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A modified entropic expression for the analysis of swelling behavior of polymeric membranes in solutions

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Abstract

The linear mixed relation for mixed molar volume and free-volume were modified to derive our new activity expression attributed to the combined combinatorial and free volume contributions. The validity and applicability of this expression were demonstrated by calculating the solvent activity in polymer solutions and analyzing the swelling behaviors for polymeric membranes. The average absolute deviation (AAD) of these calculated results from the experimental values of solvent activities for polymer solutions was employed for comparison. It is shown that the modified model can yield better results than the original one for most of the systems considered. The swelling behavior of poly vinyl alcohol (PVA) membranes in water/glycol (EG) mixture over a wide range of concentrations was analyzed. The activity of solvents in the liquid and the membrane was calculated by the UNIQUAC model and this present modified model, respectively. The estimations are consistent with experimental data roughly at temperatures of 333 and 343 K. It is found that the modified model is a suitable alternative to the Flory–Huggins equation for the analysis of the swelling behaviors of polymeric membranes in solutions.

Keywords: Modified FV fraction; Modified entropic expression; Swelling behavior

1. Introduction

Knowing the value of solvent activities in polymer solutions is important to polymerization process and the understanding of swelling characteristics of polymeric membranes. Laboratory determination of these data can be potentially expensive and time consuming, so it is desirable to predict the solvent activities in polymer solutions by simple activity model equations. The most widely used models for polymer solutions can be grouped under two categories: (1) Equation of state based on the lattice-fluid theory of polymer solutions, such as GC-Flory [1] and GCLF [2] models; (2) activity models based on group contribution, such as UNIFAC [3,4], UNIQUAC [5,6] and UNIFAC-ZM [7,8].

Of these two type equations, the second one, which requires less model parameters and is comparatively simple since it does not take the effect of pressure into consideration, can bring out reasonable solvent activity predictions. Thus, this kind of model expression is popular and is taken as a good choice to describe the phase behavior for polymer solutions. These group contribution models incorporated with the free-volume (FV) definition have gained increasing attention and have been investigated extensively [9–12]. The UNIQUAC-FV model is successfully applied to systems that exhibit both an upper critical solution temperature (UCST) and a lower critical solution temperature (LCST) [13]. UNIQAC related models can be used to describe binary to ternary phase behavior for polymer solutions [14,15]. Though they can be used to characterize phase behavior for some polymer solutions successfully, FV based models generally under-estimate solvent activity, so modifications to the FV fraction expression are required to improve calculated results.

The aim of this present article is to study the applicability of several group contribution activity models used in polymer solutions taking account of the free-volume effects, such as UNIFAC-FV [9,10] and ENTROPIC-FV (EFV) [11,12]. A modified activity expression attributed to the combined combinatorial and free-volume contributions was

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Symbols

PVAc	poly(vinyl acetate)	PIB	polyisobutylene
PEO	poly(ethylene oxide)	PS	polystyrene
PP	polypropylene	TCC	tetrachloride carbon
PVC	poly(vinyl chloride)	Temp	temperature
VA	vinyl acetate	ADD	$=\dfrac{1}{N}\sum\left\lvert\dfrac{a_{\mathrm{i,cal}}-a_{\mathrm{i,exp}}}{a_{\mathrm{i,exp}}}\right\rvert\times 100\%$
PDMS	poly(dimethylsiloxane)		

proposed in this study and the calculated results by this model were presented for comparison. The swelling behavior of poly vinyl alcohol (PVA) membranes in water/glycol (EG) mixture over a wide range of concentrations was analyzed by this modified expression.

2. FV related models and its modified treatment description

UNIFAC-FV model was proposed by Oishi and Prausnitz [9] as follows

$$\ln a_i = \underset{\text{combinatorial}}{\ln a_i^C} + \underset{\text{UNIFAC residual}}{\ln a_i^R} + \underset{\text{free}-\text{volume}}{\ln a_i^{\mathrm{FV}}} \tag{1}$$

where superscript FV stands for the free volume.

EFV model equation was proposed by Elbro et al. [16], it was based on UNIFAC-FV model [9] with integrating the combinatorial with the free-volume terms into one term with the residual term remaining to be unchanged. The activity of component i can be expressed in terms of EFV model equations as follows:

$$\ln a_i = \ln a_i^R + \ln a_i^{C+\mathrm{FV}} \tag{2}$$

The second term on the right side of Eq. (2) is given by

$$\ln a_i^{C+\mathrm{FV}} = \ln \varphi_i^{\mathrm{FV}} + 1 - \frac{\varphi_i^{\mathrm{FV}}}{x_i} \tag{3}$$

The free-volume fraction φ_i^{FV} is defined by

$$\varphi_i^{\mathrm{FV}} = \frac{x_i(V_i - V_{i\mathrm{w}})}{\sum x_j(V_j - V_{j\mathrm{w}})} \tag{4}$$

where V_i and $V_{i\mathrm{w}}$ are the molecular volume and van der Waals (vdW) volume, respectively.

The residual part can be expressed by [9]

$$\ln a_i^R = \sum_k \nu_k^i \left[\ln \Gamma_k - \ln \Gamma_k^i\right] \tag{5}$$

where ν_k^i is the number of type k in molecular i; Γ_k is the activity coefficient of group k at the mixture composition; and, Γ_k^i is the activity coefficient of group k at a group composition corresponding to pure component i.

The activity coefficient group Γ_k is given by

$$\ln \Gamma_k = Q_k\left[1 - \ln\left(\sum_m \theta_m \tau_{mk}\right) - \sum_m\left(\frac{\theta_m \tau_{km}}{\sum_j \theta_j \tau_{jm}}\right)\right] \tag{6}$$

where m and j are the number of groups in the solution; θ_m is the group surface area fraction of group m in the given solution; and, τ_{mk} is the group interaction parameter for the interaction of group m with group k.

The group surface area fraction θ_m for group m is

$$\theta_m = \frac{Q_m X_m}{\sum_k Q_k X_k} \tag{7}$$

where X_m is the mole fraction of group m in the solution which is calculated from the following equation

$$X_m = \frac{\sum_j \left(\nu_m^j w_j / M_j\right)}{\sum_j \left(w_j / M_j \sum_n \nu_n^j\right)} \tag{8}$$

where ν_m^j is the number of groups of type m in component j; n is the number of groups in the mixture; w_j is the mass fraction of component j in the polymer solution; and, M_j is the molecular weight of component j.

The estimations by this model were consistent with experimental data for some polymer solutions, while not for some others. As such, a lot of modifications [12,17,18] were made to improve the predictions. Several modifications were focused on the FV fraction term considering that the model gave under-estimations for some systems. Two of these are listed as follows. The first one (EFV-1.2) has been proposed by Kouskoumvekaki et al. [17]. The authors used the combinatorial term of Elbro et al. to predict the activity coefficients in nearly athermal polymer/solvent solutions and asymmetric alkane systems. It is shown that the results are improved when a hard-core volume larger than the van der Waals volume is employed. They have concluded that the optimum free volume for this combinatorial term is

$$\varphi_i^{\mathrm{FV}} = \frac{x_i(V_i - 1.2V_{i\mathrm{w}})}{\sum x_j(V_j - 1.2V_{j\mathrm{w}})} \tag{9}$$

The second modification (EFV-0.9) follows the suggestion of Sheng et al. [18] that better representation of the combinatorial effects can be achieved by employing an exponent equal to 0.9 in the free-volume fractions

$$\varphi_i^{\mathrm{FV}} = \frac{x_i(V_i - V_{i\mathrm{w}})^{0.9}}{\sum x_i(V_i - V_{i\mathrm{w}})^{0.9}} \tag{10}$$

The effect of the FV fraction on solvent activity prediction is inconclusive. Following description can make you understood clearly. Both sides of Eq. (3) being taking the derivative of φ_i^{FV} gives

$$\frac{\partial \ln a_i^{C+\mathrm{FV}}}{\partial \varphi_i^{\mathrm{FV}}} = \frac{1}{\varphi_i^{\mathrm{FV}}} - \frac{1}{x_i} = \frac{1}{x_i}\left[\frac{\sum\limits_j x_j(V_j - V_{j\mathrm{w}})}{V_i - V_{i\mathrm{w}}} - 1\right] = \frac{A_i}{x_i} \tag{11}$$

A_{i} can be greater or less than zero, which depends on the value of $V_{\mathrm{i}} - V_{i\mathrm{w}}$. $A_i \leq 0$ if $V_i - V_{i\mathrm{w}}$ is the largest one for $i = 1,2,\ldots,n$; if it is the smallest one, $A_i \geq 0$. So $a_i^{C+\mathrm{FV}}$ can be increased or decreased with φ_i^{FV} increasing, which relies on the characteristics of polymer solutions. The linear mixed relation for mixed molar volume and free-volume were modified to derive our new activity expression for improved description of the phase behavior of polymer solutions. A adjustable parameter, λ, which is reflective of free-volume mixing and is close to unity, is thus incorporated into the φ_i^{FV} terms in Eq. (3) in this present article, which gives (the derivation is detailed in Appendix A)

$$\ln a_i^{C+\mathrm{FV}} = \ln\frac{\varphi_i^{\mathrm{FV}}}{\lambda} + 1 - \frac{\varphi_i^{\mathrm{FV}}}{\lambda x_i} \tag{12}$$

This expression is the same as the original EFV when lambda is set to be unity.

3. Calculation and discussion

Four models were chosen to study the phase behavior for 31 polymer solution systems, including both weak and strong polar organic solvent systems. The adjustable parameters c_1 and b used in the UNIFAC-FV model were set to be 1.1 and 1.28 [9] in these simulations. The binary interaction parameters used for a_i^R calculation and group volume and surface area parameters used for $a_i^{C+\mathrm{FV}}$ calculation were obtained from the database [19,20]. The polymer density, which plays an important role in these calculations based on these FV models, is a function of temperature, polymerization degree, crystallinity of polymer. So the values of the density of these polymers were obtained from the experimental data [21–25] for accuracy even they could be estimated from empirical equations [26,27]. The van der Waals volume, $V_{i\mathrm{w}}$, can be estimated by Bondi method [28].

3.1. Comparison of these models

UNIFAC-FV, EFV, EFV-1.2, and EFV-λ models were used to evaluate the solvent activities for 31 polymer solution systems. The optimal value of lambda was found to be 0.95 by fitting to experimental data, which reflected in Fig. 1. It is indicated in this figure that the average AAD for the 31 polymer solution systems reach the minimum value when the value of λ get to 0.95. It is shown in Table 1 that EFV-1.2 model is better in activity prediction for some polymer solutions than the original EFV model. EFV-1.2 gave the AAD values of 1.06, 1.59 and 11.01%, EFV the AAD values of 5.19, 4.01 and 21.87% for polymer solutions of PDMS (26,000)/benzene, PIB (2,250,000)/pentane and PP (205,000)/$\mathrm{CCl_4}$, respectively. This may be attributed to the fact that the difference between the vdW volume and the hard-core volume was diminished with the former multiplied by 1.2. On the other hand, the EFV-1.2 model made a poorer prediction for some others. For systems of hexane in PDMS at various molecular weights, the EFV-1.2 model yields poorer predictions than the original EFV method. These results are in agreement with those from Kouskoumvekaki et al. since the adjustable parameter of 1.2 is not the optimal value for these systems [17]. This present model ($\lambda = 0.95$) produces also poorer results than the original EFV method ($\lambda = 1.0$) since the value of 0.95 for the adjustable parameter λ is not the optimal value for these same systems, as indicated in Fig. 2. These poorer estimations by EFV-1.2 model for these systems may be due to the fact that the difference between the vdW volume and the hard-core volume was increased with the former multiplied by 1.2. The hard-core volume and the vdW volume were estimated in order to clarify the explanation further. For PDMS (26,000)/benzene and PIB (1170)/pentane, the solvent vdW and hard-core volumes are 48.36 and 70.02 for the former, 58.03 and 84.03 for the latter, respectively. The difference between the vdW volume and the hard-core volume is reduced when the former multiplied by 1.2, and this is in

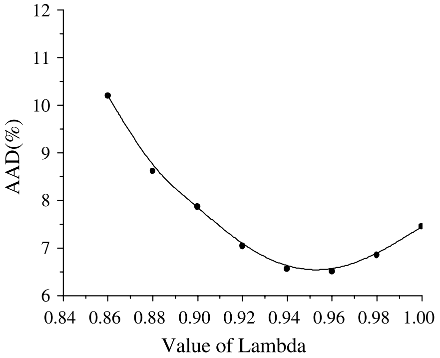

Fig. 1. The value of AAD under different λ for 31 polymer/solvent systems.

Table 1
Comparison of calculated results for four different combined combinatorial and FV expressions

System	Temperature (K)	N	AAD (%)				Refs.
			EFV	EFV-1.2	This work	UNIFAC-FV	
PDMS (15,650)/benzene	303.15	8	4.71	0.50	0.32	13.53	[21]
PDMS (26,000)/benzene	303.15	8	5.19	1.06	0.60	13.93	[21]
PDMS (15,650)/hexane	303	8	1.23	5.38	3.49	1.36	[21]
PDMS (6650)/benzene	303.15	8	4.80	1.94	1.48	12.05	[21]
PDMS (26,000)/hexane	303	8	1.68	4.85	3.01	0.74	[21]
PDMS (3350)/hexane	303.15	8	2.13	2.85	2.34	1.95	[21]
PDMS (6650)/hexane	303.15	8	1.05	5.03	3.60	2.01	[21]
PDMS (89,000)/hexane	303.15	8	1.98	4.79	2.75	0.42	[21]
PEO (5700)/benzene	333.15	8	5.86	12.19	9.09	3.52	[23]
PIB (100,000)/cycolhexane	298.15	10	3.15	3.10	1.30	3.70	[21]
PIB (1170)/pentane	298.15	6	10.85	6.30	8.91	11.18	[21]
PIB (2,250,000)/pentane	298.15	12	4.01	1.59	2.79	3.81	[21]
PIB (40,000)/benzene	298.15	11	10.18	3.97	7.30	2.67	[21]
PIB (40,000)/cyclohexane	298.15	8	7.49	1.20	4.53	4.61	[21]
PIB (40,000)/pentane	298.15	9	14.74	4.66	12.12	8.41	[21]
PIB (50,000)/benzene	298.15	16	9.14	7.71	5.38	5.94	[21]
PIB (50,000)/cyclohexane	298.15	11	5.52	3.51	2.41	1.92	[21]
PIB (50,000)/hexane	298.15	8	2.60	12.33	2.71	7.44	[21]
PIB (50,000)/toluene	298.15	7	13.34	11.66	12.25	11.14	[21]
PP (15,000)/TTC	303.15	6	7.51	4.84	6.79	10.10	[21]
PP (205,000)/TTC	303.15	7	21.87	11.01	18.84	16.17	[21]
PS (15,400)/toluene	298.15	6	5.52	4.53	3.23	7.40	[23]
PVAc (143,000)/VA	303.15	10	3.26	6.56	3.89	4.29	[21]
PVAc (143,000)/benzene	303.15	9	8.13	7.15	6.84	9.98	[21]
PVAc (48,000)/benzene	303.15	8	2.78	4.05	2.48	3.48	[21]
PVAc (74,000)/benzene	333.15	7	4.51	9.03	5.00	5.44	[24]
PVAc (74,000)/methanol	313.15	11	23.58	39.69	28.11	26.16	[24]
PVAc (74,000)/ethanol	293.15	15	6.82	11.98	4.67	40.98	[24]
PVAc (9000)/acetone	303.15	5	3.16	4.54	1.10	1.90	[23]
PVAc (170,000)/propanol	303.15	5	21.66	27.65	17.83	13.16	[25]
PVC (34,000)/toluene	316.35	8	17.95	9.53	15.02	17.55	[21]
Overall			7.63	7.59	6.46	8.79	

agreement with the results indicated in Table 1. To the contrary, the solvent vdW and hard-core volumes are 21.71 and 21.97 for PVAc (74,000)/methanol, 49.30 and 49.98 for PVAc (170,000)/propanol, respectively. Larger difference between the vdW and hard-core volume tends to arise if the former multiplied by 1.2 for this case, and this is also in accord with the results indicated in Table 1. There are also the cases that EFV-1.2 and EFV models gave estimations not quite different for some systems. As an example, the AAD values evaluated by EFV-1.2 and EFV models were 3.15 and 3.10% for PIB (100,000)/cyclohexane, respectively.

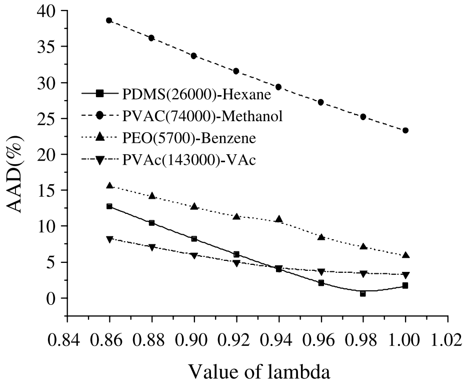

Fig. 2. ADD vs. the value of λ.

The modified model ($\lambda = 0.95$) proposed in this article achieved better results for most of the systems considered than those estimated by the original EFV method ($\lambda = 1.0$). For example, the former produces AAD values of 0.60, 1.30 and 3.23% and, the latter of 5.19, 3.15 and 5.52% for the polymer solution systems of PDMS (26,000)/benzene, PIB (100,000)/cyclohexane, and PS (15,400)/toluene, respectively. This may attribute to the fact that 0.95 is the optimal value for the adjustable parameter instead of 1.0, as reflected in Fig. 1.

The denominator multiplied by 0.95 in the φ_i^{FV} term makes its value become larger, which results in improved predictions for most of systems and worse estimations for some others, such as PEO (5700)/benzene and PDMS (26,000)/hexane for the worse examples. The reason for these poorer predictions may be that 0.95 is not the optimal value for the adjustable parameter for such specific systems, as depicted in Fig. 2. One can find in this figure that the

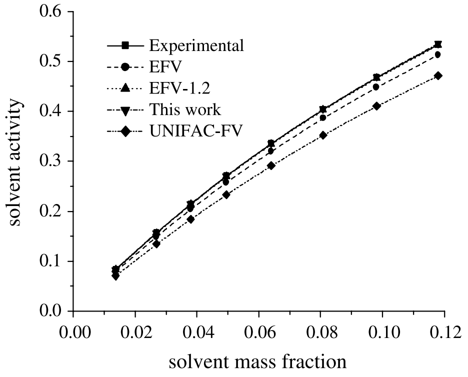

Fig. 3. Experimental and calculated activities of benzene in PDMS (15,650) + benzene system at 303.15 K.

optimal value for λ is greater than one for PEO (5700)/ benzene mixture and in between 0.95 and 1 for PDMS (26,000)/hexane system.

The calculated results by these four models are displayed against the experimental data in Figs. 3–6 for four systems of PDMS (15,650)/benzene, PIB (100,000)/cyclohexane, PS (15,400)/toluene and PVAc (9000)/acetone, respectively. It is shown that all these models can roughly give estimations representing experimental dada, while this present method reproduces characteristics being closest to experimental observations.

3.2. Effect of the van der Waals volume

It is shown that the calculated values of solvent activity are sensitive to the FV. Since the molecular volume can be obtained with accuracy, while the vdW volume, essentially a measure of molecule's hard-core volume which can be calculated by Bondi, is not always reflective of real situations due to the packing of molecules, a higher than the vdW volume inaccessible volume represents more adequately the hard-core volume. This target is to elucidate how the vdW volume to affect solvent activity prediction. In order to get further understanding of the effect of V_{iw} on the solvent activity prediction, the value of V_{iw} was changed to see the variation in calculated results. One may roughly think that the model is a good one if the solvent activity is less sensitive to V_{iw}.

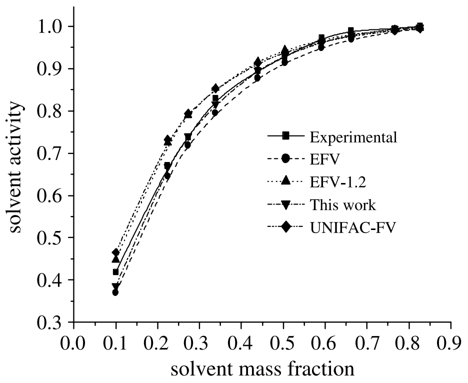

Fig. 4. Experimental and calculated activities of cyclohexane in PIB (100,000) + cyclohexane system at 298.15 K.

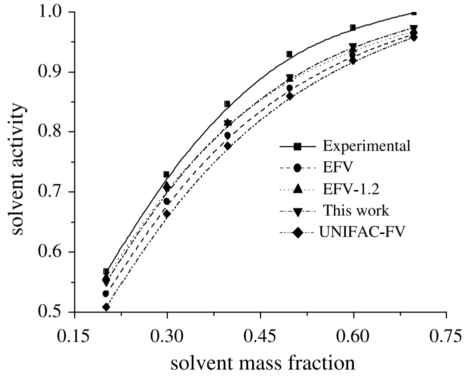

Fig. 5. Experimental and calculated activities of toluene in PS (15,400) + toluene system at 298.15 K.

It is indicated in Fig. 7 that the calculated results from EFV-1.2 are closer to the experimental data than those from EFV and the present models when the vdW volume was increased with it multiplied by two. The same point can also be seen from Fig. 8, activity ratios (the ratio of the solvent activity at $2V_{iw}$ to that at V_{iw}) calculated from EFV-1.2 are closer to unity than those from EFV and this proposed method, the latter two models make little difference in terms of the activity ratios. So EFV-1.2 is preferred in terms of the sensitivity to the vdW volume when it is over-estimated. The situation is quite different when V_{iw} was reduced with it divided by two. Predictions from this present method were closer to these experimental data, as indicated in Fig. 9. The activity ratios calculated from EFV-1.2 were further away from unity than those calculated from the other models, as displayed in Fig. 10. So EFV-λ ($\lambda = 0.95$) is preferred and EFV-1.2 is the last choice when the vdW volume is under-estimated.

3.3. Effect of solvent free-volume

The solvent free-volume was changed to study its effects

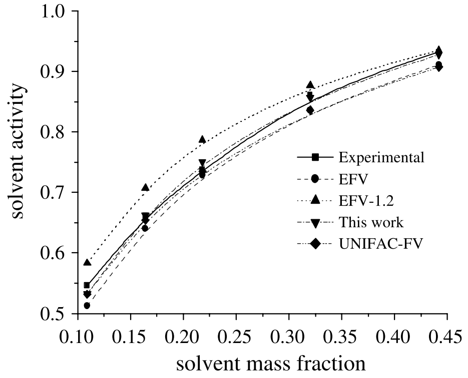

Fig. 6. Experimental and calculated activities of acetone in PVAc (9000) + acetone system at 303.15 K.

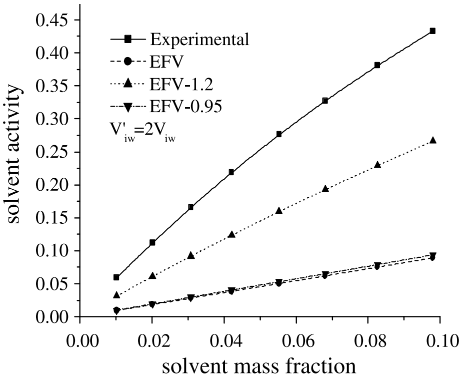

Fig. 7. Effect of increasing vdW volume on calculated activities of hexane in PDMS (26,000)+hexane system at 303 K.

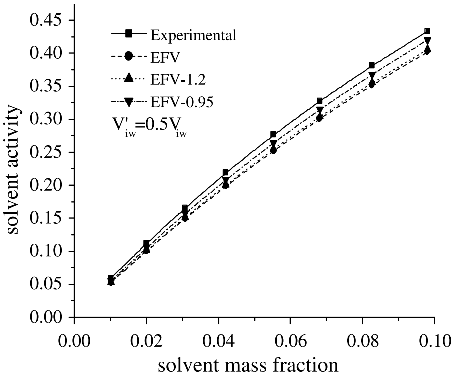

Fig. 9. Effect of decreasing vdW volume on calculated activities of hexane in PDMS (26,000)+hexane system at 303 K.

on the solvent activity estimation. Studying different $V_i - V_{i\mathrm{w}}$ (different solvents in same way) in the same polymers may lead to meaningful conclusions. EFV $-\lambda$ ($\lambda = 0.95$) was employed to evaluate the activities of hexane in PIB (50,000)/hexane system at 298.15 K and in PDMS (26,000) /hexane system at 303 K, respectively. The calculation was performed at different $V_i - V_{i\mathrm{w}}$ of hexane with other physical and structural parameters keeping fixed. It is found from Figs. 11 and 12 that the solvent free-volume has significant influence on the calculation. It is interesting to note that the variation of the solvent activity for different polymers is similar. The value of these activities was increased with the free-volume increasing, and decreased with the decrease in the free-volume. The result can be explained from Eq. (4) in conjunction with Eqs. (2) and (3). Eq. (4) being derivative to $V_i - V_{i\mathrm{w}}$ gives

$$\frac{\partial \varphi_i^{\mathrm{FV}}}{\partial (V_i - V_{i\mathrm{w}})} = \frac{x_i\left[\sum (V_j - V_{j\mathrm{w}}) - x_i(V_i - V_{i\mathrm{w}})\right]}{\left[\sum x_j(V_j - V_{j\mathrm{w}})\right]^2} > 0 \qquad (13)$$

The different curves have similar shape in Fig. 11, while have different shapes in Fig. 12. This may reflect that there are different interactions between different polymers and the same solvent. This further suggests that the solvent mass fraction has different impact on the value of solvent activity for different polymers.

3.4. Analysis of swelling behavior of PVA membranes in water/glycol (EG) mixture using the modified model

In the frame of phase equilibrium the chemical potential of component i in the liquid phase is equal to that in polymeric membranes at sorption–desorption equilibrium and, it can be expressed by

$$\mu_i^{\mathrm{L}} = \mu_i^{\mathrm{M}} \qquad (14)$$

or

$$x_i^{\mathrm{L}}\gamma_i^{\mathrm{L}} = x_i^{\mathrm{M}}\gamma_i^{\mathrm{M}} \qquad (15)$$

where μ_i^{L} and μ_i^{M} are the chemical potential of component i in the liquid mixture and the membrane, respectively; x_i^{L} and x_i^{M} are the mole fraction of component i in the liquid mixture and the membrane, respectively; γ_i^{L} and γ_i^{M} are the activity coefficient of component i in the liquid mixture and the membrane, respectively.

The modified model presented in this paper was applied to the system of H_2O/EG/PVA mixture and then the

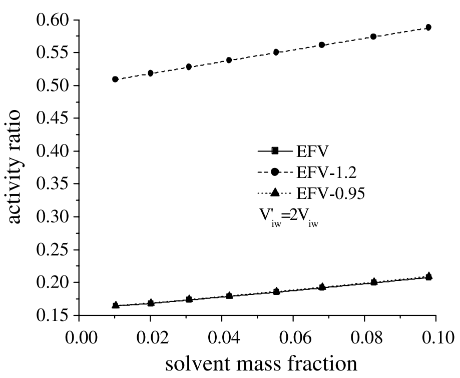

Fig. 8. Ratio of activities of hexane in PDMS (26,000)+hexane system at 303 K when the vdW volume was multiplied by 2.

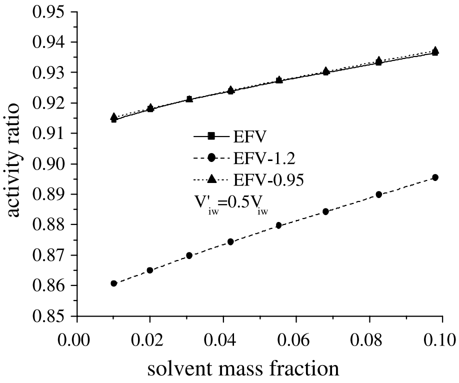

Fig. 10. Ratio of activities of hexane in PDMS (26,000)+hexane system at 303 K when the vdW volume was multiplied by 0.5.

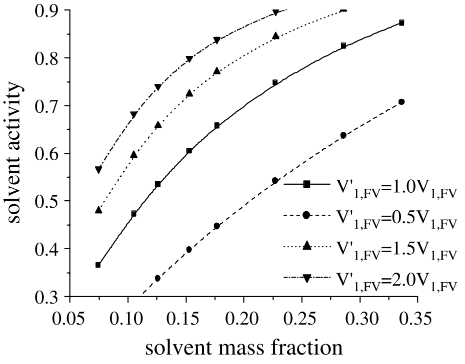

Fig. 11. Effect of solvent free-volume on calculated activities of hexane in PIB (50,000) + hexane system at 298.15 K.

calculations were compared with the experimental data [29]. Molecular volume of water and EG, the binary interaction parameters required for a_i^R calculation were all taken from Ref. [19] except stated otherwise. Molecular volume of PVA was estimated by the Tait equation [27]. The modified UNIQUAC equation was used to estimate the activity of the small molecular solvents of water and EG in the liquid mixture.

The present method was used to calculate the sorption data of H_2O/EG mixture in PVA membrane. Calculated results from the model at temperatures of 333 and 343 K are displayed in Figs. 13 and 14 against the experimental data [29], respectively. The share characters in the two figures are that the calculated results for the amount of adsorption of EG are less than experimental observations; on the contrary, those for water are larger than experimental data. While in generally speaking, this proposed method can reproduce those experimental swelling behavior for PVA membranes in water/EG mixture since the maximum relative absolute deviation for these estimated sorption data from those experimental observations is around 11%.

4. Conclusion

A modified EFV model was presented in this article with the modification to the linear mixed relation for mixed molar volume and the free-volume. Compared with EFV, EFV-1.2 and UNIFAV-FV models, the proposed combined combinatorial and free volume contributions EFV-λ in this work can generally make improved predictions in the solvent activities for most of the polymer solutions considered when the lambda is set to be the value of 0.95 instead of 1.0 which corresponds to the original EFV model, such as PDMS (26,000)/benzene, PIB (50,000)/benzene and PS (15,400)/toluene, as indicated in Table 1. The sensitivity analysis of the prediction in the solvent activity to the van der Waals volume and the free-volume was performed for several different ENTROPIC expressions, respectively. It is proved that EFV-1.2 is preferred when the vdW volume is overestimated; to the contrary, the present method is preferred. In the analysis of swelling behavior for polymeric membrane, the estimations by the modified model can generally represent the sorption behavior of water/EG in the PVA membranes.

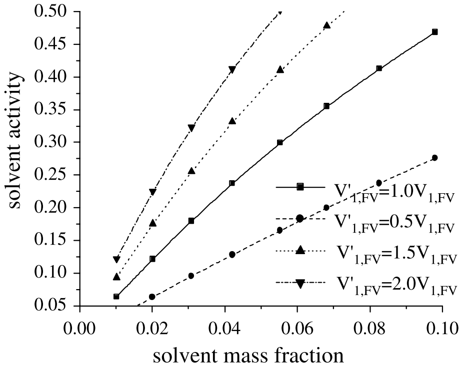

Fig. 12. Effect of solvent free-volume on calculated activities of hexane in PDMS (26,000) + hexane system at 303 K.

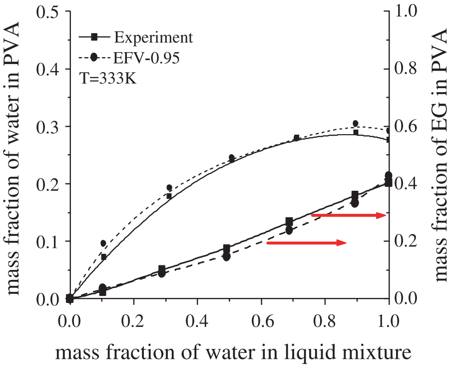

Fig. 13. Experimental and calculated water and EG solubility in PVA membrane at 333 K.

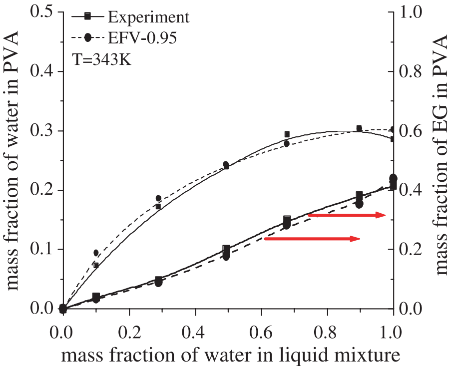

Fig. 14. Experimental and calculated water and EG solubility in PVA membrane at 343 K.

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Appendix A

From the van der Waals partition function, the contribution to molar excess Helmholtz free energy from the combined combinatorial and free volume part can be expressed [Fluid Phase Equilib 1997;127:103–21]

$$\frac{a^E}{RT}=\sum_i x_i\ln\frac{V_i}{V_{\text{mix}}}+\sum_i x_ic_i\ln\left(\frac{V_{fi}V_{\text{mix}}}{V_iV_{f\text{mix}}}\right) \tag{A1}$$

c_i is pure component parameter, Eq. (A1) can be written as follows when c_{mix},V_{mix} and $V_{f\text{mix}}$ and are linear functions of their pure component parameters, respectively

$$\frac{a^E}{RT}=\sum_i x_i\ln\frac{\varphi_i^{\text{vol}}}{x_i}+\sum_i x_ic_i\ln\left(\frac{\varphi_i^{\text{FV}}}{\varphi_i^{\text{vol}}}\right) \tag{A2}$$

At low pressures, we can use the excellent approximation $a^E=g^E$. Finally, using Eq. (A2) the activity coefficient corresponding to the combined combinatorial and free volume contribution can be easily derived through the following general thermodynamic relation

$$\ln\gamma_i=\frac{\partial}{\partial n_i}\left(\frac{ng^E}{RT}\right) \tag{A3}$$

$$\begin{aligned}\ln\gamma_i^{C+\text{FV}}&=\ln\frac{\varphi_i^{\text{vol}}}{x_i}+1-\frac{\varphi_i^{\text{vol}}}{x_i}+c_i\ln\left(\frac{\varphi_i^{\text{FV}}}{\varphi_i^{\text{vol}}}\right)\\&\quad+c_{\text{mix}}\left(\frac{\varphi_i^{\text{vol}}}{x_i}-\frac{\varphi_i^{\text{FV}}}{x_i}\right)\end{aligned} \tag{A4}$$

Eq. (A4) can be further simplified into Eq. (A5) when $c_i=1$

$$\ln\gamma_i^{C+\text{FV}}=\ln\frac{\varphi_i^{\text{FV}}}{x_i}+1-\frac{\varphi_i^{\text{FV}}}{x_i} \tag{A5}$$

V_{mix} and $V_{f\text{mix}}$ are mixed volume and free volume, respectively. One of the key conditions in the derivation of Eq. (A5) is that V_{mix} and $V_{f\text{mix}}$ are linear functions of their pure component parameters, respectively. While there are for most cases actually exist [Chem Eng Sci 1996;51:4923–31]

$$V^E=V_{\text{mix}}-\sum x_iV_i,\quad V_f^E=V_{f\text{mix}}-\sum x_iV_{fi}$$

Since V^E [Polymer 2003;44:3891–900. Thermochim Acta 2003;403:223–9] and V_f^E [Polymer 2005;46:859–68] are not zero for non-ideal solutions, We have modified the linear mixed relation as follows

$$V_{\text{mix}}=\beta\sum x_iV_i,\quad V_{f\text{mix}}=\lambda\sum x_iV_{fi} \tag{A6}$$

where β and λ are supposed to be parameters. Substituting Eq. (A6) into Eq. (A1) gives

$$\begin{aligned}\frac{a^E}{RT}&=\sum_i x_i\ln\frac{V_i}{V_{\text{mix}}}+\sum_i x_ic_i\ln\left(\frac{V_{fi}V_{\text{mix}}}{V_iV_{f\text{mix}}}\right)\\&=\sum_i x_i\ln\frac{V_i}{\beta\sum x_iV_i}\\&\quad+\sum_i x_ic_i\ln\left(\frac{V_{fi}}{V_i}\,\frac{\beta\sum x_iV_i}{\lambda\sum x_iV_{fi}}\right)\\&=\sum_i x_i\ln\frac{\varphi_i^{\text{vol}}}{\beta x_i}+\sum_i x_ic_i\ln\left(\frac{\beta}{\lambda}\,\frac{\varphi_i^{\text{FV}}}{\varphi_i^{\text{vol}}}\right)\end{aligned} \tag{A7}$$

Substituting Eq. (A7) into Eq. (A3) gives

$$\begin{aligned}\ln\gamma_i^{C+\text{FV}}&=\ln\frac{\varphi_i^{\text{vol}}}{\beta x_i}+1-\frac{\varphi_i^{\text{vol}}}{\beta x_i}+c_i\ln\left(\frac{\beta\varphi_i^{\text{FV}}}{\lambda\varphi_i^{\text{vol}}}\right)\\&\quad+c_{\text{mix}}\left(\frac{\varphi_i^{\text{vol}}}{\beta x_i}-\frac{\varphi_i^{\text{FV}}}{\lambda x_i}\right)\\&=\ln\frac{\varphi_i^{\text{vol}}\beta\varphi_i^{\text{FV}}}{\beta x_i\lambda\varphi_i^{\text{vol}}}+1-\frac{\varphi_i^{\text{FV}}}{\lambda x_i}\\&=\ln\frac{\varphi_i^{\text{FV}}}{\lambda x_i}+1-\frac{\varphi_i^{\text{FV}}}{\lambda x_i}\end{aligned} \tag{A8}$$

References

[1] Holten-Andersen J, Rasmussen P, Fredenslund Aa. Phase equilibria of polymer solutions by group contribution. Part 1. Vapor–liquid equilibria. Ind Eng Chem Res 1987;26:1382–90.

[2] Hamedi M, Lu1tzow N, Betz HS, Duda JL, Danner RL. Thermodynamic behavior of ethylene–styrene interpolymers. Ind Eng Chem Res 1999;40:3002–8.

[3] Fredenslund Aa, Jones RL, Prausnitz JM. Group contribution estimation of activity coefficients in nonideal liquid mixtures. AIChE J 1975;21:1086–99.

[4] Vicente MS, Gottifredi JC. Estimation of solvent activities in polymers solutions using a group-contribution method. Sep Purif Technol 2001;22–23:671–9.

[5] Abrams DS, Prausnitz JM. Statistical thermodynamics of liquid mixtures: A new expression for the excess Gibbs energy of partly or completely miscible systems. AIChE J 1975;21:116–27.

[6] Rolemberg MP, Kralhenbulhl MA. Vapor–liquid equilibria of binary and ternary mixtures of benzene, cyclohexane and chlorobenzene at 40.0 and 101.3 kPa. J Chem Eng Data 2001;46:256–60.

[7] Wibawa G, Takishima S, Sato Y, Masuoka H. Revision of UNIFAC group interaction parameters of group contribution models to improve prediction results of vapor–liquid equilibria for solvent–polymer systems. Fluid Phase Equilib 2002;202:367–83.

[8] Pappa GD, Voutsas EC, Tassios DP. Prediction of activity coefficients in polymer and copolymer solutions using simple activity coefficient models. Ind Eng Chem Res 1999;38:4975–84.

[9] Oishi T, Prausnitz JM. Estimation of solvent activities in polymer solutions using a group-contribution method. Ind Eng Chem Process Des Dev 1978;17:333–9.

[10] Kontogeorgis GM, Fredenslund Aa. Simple activity coefficient model for the prediction of solvent activities in polymer solutions. Ind Eng Chem Res 1993;32:362–72.

[11] Bogdanic G, Vidal J. A segmental interaction model for liquid–liquid equilibrium calculations for polymer solutions. Fluid Phase Equilib 2000;173:241–52.

[12] Tritopoulou EA, Pappa GD, Voutsas EC, Economou IG, Tassios DP. Modeling of liquid–liquid phase equilibria in aqueous solutions of poly(ethylene glycol) with a UNIFAC-based model. Ind Eng Chem Res 2003;42:5399–408.

[13] Pappa GD, Voutsas EC, Tassios DP. Liquid–liquid phase equilibrium in polymer–solvent system: correlation and prediction of the polymer molecular weight and the temperature effect. Ind Eng Chem Res 2001; 40:4654–63.

[14] Jonquieres A, Perrin L, Arnold S, Lochon P. Comparison of UNIQUAC with related models for modeling vapor sorption in polar materials. J Membr Sci 1998;150:125–41.

[15] Jonquieres A, Perrin L, Arnold S, Clement R, Lochon P. From binary to ternary systems: General behavior and modeling of membrane sorption in purely organic systems strongly deviating from ideality by UNIQUAC and related models. J Membr Sci 2000;174:255–75.

[16] Elbro HS, Fredenslund Aa, Rasmussen P. A new simple equation for the prediction of solvent activities in polymer solutions. Macromolecules 1990;23:4707–14.

[17] Kouskoumvekaki IA, Michelsen ML, Kontogeorgis GM. An improved entropic expression for polymer solutions. Fluid Phase Equilib 2002;202:325–35.

[18] Sheng YJ, Panagiotopoulos AZ, Tassios DP. Activity coefficients in nearly athermal model polymer/solvent systems. AIChE J 1995;41: 2306–11.

[19] Poling BE, Prausnitz JM, O'Connell JP. The properties of gases and liquids. 5th ed. New York: McGraw-Hill; 2001.

[20] Prausnitz JM. Computer calculations for multicomponent vapor–liquid and liquid–liquid equilibria. Prentice-Hall: Englewood Cliffs, NJ, USA; 1980.

[21] Wen H, Elbro HS, Alessi P. Polymer solution data collection. Part 1. Vapor–liquid equilibrium, DECHEMA chemistry data series, Frankfurt am Main, Germany 1992.

[22] Lu HZ. Handbook of petrochemical basic data. Beijing, China: Chemical Industry Press; 1992.

[23] Tochigi K, Futakuchi H, Kojima K. Prediction of vapor–liquid equilibrium in polymer solutions using a Peng–Robinson group contribution model. Fluid Phase Equilib 1998;152:209–17.

[24] Saure R, Schlunder EU. Sorption isotherms for methanol, benzene and ethanol on poly(vinyl acetate) (PVA). Chem Eng Process 1995;34: 305–16.

[25] Chang BH, Bae YC. Solvent activities of ordinary and associated binary polymer solutions: Group-contribution method. Fluid Phase Equilib 2003;207:247–61.

[26] Romdhane IH, Danner RP. Solvent volatilities from polymer solutions by gas–liquid chromatography. J Chem Eng Data 1991;36(1):15–20.

[27] Rodges PA. Pressure–volume–temperature relationship for polymeric liquid: Review of equations of state and their characteristic parameters for 56 polymers. J Appl Polym Sci 1993;48:1061–80.

[28] Bondi A. Physical properties of molecular crystals, liquids and glasses. New York: Wiley; 1968.

[29] Fengrong C, Hongfang C. Pervaporation separation of ethylene glycol-water mixtures using crosslinked PVA–PES composite membranes. Part II. The swelling equilibrium model of the dense active layer in ethylene glycol/water mixtures. J Membr Sci 1996;118: 169–76.