.976	-283.070	222.305	-300.459	50.025	3.168	0.906	2.555
U	-535.483	42.144	-279.045	-241.286	-326.386	-379.363	0.376	0.688	1.104
V	-1280.354	-857.772	-297.393	-542.699	-351.290	-866.579	0.504	0.359	1.147
W	-1178.423	-884.679	-328.096	-576.481	-378.469	-759.859	1.958	0.598	0.310
X	-1086.219	-912.434	-346.082	-648.970	-376.469	-641.542	1.690	1.568	0.213

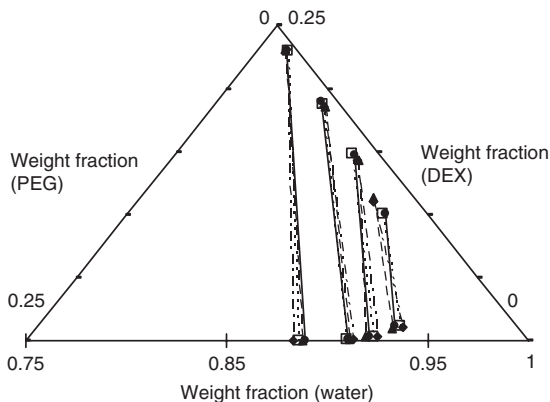


Figure 1. The ternary phase diagram for the ATPS of PEG 6000 + DEX 500 with number average molecular weight 179,347 along with the equilibrium tie-lines obtained from the UNIQUAC-based models at 283.15: experimental data (□); results of the modified UNIQUAC-NRF (●); results of the original UNIQUAC-NRF (▲); results of the UNIQUAC (◆).

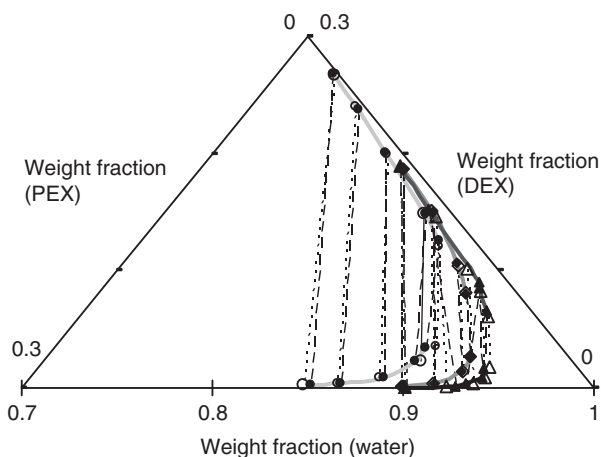


Figure 2. The ternary phase diagram for the ATPS of PEG6000 + DEX with different molecular weight of DEX along with the equilibrium tie-lines obtained from the the modified UNIQUAC-NRF model at 293.15 K; DEX 24: experimental data (---○---); results of the model (---●---); DEX 37: (---◇---); results of the model (---◆---); DEX 68: experimental data (---△---); results of the model (---▲---).

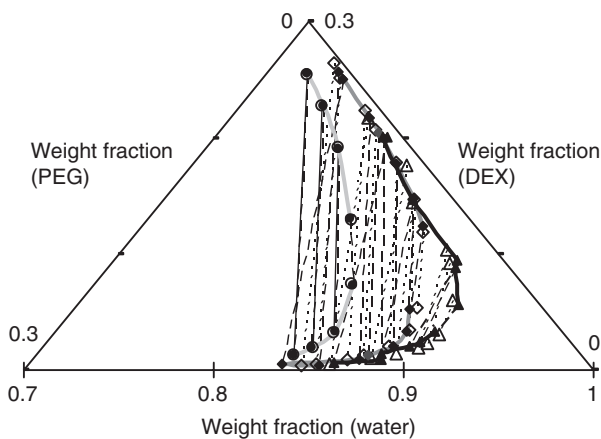


Figure 3. The ternary phase diagram for the ATPS of PEG + DEX17 with number average molecular weight 23,000 with different molecular weight for PEG at 293.15 correlated by the modified UNIQUAC-NRF model; PEG 4000: experimental data (---○---); results of the model (---●---); PEG 6000: (---◇---); results of the model (---◆---); PEG 20000: experimental data (---△---); results of the model (---▲---).

ternary interaction parameters into account. In order to do a fair comparison between the results, the same minimisation procedure and the same experimental data were used for the models studied here. The results of the modified UNIQUAC-NRF model are in good agreement with experimental data in comparison to those obtained from the original UNIQUAC and the UNIQUAC-NRF activity coefficient models.

Abbreviations

PEG	Polyethylene glycol
DEX	Dextran
NRF	Nonrandom factor

List of symbols

A_{ij}	Interaction parameter between molecules i and j
g^E	Molar excess Gibbs free energy
l	Size parameter in UNIQUAC equation
M_i	Molecular weight of component i
N	Number of experimental points
q	Surface parameter
R	Gas constant
r	Volume parameter
T	Absolute temperature
u_{ij}	Binary interaction parameter between molecules i and j
w	Weight fraction
x	Mole fraction
z	Coordination number

Greek letters

γ	Molar-based activity coefficient
Ω	Weight-based activity coefficient
Γ	Nonrandom factor
ϕ	Volume fraction
θ	Surface area fraction
a_i	Activity of component i
τ_{ij}	Binary interaction parameter between molecules i and j
τ_{jki}	Ternary interaction parameter between molecules k , j , and i

Superscripts

Calcd	Calculated value
expt.	Experimental value
I, II	Two aqueous phases in equilibrium

Subscripts

i, j, k, l, m, p	Component index
'	Weight fraction index

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