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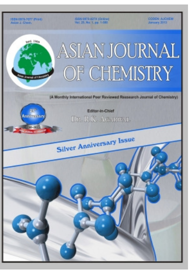

A Modified UNIFAC Model for Polymer Solutions

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For not considering the effect of free volume, the predictive results of the UNIFAC model in polymer solution systems are not acceptable. To improve the predictive accuracy, a free-volume term derived from the van der Waals partition function is added into the UNIFAC model, experimental data of 19 polymer solution systems are used to test the modified model, which is compared with the UNIFAC model, the UNIFAC-FV model and the Entropic-FV-1.2 model, and the results showed that the modified model is mostly better than other models. Furthermore, the model is valid for the whole range of polymer concentration (from dilute solution up to saturation).

Key Words: Polymer solution, van der Waals partition function, UNIFAC model, Entropic-FV-1.2 model.

INTRODUCTION

Vapour-liquid equilibrium (VLE) of polymer solution systems is of fundamental importance to design processes such as the removal of solvent from products in polymer industry[1]. However, as polymer solutions are more complicated than low molecular fluid systems, the experimental data of polymer solution systems are difficult to be obtained. Therefore, fast and reliable predictive methods to design polymeric processes are necessary.

During the last few years, many thermodynamic models have been developed and activity coefficient models[2] have received a great of attention because they need a small number of group parameters. Among them, the UNIQUAC model[3] and the UNIFAC model[4] are the most widely used methods. The former, proposed by Abrams and Prausnitz, is an important local composition model derived by combining the Wilson equation with the Guggenheim's quasichemical approach and its interaction parameters should be calculated by a non-linear regression technique. Based on the UNIQUAC model, the UNIFAC model was first proposed by Fredenslund *et al.*[4] and much more conveniente because of no regression. The two models have been successfully used for low molecular weight molecules, but have some limitations in polymer solutions. This phenomenon mainly stems from the lack of consideration for the free volume, which is important in systems containing molecules with large differences. To achieve satisfactory results, Oishi and Prausnitz modified the UNIQUAC and UNIFAC models by introducing a free volume term based on Flory's equation[5] and the modified models can also give a further improvement in comparison with the original models.

In this work, a new free volume term derived from the generalized van der Waals partition function[6] is added to the UNIFAC model to develop a modified UNIFAC model. To evaluate the model, experimental data of 19 polymer solution systems are used and its predictive results are compared with those from the UNIFAC model, the UNIFAC-FV[7] and the Entropic-FV-1.2 model[8]. To know how to modify the original models efficiently, effects of free volumes and molar volumes of both solvent and polymer on the predictive results are also investigated.

Thermodynamic models

UNIFAC model: The UNIFAC model proposed by Fredenslund *et al.* is based on the assumption that the molecules in a mixture can be divided into functional groups and the behaviour of the mixture depends on the local composition and interaction of these groups. The activity α_i is divided into a combinatorial part α_i^c and a residual part α_i^R

$$\ln\alpha_i = \ln\alpha_i^c + \ln\alpha_i^R \qquad (1)$$

As many group parameters have been calculated and estimated, the UNIFAC model is now widely used for low molecular fluid systems.

UNIFAC-FV model: To improve its predictive accuracy of the UNIFAC model, Oishi and Prausnitz considered the effect of free volume and added a free volume term derived from the Flory equation to the combinatorial and residual terms of the UNIFAC model and obtained the UNIFAC-FV model. The activity α_i can be calculated from the following expression:

$$\ln \alpha_i = \ln \alpha_i^{\ c} + \ln \alpha_i^{\ R} + \ln \alpha_i^{\ FV} \tag{2}$$

The Entropic-FV-1.2 model: The Entropic-FV model[9] proposed by Elbro *et al.* combines the combinatorial and free-volume effects into combinatorial-FV expression compared with the UNIFAC-FV model. To improve the predictive accuracy of the model, Kouskoumvekaki *et al.*[8] proposes the Entropic-FV-1.2 model by optimizing the relationship between hardcore volume and van der Waals volume. The activity of the component i can be expressed as:

$$\ln \alpha_i = \ln \varphi_i^{fv} + 1 - \frac{\varphi_i^{fv}}{\chi_i} + \sum_k \nu_k^1 \left(\ln \Gamma_k - \ln \Gamma_k^1 \right) \tag{3}$$

A modified model based van der Waals partition function: Beret and Prausnitz[10] and later Donohue and Prausnitz[11] developed a semi-theoretical equation of state.

$$Q = \frac{1}{N! \Lambda^{3N}} (V_f)^N \left(\frac{V_f^{c-1}}{V^{c-1}} \right)^N \left(\exp\left(-\frac{E_0}{2KT} \right) \right)^{Nc} f(T)^N \tag{4}$$

From eqn. 4, the following two equations can be obtained:

$$Q^{com} = (V)^N \tag{5}$$

$$Q^{com-FV} = \left(\frac{V_f^c}{V^{c-1}} \right) \tag{6}$$

In our previous work[12], the mixing rules of both volume and free volume are written as:

$$V_{mix} = \mu \sum x_i V_i \qquad V_{fmix} = \lambda \sum x_i V_{fi} \tag{7}$$

Substituting eqn. 7 into eqns. 5 and 6, the following expressions can be deduced:

$$\ln r_i^{comb-FV} = \ln \frac{\phi_i^{FV}}{\lambda x_i} + 1 - \frac{\phi_i^{FV}}{\lambda x_i} \tag{8}$$

$$\ln r_i^{comb} = \ln \frac{\phi_i^{vol}}{\mu x_i} + 1 - \frac{\phi_i^{vol}}{\mu x_i} \tag{9}$$

Subtracting eqn. 9 from eqn. 8, the free volume term of activity coefficient of component i is given:

$$\ln r_i^{FV} = \ln \frac{a\phi_i^{FV}}{b\phi_i^{vol}} + \frac{\phi_i^{vol}}{a x_i} - \frac{\phi_i^{FV}}{b x_i} \tag{10}$$

For calculating conveniently, eqn. 10 is changed into

$$\ln r_i^{FV} = \ln \frac{a\phi_i^{FV}}{b\phi_i^{vol}} + \frac{\phi_i^{vol}}{x_i} - \frac{\phi_i^{FV}}{x_i} \tag{11}$$

μ/λ is set to be β, thus a modified model can be obtained by incorporating eqn. 11 into the UNIFAC model.

$$\ln \alpha_i = \ln \phi_i + \frac{zq_i}{2} \ln \frac{\theta_i}{\phi_i} + l_i - \left(\frac{\phi_i}{x_i} \right) \sum_{j=1}^{n} (x_j l_j) + \sum_k \nu_k^i \left(\ln \Gamma_k - \ln \Gamma_k^i \right)$$
$$+ \ln \frac{\beta \phi_i^{FV}}{\phi_i^{vol}} + \frac{\phi_i^{vol}}{x_i} - \frac{\phi_i^{FV}}{x_i} \tag{12}$$

The modified model consists of three terms: combinational term, residual term and new free-volume term. β is the only variable parameter and can be determined by the regression of experimental data of polymer solution systems. In addition, the model is very simple because that no additional information is needed compared with the classical models such as the UNIFAC-FV.

RESULTS AND DISCUSSION

Determination of β parameter: In this study, a total of 19 experimental data of polymer solution systems was used to determine β parameter. The influence of β value on the average absolute deviations (AAD) between calculated and experimental activity was investigated, and the results are shown in Fig. 1. When the β value is 1, 1.03, 1.05, 1.08, 1.1, the average AAD is 9.15, 8.84, 8.78, 9.15, 9.82 %, respectively. Furthermore, when β value is lower than 1 or higher than 1.1, the error will be much larger. Therefore, the results are the best when the β value in this study is set to be 1.05.

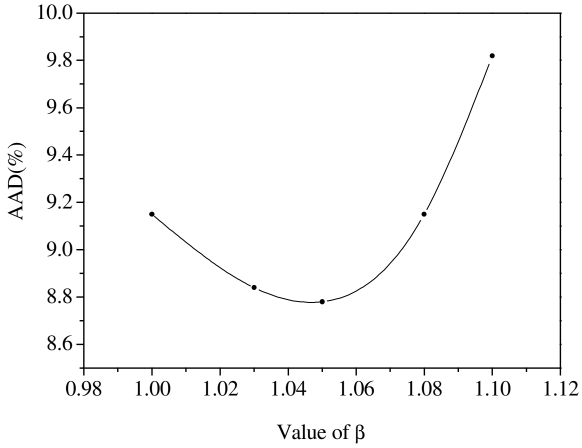

Fig. 1. Value of average absolute deviation under different value of β for 19 different polymer/ solvent systems

Fig. 2 shows the effect of β value on the average absolute deviation between calculated and experimental activity in the following four polymer solution systems: PVAc(170000)/ propanol, PVAc(48000)/ benzene, PDMS(6650)/benzene and PDMS(6650)/hexane. For the first two polymer solution systems, when β value is about 1.05, the average absolute deviation is the smallest. However, for the last two polymer solution systems, the average absolute deviation is not the smallest when β value is about 1.05. Fortunately, for most systems, the average absolute deviation is the smallest when β value is 1.05. Therefore, β value of 1.05 is appropriate and the predictive accuracy is acceptable.

Evaluation of the modified model: The purpose of this section is to present an evaluation of the group contribution model capability for predicting phase equilibria of polymer solutions and 19 polymer solutions are considered. Applications of the UNIFAC-FV model, the Entropic-FV model, the Entropic-FV-1.2 model and the model proposed in this work require accurate knowledge of molar volumes of both solvent and polymer. For the solvents, the molar volume estimation methods are available and acceptable. For the polymers, the experimental densities data for the polymers used in this work

TABLE-1
COMPARISON OF THE PREDICTIVE ACCURACY OF THE MODEL PROPOSED IN THIS WORK, THE ORIGINAL UNIFAC MODEL, THE UNIFAC-FV MODEL AND THE ENTROPIC-FV MODEL

Systems	Temp. (K)	Average absolute deviations (%)[a]				
		UNIFAC	UNIFAC-FV	EFV-1.2	This work	Reference
PDMS(15650)/Benzene	303.15	16.38	13.53	0.50	5.58	13
PDMS(26000)/Benzene	303.15	16.68	13.93	1.06	6.01	13
PDMS(6650)/Benzene	303.15	14.42	12.05	1.94	5.16	13
PDMS(15650)/Hexane	303.00	6.06	1.36	5.38	10.50	13
PDMS(26000)/Hexane	303.00	6.65	0.74	4.85	9.74	13
PDMS(6650)/Hexane	303.15	4.56	2.01	5.03	11.30	13
PEO(5700)/Benzene	343.15	9.60	3.52	12.19	4.73	15
PHP(224100)/Toluene	303.15	16.46	6.76	12.13	6.10	13
PIB(100000)/Cyclohexane	298.15	15.51	3.70	3.10	6.00	13
PIB(50000)/Cyclohexane	298.15	23.94	1.92	3.51	2.92	13
PP(15000)/Methane, tetrachlore	303.15	18.73	10.10	4.84	10.04	13
PVAc(143000)/Benzene	303.15	17.87	9.98	7.15	8.55	13
PVAc(48000)/Benzene	303.15	11.37	3.48	4.05	1.27	13
PVAc(74000)/Benzene	333.15	18.89	5.44	9.03	6.29	5
PVAc(9000)/Acetone	303.15	21.92	1.90	4.54	6.70	15
PVAc(170000)/Propanol	303.15	8.29	13.16	27.65	7.71	16
PVAc(74000)/Methanol	293.15	18.15	13.53	22.65	12.53	5
PVAc(74000)/Methanol	313.15	19.50	26.16	38.27	23.55	5
PVAc(74000)/Methanol	323.15	21.25	25.26	39.69	22.23	5
Average	–	15.06	10.06	8.87	8.78	–

[a] $\%AAD = (1/N)\sum\left(\left|\alpha^{calc.} - \alpha^{exp.}\right| / \alpha^{exp.}\right)\times 100\%$

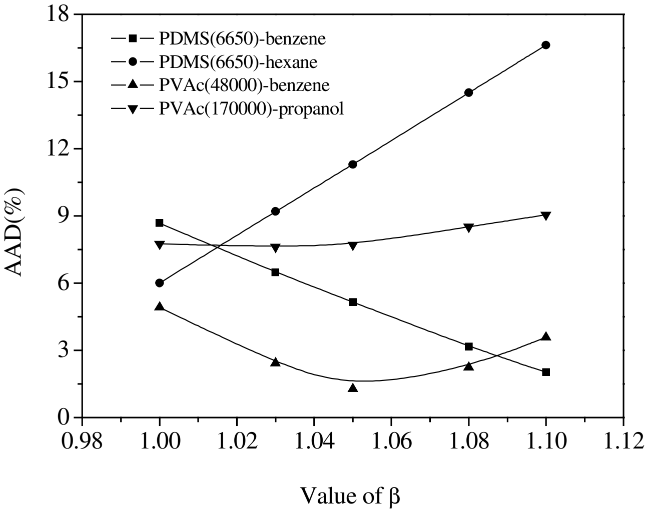

Fig. 2. Absolute average deviation (AAD) *vs.* the value of β

are mostly taken from the DECHEMA Chemistry Data Series[13]. In addition, the applied volume and surface area parameters of polymers and solvents were calculated from the size parameters of the groups involved in the molecules. These size parameters were taken from the UNIFAC Parameter Tables[14].

Table-1 presents the absolute average deviation (AAD) of the correlation of the vapour-liquid equilibrium experimental data of polymer solution systems using the model proposed in this work. The data are compared with the results obtained from the UNFAC model, the UNIFAC-FV and the Entropic-FV-1.2 model. The total average absolute deviation was 8.78 % for the model in this work, 8.87 % for the Entropic-FV-1.2, 10.06 % for the UNIFAC-FV, 15.06 % for the UNIFAC. The results show that the model proposed in this work can accurately correlate the vapour-liquid equilibrium experimental data of polymer solution systems over a wide range of temperature with better accuracy than other models.

Figs. 3-6 compare correlated data with experimental data: PVAc(48000)/benzene, PVAc(170000)/propanol, PVAc(74000)/ methanol and PEO(5700)/benzene. For most systems, the model proposed in this work is of comparable accuracy with the UNIFAC, UNIFAC-FV and Entropic-FV-1.2 models. As shown in Figs. 3 and 4, the model provides fairly good prediction of phase equilibria of polymer solutions. However, for several systems the improvement is not so large. For examples, for PVAc(74000)/methanol and PEO(5700)/benzene, the correction is not available as shown in Figs. 5 and 6. Fortunately, for most systems, the correction is appropriate and the predictive accuracy is acceptable.

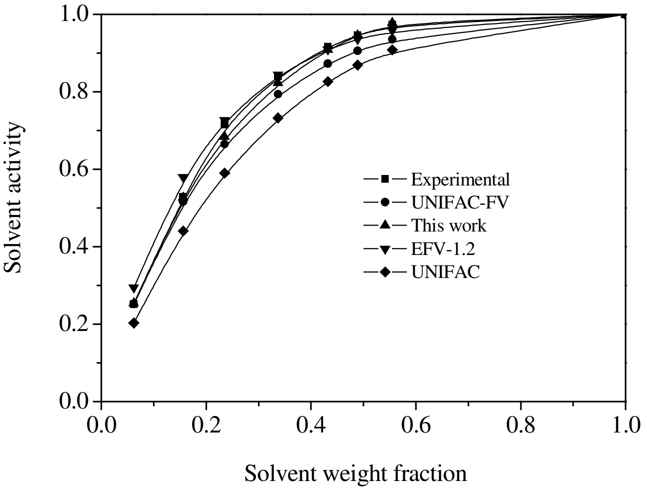

Fig. 3. Experimental and calculated activities of benzene in PVAc(48000)/ benzene at 303.15 K

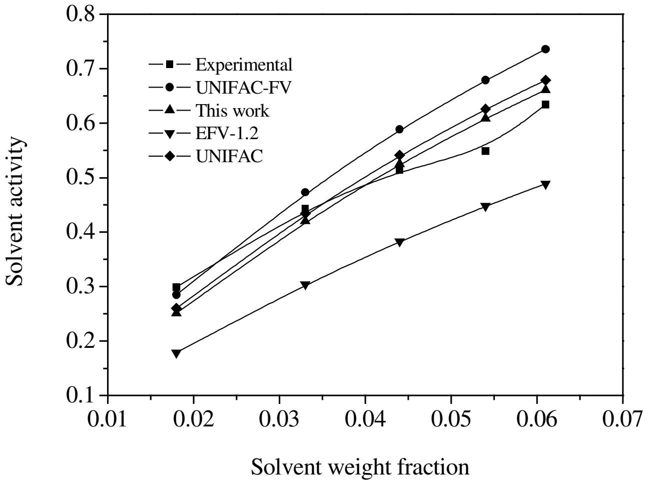

Fig. 4. Experimental and calculated activities of propanol in PVAc(170000) /propanol at 303.15 K

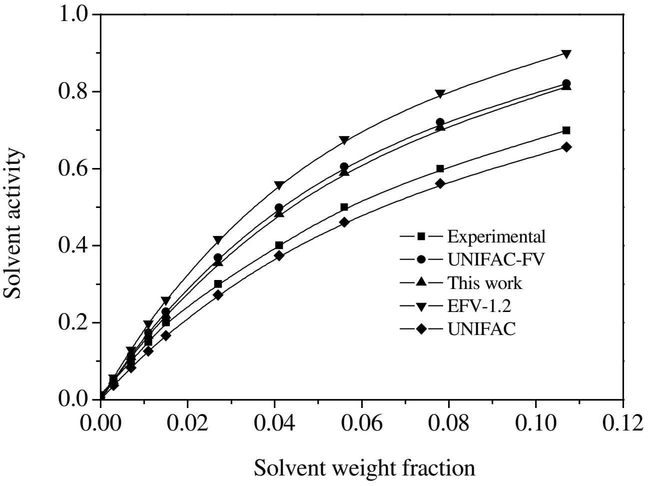

Fig. 5. Experimental and calculated activities of methanol in PVAc(74000)/ methanol at 323.15 K

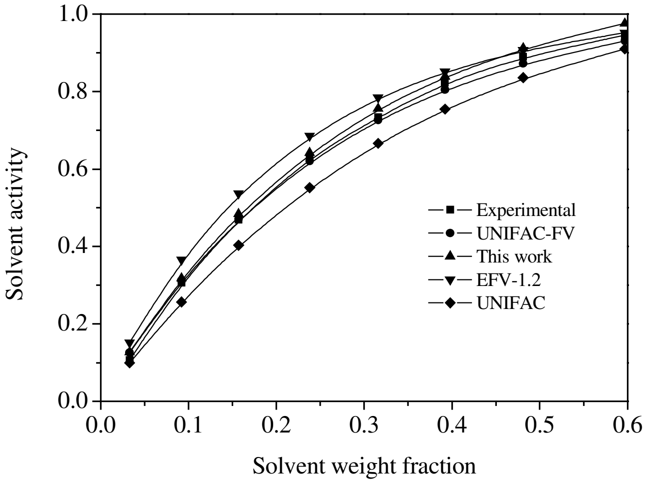

Fig. 6. Experimental and calculated activities of benzene in PEO(5700)/ benzene at 343.15 K

Conclusion

A modified model for prediction of vapour-liquid equilibria in polymer solutions is developed and 19 experimental data of polymer solutions are used to evaluate the model proposed in this study. The results show that the model can accurately correlate experimental data of polymer solution systems over a wide range of concentration and no additional information is required.

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