

行政院國家科學委員會專題研究計畫成果報告

高分子薄膜在酒精/水溶液之膨脹行為

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一、中文摘要

聚(乙烯-乙醇醇), 聚(乙烯-乙醇酯), 和聚胺酯三種疏水性高分子在水和酒精混合溶液中的膨潤行為是本研究的重點。除實驗的觀測外, 根據高分子熱力學 Flory-Huggins 理論所推衍的理論膨潤度也和實驗點做比較和討論, 在 PU 和 EVAc 系統中的理論膨潤度用無修正的 Flory-Huggins 理論即能完整預測出來, 但在 EVAL 的系統中卻需在加入一個三成分作用力參數才能準確預測出。由實驗及模擬結果中發現, 疏水性高分子和水之間的作用會引起水結構的改變而致不同的系統有不同的膨潤趨勢。

關鍵詞：膨潤, 三成分作用力參數, 水結構

Abstract

Swelling behavior of poly(ethylene-co-vinyl alcohol) (EVAL), polyurethane (PU) and poly(ethylene-co-vinyl acetate) (EVAc) in ethanol/water mixtures was investigated. The theoretical swellings derived from Flory-Huggins theory show good agreement with the swelling behavior of PU and EVAc in ethanol/water mixtures. However, the agreement between theoretical and experimental swelling values for EVAL is reasonably established when the Flory-Huggins equation was modified by incorporating a ternary interaction parameter t_7 . It is concluded that the hydrophobic interactions between polymer and water are a major factor to influence the polymer swelling due to changes in the structuring of water around hydrophobic polymers

Keywords: swelling, ternary interaction parameter, water structure

INTRODUCTION

It is the main aim of the present work to perform experimental investigation on the effect of the water/ethanol mixture on the swelling of the polymeric membrane. It is well known that the water molecule is easily incorporated into the hydrophilic polymer membranes due to the strong affinity between the water molecule and the hydrophilic polymers. the swelling behavior of hydrophobic polymer in water/ethanol mixtures is very complex because the liquid molecule in the polymer is far from randomly distributed as a result of the interaction between the liquid molecule and the polymer. Thus, another objective of this paper is to describe and to predict the complex swelling behavior on the basis of a suitable thermodynamic model. Theoretical values of polymer swelling have been derived from Flory-Huggins thermodynamics. The equations derived for the prediction of the theoretical swelling curves are based on the Flory-Huggins theory modified with a ternary interaction parameter, t_7 . We found the Flory-Huggins theory with a zero value of the ternary interaction parameter could correctly predict the swelling behavior of PU and EVAc in water/ethanol mixtures. However, in the water-ethanol-EVAL system, no good agreement was found between the theoretical predictions and experimentally obtained swelling data.

MATERIALS AND METHODS

PU used in this study was synthesized by 4,4-dicyclohexylmethane diisocyanate (H12MDI, Mobay Co.), hydroxyl-terminated polybutadiene (HTPB, ARCO Co.) and 1,2-butanediol (Merck Co.) under the catalysis of dibutylzinc-dilaurat (DBTDL, Merck Co.). EVAL was obtained from Kuraray Co. Ltd., Japan (EP-E105A). EVAc was obtained from E.I. Dupont de Nemours & Co., Wilmington, DE (ELVAX-170).

Dense membranes prepared by solvent evaporation were used for swelling measurement. A piece of a known weight membrane was immersed into a flask containing the water/ethanol mixture of known composition that was present in large excess compared to the amount of membrane. The swelling equilibrium was established until no further weight increase was observed. Results of water/ethanol in the EVAc were taken from reference [1]. The swelling degree has been expressed as a relative weight increase (gm of liquid / gm of dry polymer).

THEORY

The chemical potential, $\Delta \sim_i$ ($\sim_r \sim_i^o$) in the membrane phase and surrounding fluid phase are given:

$$\begin{aligned} \frac{\Delta \sim_1}{RT} = & \ln w_1 + 1 - w_1 - \frac{V_1}{V_2} w_2 - \frac{V_1}{V_3} w_3 + (w_2 t_{12} + w_3 t_{13})(w_2 + w_3) - \frac{V_1}{V_2} w_2 w_3 t_{23} \\ & - h_1 h_2 w_2 \frac{d t_{12}}{d h_2} - w_1 w_2 w_3 \frac{\partial t_{13}}{\partial w_2} - w_1 w_3^2 \frac{\partial t_{13}}{\partial w_2} - w_1 w_3 \frac{\partial t_{13}}{\partial w_3} - \frac{V_1}{V_2} w_2^2 w_3 \frac{\partial t_{23}}{\partial w_2} \\ & - \frac{V_1}{V_2} w_2 w_3^2 \frac{\partial t_{23}}{\partial w_3} - w_1 w_2^2 w_3 \frac{\partial t_T}{\partial w_2} - w_1 w_2 w_3^2 \frac{\partial t_T}{\partial w_3} + t_T w_2 w_3 (1 - 2w_1) \end{aligned} \quad (1)$$

$$\begin{aligned} \frac{\Delta \sim_2}{RT} = & \ln w_2 + 1 - w_2 - \frac{V_2}{V_1} w_1 - \frac{V_2}{V_3} w_3 + \left(\frac{V_2}{V_1} w_1 t_{12} + w_3 t_{23} \right) (w_1 + w_3) - \frac{V_2}{V_1} w_1 w_3 t_{13} \\ & + \frac{V_2}{V_1} h_1 h_2 w_1 \frac{d t_{12}}{d h_2} + \frac{V_2}{V_1} w_1 w_3 (w_1 + w_3) \frac{\partial t_{13}}{\partial w_2} - \frac{V_2}{V_1} w_1 w_3^2 \frac{\partial t_{13}}{\partial w_3} + w_2 w_3 (w_1 + w_3) \frac{\partial t_{23}}{\partial w_2} \\ & - w_2 w_3^2 \frac{\partial t_{23}}{\partial w_3} + \frac{V_2}{V_1} w_1 w_2 w_3 (w_1 + w_3) \frac{\partial t_T}{\partial w_2} - \frac{V_2}{V_1} w_1 w_2 w_3^2 \frac{\partial t_T}{\partial w_3} + \frac{V_2}{V_1} t_T w_1 w_3 (1 - 2w_2) \end{aligned} \quad (2)$$

the chemical potential of each liquid component in these two phases are equal, i.e.,

$$\sim_1^l = \sim_1^m \quad (3)$$

$$\sim_2^l = \sim_2^m \quad (4)$$

where \sim_i^l and \sim_i^m are the chemical potentials of component i in the liquid mixture phase and the membrane phase, respectively. Since volume fractions of all components in the membrane phase (w_i^m) add up to 1, we have:

$$w_1^m + w_2^m + w_3^m = 1 \quad (5)$$

Interaction Parameters. The binary interaction parameters between water and ethanol, t_{12} , at 37°C and 32°C are calculated from the excess Gibbs energy data using the group contribution method of UNIFAC [2]. Assuming that t_{12} has the functional form

suggested by Koningsveld and Kleintjens [3], parameters a , b , and c in Eqn.(8) can be found by least square regression.

$$t_{12} = a - \frac{b}{1 - c w_2} \quad (6)$$

For a ternary system, χ_{12} is assumed to be function only of $w_2 / (w_1 + w_2)$. Thus, t_{12} is obtained by replacing w_2 with $h_2 = w_2 / (w_1 + w_2)$ in eqn. (6).

Binary interaction parameters between pure liquid and polymer, t_{13} and t_{23} , are considered as concentration independent due to low sorption in this study. Thus, t_{13} and t_{23} can be determined using data from equilibrium swelling experiments of the pure components in the corresponding membrane [14]. The following equation is employed:

$$\ln w_i + \left(1 - \frac{1}{x_n} \right) w_3 + t_{i3} w_3^2 = 0 \quad i=1 \text{ or } 2 \quad (7)$$

RESULTS AND DISCUSSION

As shown in Fig. 1, the shape of the swelling curves is quite different for these polymers studied here in water/ethanol mixtures. In case of EVAc, the polymer swelling exhibits positive deviation from ideal, which is above the swelling of either pure constituent. EVAc shows an opposite behavior. On the other hand, in case of PU, the deviation from ideal is not evident.

In order to explain the difference in swelling behavior of hydrophobic polymers in water/ethanol mixtures, the equations derived in the theory section were analyzed under various conditions. The physical constants required in computations are given in Table 1. Nonlinear regression was then used with eqn. (6) to find the parameters a , b , and c , and the results are given in Table 2. Influence of the affinity of water towards the hydrophobic polymer on the polymer swelling is given in Figure 2. Figure 3 shows another case how a theoretical swelling curve may continuously change with t_{13} from 1.5 to 5.0, still keeping t_{23} at a constant but lower value (1.0).

Water molecules experience strong hydrogen bonding that means that water

molecules may penetrate the polymer accompanied by clustered molecules. The extent of clustering will depend on the type of polymer and other penetrant molecules present. In case of EVAc, the water molecules in the solution around EVAc are far from randomly distributed as a result of the hydrophobic interaction between the water molecules and EVAc. Therefore, very limited water sorbed in such a strongly hydrophobic polymer (Figure 1 (c)) is primarily attributed to more structured water clusters surrounding polymer due to the hydrophobic hydration. Further, when ethanol is added to water ethanol molecules like to stay in the solution due to the strong interaction between ethanol and water. Therefore, the restriction of ethanol molecules will decrease the EVAc swelling. The decrease of the EVAc swelling implies that intramolecular hydrophobic interactions of the ethylene groups are increased which in turn may promote further shrink of the EVAc. Hence, the total swelling is always negative from ideal.

The negative deviation from the ideal for the EVAL swelling in water/ethanol mixtures was not observed, even above the swelling of either pure constituent (Figure 1). This behavior could already be expected because of the higher affinity between water and EVAL in comparison with water and PU. Therefore, as the polymer hydrophobicity decreases, ethanol can disturb the structured water cluster to increase the polymer swelling in water/ethanol mixture.

In Figure 4 the experimental swelling values and the theoretical results with different t_T values for the total swelling of water/ethanol mixtures in the EVAL are given. Regardless of the t_T value, all of the calculation results show that the degree of swelling increases to a maximum value and then decreases as the weight fraction of water in the liquid mixture is increased. Then a try-and-error procedure was used to obtain the concentration-dependent t_T , in which experimental data points on the swelling curve were fitted. The best fit is obtained by using $t_T = -1.0 + 0.02w_2 + 1.39w_3$. Figure 5

shows that the computed swelling values match closely the experimental data points over the entire composition range, suggesting that a reliable curve fitting has been obtained. In sum, Although the t_T value is only an estimate, our study indicates that t_T is a concentration-dependent parameter and might even describe the microscopic behavior of water-ethanol-EVAL system to coincide with the experimental data.

REFERENCES

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Table 1. Physical properties of water, ethanol, EVAL, PU and EVAc.

Component	Molecular weight	Density (g/cm ³)
Water	18	1
Ethanol	44	0.78
EVAL	56000	1.14
PU	70000	0.99
EVAc	48100	0.96

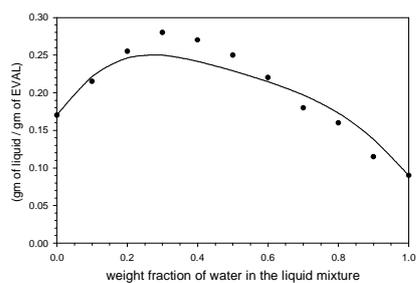
Table 2a. Summary of binary interaction parameters at 37°C.

	χ_{ij}
Water-EVAL	1.784
Water-PU	3.723
Ethanol-EVAL	1.274
Ethanol-PU	1.223
Water-Ethanol	$0.777 + 0.197 / (1.0 - 0.704h_2)$

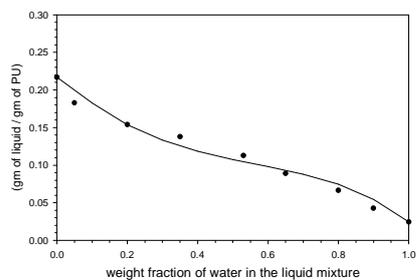
$$h_2 = w_2 / (w_1 + w_2).$$

Table 2b. Summary of binary interaction parameters at 32°C.

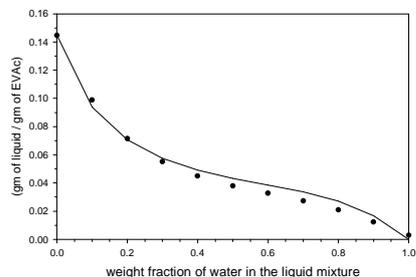
	χ_{ij}
Water-EVAc	4.908
Ethanol-EVAc	1.451
Water-Ethanol	$0.786 + 0.191 / (1.0 - 0.706h_2)$



1 (a)



1 (b)



1 (c)

Fig. 1 Experimental data (●) and theoretical values according to the Flory-Huggins theory with $t_T = 0$ (—) for the total swelling of (a) EVAL, (b) PU and (c) EVAc in water/ethanol mixtures as a function of the weight fraction of water in the liquid

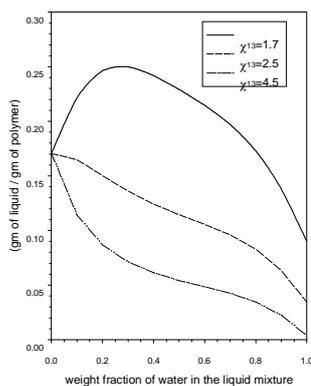
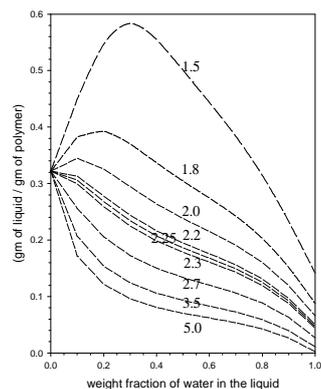


Figure 2. Theoretical swelling curves of hydrophobic polymers in water/ethanol mixtures, where $t_{23} = 1.27$ and $t_{13} = 1.7, 2.5$ and 4.5 , respectively.

Figure 3. Effect of t_{13} on the swelling curves of



hydrophobic polymers in water/ethanol mixtures at $t_{23} = 1.0$. The numbers shown denote the value

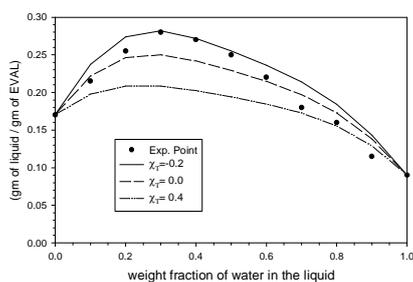


Figure 4. Experimental data (●) and theoretical values with different t_T values for the total swelling of EVAL in water/ethanol mixtures as a function of the weight fraction of water in the liquid.

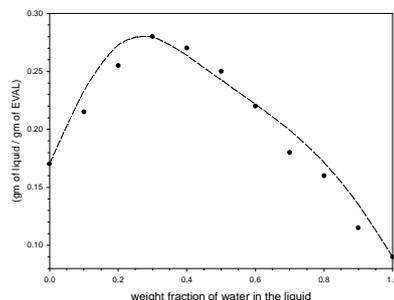


Figure 5. Experimental data (●) and theoretical values using $t_T = -1.0 + 0.02w_2 + 1.39w_3$ (----) for the total swelling of EVAL in water/ethanol mixtures as a function of the weight fraction of water in the liquid.