

Hydrophilic Behavior of HSPAN/PVA Membrane*

JOHN E. TURNER and MITCHEL SHEN, *Department of Chemical Engineering, University of California, Berkeley 94720*, and CHEN-CHONG LIN,** *Department of Chemical Engineering National Taiwan University, Taipei, Taiwan*

Synopsis

The hydrophilic behavior including water absorption, swelling, and dielectric spectrum of pure HSPAN as well as HSPAN/PVA blends are investigated. The HSPAN/PVA membranes still absorb a considerable amount of water. The effect of water upon mechanical properties is also investigated for these membranes. Formalization of membrane enhances mechanical properties and reduces weight losses during swelling with much loss in the water absorption ability of PVA. This kind of blend shows promise as material for hydrophilic membranes.

INTRODUCTION

Starch, being an abundant natural polymer, has been a focus of considerable attention for many years. Graft copolymer of acrylonitrile on starch (SPAN), which can be prepared by the ceric ion initiation method,^{1,2} is one of the most promising materials available on the market. This copolymer is dispersible when hydrolyzed by an aqueous base, whereby the nitrile groups are converted to a mixture of carboxamide and alkali metal carboxylate.^{3,4} This hydrolyzed starch-polyacrylonitrile graft copolymer (HSPAN) prepared from granular starch is not a very good film former but will swell in water with an increase of 30 times in surface area of the samples while retaining its geometric integrity.⁵ On the other hand, poly(vinyl alcohol) (PVA), another hydrophilic polymer, has good film-forming characteristics. In order to strengthen HSPAN, PVA is blended. The resulting film is an interesting composite membrane which showed sufficiently encouraging performance in molecular separation to warrant further investigation. For instance, Lin investigated the use of this blend in reverse osmosis membrane.⁶

EXPERIMENTAL

Sample Preparation

HSPAN. This was obtained by hydrolyzing SPAN with NaOH. Sample S is supplied by General Mills (trade name SGP-502). Sample T was synthesized by grafting polymerization onto granular starch at Taiwan University. The characteristics of these two samples are listed in Table I.

HSPAN Membranes. Pure HSPAN is very difficult to form as film. It is,

* In commemoration of Professor Mitchel Shen, who passed away on August 7, 1979.

** Visiting Professor of the Department of Chemical Engineering, Louisiana State University, 1979/1980.

TABLE I
 Structural Difference Between HSPAN Samples S and T

	Sample S	Sample T
Type of starch	corn	corn
Percent add-on	52	49
\bar{M}_v of side chains	8.0×10^5	1.5×10^5
Grafting frequency	4623 AGU/graft	924 AGU/graft
Conversion of nitrile groups to:		
Acrylamide	50%	25%
Sodium acrylate	50%	75%
Moisture regain at 84.3% RH	80%	36%

therefore, prepared by spin casting it as an aqueous dispersion. A dispersion of 1–3% HSPAN solution is placed in the cup of the spin caster which is lined with a Teflon sheet. After casting, the Teflon liner is easily removed and a film about 0.007 mm thick is peeled away. Dry film is very brittle and difficult to handle. The HSPAN/PVA composite membranes are prepared by casting an aqueous blend of HSPAN and PVA in appropriate ratio on a flat glass plate coated with Mylar. The glass plate is floating on mercury. After drying at room temperature, the films are peeled from the Mylar surface and vacuum dried. Thickness of the dried films is 0.20–0.35 mm. Films containing more than 10% PVA are much stronger than the pure HSPAN films and resist breaking upon handling.

Formalization. Some of the films containing PVA were formalized to form swellable but nonsoluble membranes. The formalization bath consists of 20% H_2SO_4 , 20% Na_2SO_4 , and 7–10% HCHO by weight. The composite membranes were immersed in the bath at room temperature for at least 20 hr before raising the reaction temperature to the desired level.

Properties Measurement

Equilibrium Swelling. Blends are allowed to soak in deionized water for 48 hr. The swollen films are then removed from water, wiped lightly to remove free surface water, and weighed.

Absorption Isotherms. Absorption data are represented as plots of moisture regain MR versus relative humidity p/p^0 . Moisture regain is defined as

$$\frac{\text{sample wet weight} - \text{dry weight}}{\text{dry weight}} \times 100 = MR (\%)$$

Gravimetric analysis is done on a Cahn R. G. Electrobalance.

Dielectric Measurements. Measurements were made on a General Radio 1615A capacitance bridge using a 1310B oscillator, a 1232A amplifier, and a null detector. Samples are conditioned in a known relative humidity environment prior to being placed into the dielectric cell.

Mechanical Testing. Effects of sorbed water upon stress–strain of HSPAN/PVA blends are investigated on an Instron universal testing machine. Because of the hydrophilic nature of these blends the moisture of the surrounding air must be regulated. This is done by placing the sample in a sealed chamber and bubbling N_2 through a saturated salt and into the chamber. All experiments are performed at $24 \pm 1^\circ\text{C}$.

Salt and Water Sorptions of Formalized HSPAN/PVA Composite Membrane. Salt or water sorption is determined by immersing the membranes in a deionized water or a salt solution at 22°C for 48 hr. These testing samples are removed from the solution and immersed, in turn, into deionized water for 1–2 sec to remove adhered salt solution on membrane surface in the case of salt sorption measurements. The membranes are now blotted, weighed, and equilibrated in a known volume of excess deionized water for one day (under magnetic agitation) in order to leach out the salt which is sorbed by the membranes. The concentration of salt in the leached solution is then determined by using a conductimeter.

RESULTS AND DISCUSSION

Equilibrium Swelling and Weight Loss

Water content of swollen blends after direct contact with deionized water is displayed in Figure 1. Several weight fractions of HSPAN (sample S) blended with PVA are studied. Weight loss during swelling in deionized water is also shown in Figure 1. The films have larger weight losses at low HSPAN weight fractions, indicating the dissolution of supporting blend during swelling.

Absorption Isotherms

Sorption isotherms of pure HSPAN and its 90% HSPAN/PVA blend are represented in Figure 2. They are typical of B.E.T. type II⁷ isotherms commonly encountered in hydrophilic polymers.⁸ As expected, the blends display moisture regains intermediate between the two pure components. Samples with higher HSPAN content absorb more water throughout the entire range of vapor activities. For example, at $a = 0.75, 70, 40,$ and 0% HSPAN/PVA blends absorb

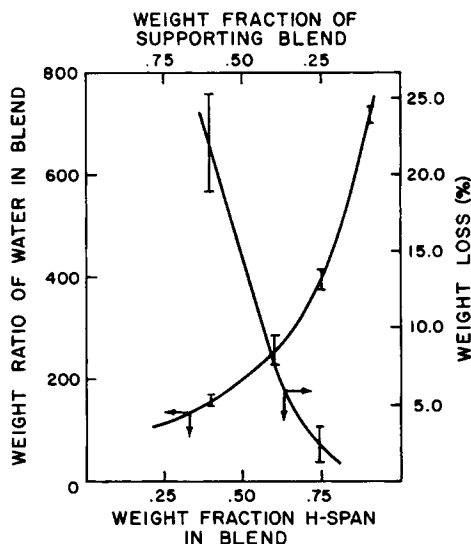


Fig. 1. Equilibrium swelling and weight loss of pure HSPAN and HSPAN/PVA blend in distilled water.

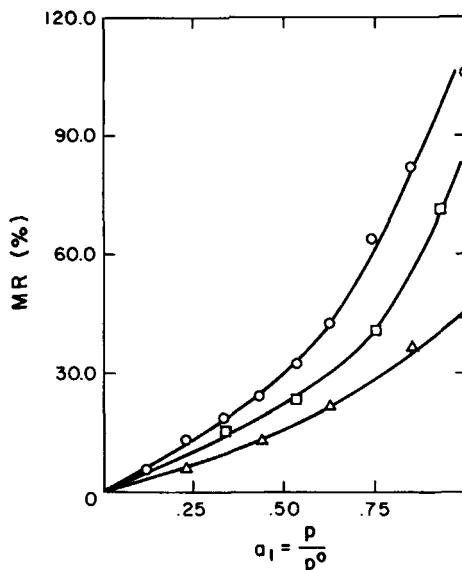


Fig. 2. Absorption isotherms of pure HSPAN and HSPAN/PVA blend: (○) 100% sample S, (■) 90% sample S/PVA, (△) 100% sample T.

72, 29, and 8% water, respectively. The General Mills product samples absorb approximately twice as much as sample T. At vapor activity = 0.843, samples S and T absorb 80 and 36% water, respectively. The reason for the difference in these properties may be a consequence of the differences in sample characteristics between the two graft copolymers presented in Table I.

It is of interest to note that sorption at higher moisture contents proceeds more rapidly, indicating a concentration-dependent diffusion coefficient. An increasing diffusion coefficient with moisture content is observed for many hydrophilic polymers.^{9,10} Similar results are shown for pure sample T in Figure 3 in which diffusion coefficient D is calculated by using Crank's¹¹ equation:

$$D = \frac{0.04919}{t_{1/2}/l^2} \quad (1)$$

where $t_{1/2}$ is half the time for absorption to take place and l is the thickness of the sample. The coefficients are seen to increase exponentially, about three orders of magnitude over the range of water contents. An exponential dependence of diffusion coefficient on water content in PVA is also reported by Spencer and Ibrahim.¹² An empirical relationship between water content and diffusion coefficient is presented:

$$D(c) = D(0) \exp(ac) \quad (2)$$

where $D(c)$ is the diffusion coefficient at concentration C ; $D(0)$ and a are constants; and $D(0) = 2.24 \times 10^{-12}$ cm²/sec at 30°C. The absorption-desorption isotherm for pure HSPAN (sample T) is shown in Figure 4.

The hysteresis loop is characteristic of many natural fibers and proteins.

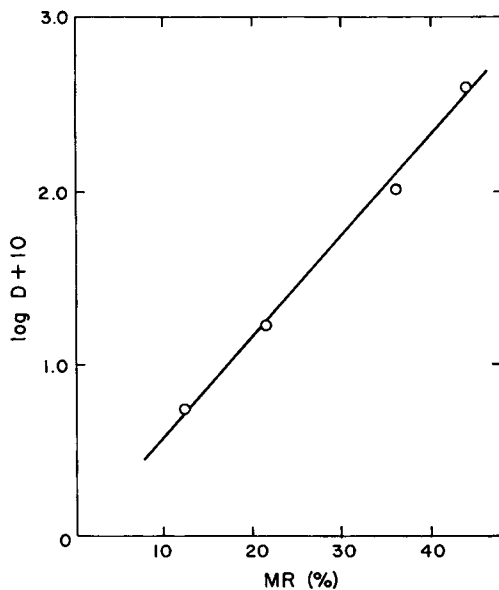


Fig. 3. Effect of water on diffusion coefficients (pure sample T).

Water Clustering

Methods for evaluating molecular interaction of polymer-penetrant systems have been proposed by Zimm¹³ and Zimm and Lundberg.¹⁴ The analysis determines the tendency of like molecules to cluster or segregate from one another. The cluster function G_{11}/\bar{V}_1 is defined as

$$\frac{G_{11}}{\bar{V}_1} = \frac{kTK}{\bar{V}_1} - \phi_2 \left(\frac{\partial(a_1/\phi_1)}{\partial a_1} \right)_{T,P} - 1 \quad (3)$$

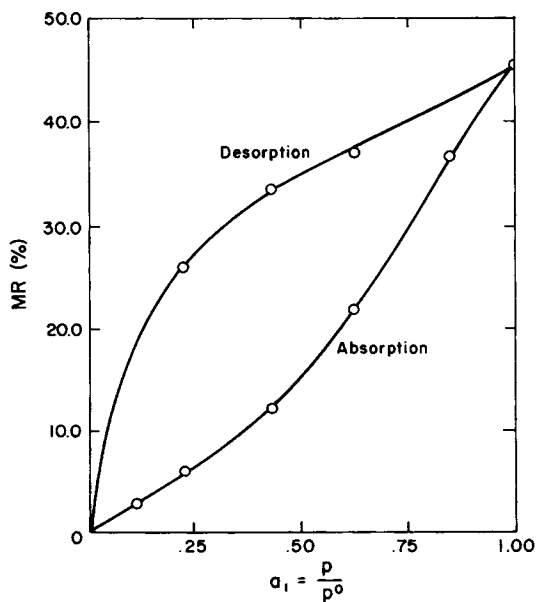


Fig. 4. Absorption-desorption hysteresis of pure sample T.

where G_{11} = cluster integral, \bar{V}_1 = molecular volume of component 1, ϕ_1 = volume fraction of component 1, ϕ_2 = volume fraction of component 2, a_1 = activity of component 1, K = isothermal compressibility of the system, and k = Boltzmann constant. K is negligible for most condensed system so the term kTK/\bar{V}_1 is usually omitted. The cluster function is the probability of finding type 1 molecules close to one another. It is a measure of the tendency for type 1 molecules to segregate or form aggregates. In this discussion, type 1 molecules refer to penetrant or water molecules. The product of the volume fraction of component 1 and its cluster function, $\phi_1 G_{11}/\bar{V}_1$, is a measure of the mean number of penetrant molecules in the neighborhood of a given penetrant in excess of the mean concentration of the same.

A more interesting parameter is the mean cluster size, $1 + \phi_1 G_{11}/\bar{V}_1$. Analysis of water clustering is made for pure HSPAN (both samples S and T), and 90% HSPAN/PVA (Fig. 5). From absorption isotherms of these polymers (Fig. 2) the activity and volume fraction data are obtained. Additivity of volume is assumed in calculating volume fraction of water in polymer from moisture regains and in determining densities of HSPAN blends. This assumption probably leads to some error. However, Starkweather found that correction for change in total volume of mixing for cellulose water systems has negligible effect upon the value of $\phi_1 G_{11}/\bar{V}_1$. Activity of the vapor is assumed to be equal to the relative humidity p/p^0 .

Pure HSPAN sample T has a mean cluster sizes near unity throughout the entire range of vapor activity. This indicates that water molecules are not associating and that water-polymer contacts predominate even at higher water contents. The mean cluster size in the pure HSPAN sample S is also fairly constant, but its value is less than unity. This arises from a negative cluster function G_{11}/\bar{V}_1 . The fact that the cluster function is negative is indicative of specific water-polymer interactions. The affinity for specific sites causes the water molecules to be more isolated from each other than they would be in a random mixture, hence a large negative cluster integral. The 90% HSPAN/PVA

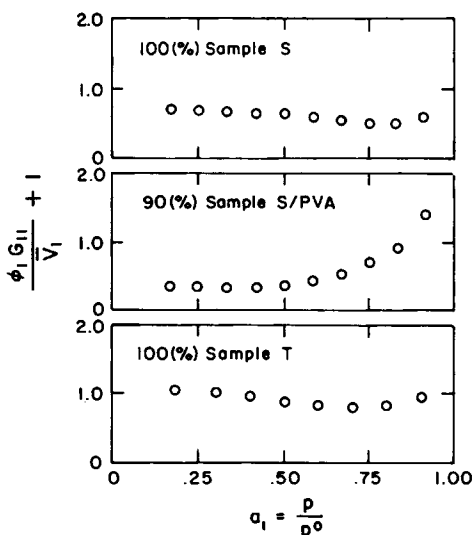


Fig. 5. Water clustering in pure HSPAN and HSPAN/PVA blend.

blend has cluster sizes of less than 1, but steadily increases to slightly more than 1 at higher water contents. The value of the cluster size does not indicate the presence of clustering of water molecules; however, it seems that water-water contacts are beginning to become favorable.

Cluster sizes for the cellulose acetate-water system from Wellons et al.¹⁶ sorption data are determined by the methods outlined above. Little clustering of water molecules is found even at higher moisture contents (maximum cluster size = 1.7 at $a_1 = 0.93$) for cellulose acetate.

Dielectric Investigation

Dielectric spectra of 90% HSPAN/PVA conditioned at 33% relative humidity are shown in Figure 6. The rapid increase in $\tan \delta$ at about 130°C in the blend is believed to be due to a dc conductivity effect.¹⁷ Similar effects have been encountered by Tran¹⁸ for HSPAN samples conditioned at 11 and 33% relative humidity.

Stress-Strain Behavior

Figure 7 shows the effect of relative humidity upon stress-strain behavior of 90% HSPAN/PVA blend. Stress is expressed as expected; absorption of water by this blend increased elongation while decreasing tensile strength. This observation is similar to the plasticizer effect in other polymers. It shows a reduction in stress and increased elongation at 20% moisture regains. Near these moisture contents the blend changes from hard and brittle plastics to soft and weak rubbers. It will be seen that the elongation is 70–160% with 6.1 MPa stress in the case of 52.9% RH conditioning.

Formalization Effect

HSPAN/PVA blend is not practical for a membrane application before it is formalized.

The increase in blending ratio of HSPAN to PVA causes more defects in the membranes and thus decreases the mechanical strength of the membranes. On

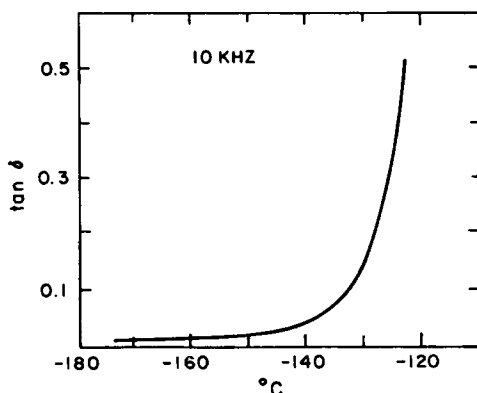


Fig. 6. Loss spectra of 90% HSPAN/PVA conditioned at 35% RH.

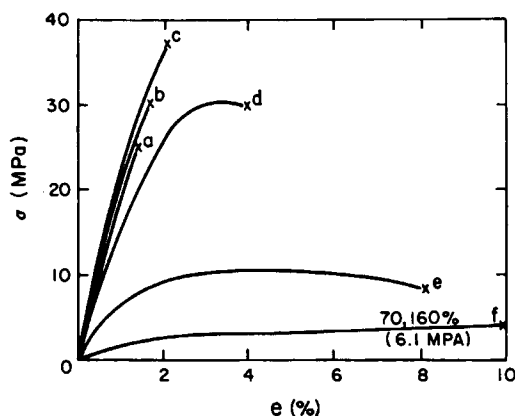


Fig. 7. Effects of relative humidity on stress-strain behavior of 90% HSPAN/PVA blends. $P_a = \text{N/m}^2$; RH conditioning (%): a = 0, b = 11.0, c = 22.5, d = 33.0, e = 42.8, f = 52.9.

the other hand, the increase in the degree of formalization would increase the intermolecular forces and make the membranes stronger and water resistant. The results are listed in Table II. In general, the greater the blending ratio and the smaller the degree of formalization, the weaker the membranes. Water content of 90% HSPAN/PVA composite membranes under the different formalization conditions are shown in Table III. As expected, an increase in the degree of formalization will largely destroy the hydrophilic groups and result in a decrease in water absorption of supporting PVA.

TABLE II
Effect of Blending Ratio and Degree of Formalization on Mechanical Properties

Blending ratio HSPAN/PVA	Formalization condition		Modulus, kg/cm	Yield stress, kg/cm ²	Ultimate strength, kg/cm ²
	$T, ^\circ\text{C}$	t, min			
0/100	50	20	4.59	233.9	308.2
10/90	50	20	1.10	60.6	168.3
20/80	50	20	0.63	41.7	81.6
30/70	50	20	0.58	24.8	56.2
0/100	50	120	7.86	282.5	311.0
10/90	50	120	2.45	164.2	169.9
20/80	50	120	0.89	67.3	93.4
30/70	50	120	0.65	35.2	71.2

TABLE III
Effect of Degree of Formalization on Water Absorption of 90% HSPAN/PVA Membrane

Run no.	Formalization				Water absorption, %
	1st		2nd		
	$T, ^\circ\text{C}$	t, hr	$T, ^\circ\text{C}$	t, hr	
1	20	4	—	—	115
2	20	4	90	2	95
3	20	20	20	1/3	73
4	20	20	50	1/3	49
5	20	20	50	2	32

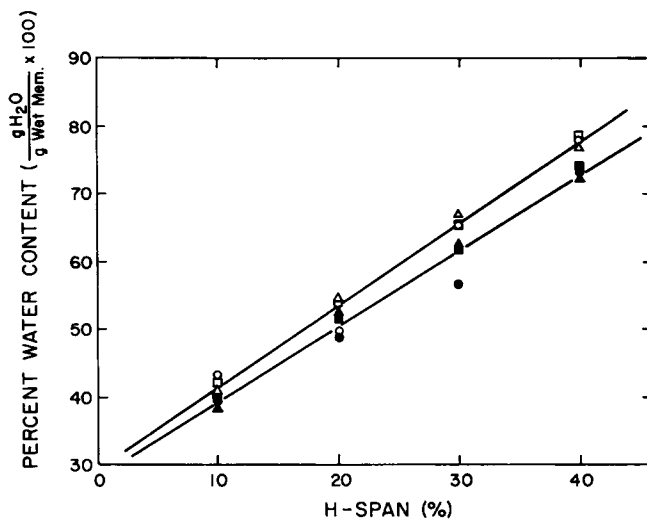


Fig. 8. Water content of HSPAN/PVA composite membranes as a function of HSPAN content in membrane: (○△□) distilled water; (●▲■) 4% NaCl solution.

Salt and Water Sorptions of Formalized HSPAN/PVC Composite Membrane

The water sorption of several formalized HSPAN/PVA composite membranes increases linearly as the weight fraction of HSPAN increases, as shown in Figure 8. The salt sorption shows the same way as water sorption, but the extent is slightly smaller. The difference in extent of sorption between pure water and salt solution is always bigger as the weight fraction is increased. This indicates that the volume of HSPAN will contract in its volume in the salt solution because of the counterion effect. It is well known that water will permeate through the membranes by the two parallel mechanisms, i.e., bulk flow and pure diffusion under high-pressure operation.¹⁹ It was found that the same mechanisms exist in formalized HSPAN/PVA composite membranes in the reverse osmosis test.²⁰

CONCLUSION

In conclusion we can state that HSPAN can be blended with PVA and still retain its ability to absorb a considerable amount of water. Analysis of clustering of sorbed water molecules shows that water-polymer contacts are favored over water-water contacts. However, HSPAN/PVA blends without formalization treatment have large weight losses upon swelling in deionized water, indicating dissolution of the supporting PVA. The weight loss of PVA can be prevented with much loss in water absorption of PVA by increasing the degree of formalization.

References

1. C. E. Brockway, *J. Polym. Sci. Part A*, **2**, 3721 (1964).
2. G. F. Fanta, R. C. Burr, C. R. Russell, and C. E. Rist, *J. Appl. Polym. Sci.*, **10**, 929 (1966).
3. L. A. Gugliemelli, M. O. Weaver, C. R. Russell, and C. E. Rist, *J. Appl. Polym. Sci.*, **13**, 2007 (1969).

4. M. O. Weaver, L. A. Gugliemelli, W. M. Doane, and C. R. Russell, *J. Appl. Polym. Sci.*, **15**, 3015 (1971).
5. M. O. Weaver, E. B. Bagley, G. F. Fanta, and W. M. Doane, *J. Appl. Polym. Sci. Appl. Polym. Symp.* **25**, 25 (1974).
6. C. C. Lin and T. S. Lee, *J. Chinese Inst. Chem. Eng.*, **8**, 149 (1977).
7. S. Brauner, *The Physical Absorption of Gases and Vapors*, Oxford University Press, London, 1945.
8. L. Valentine, *J. Polym. Sci.*, **27**, 313 (1958).
9. I. C. Watt, *J. Appl. Polym. Sci.*, **8**, 1737 (1964).
10. T. Gillespie and B. M. Williams, *J. Polym. Sci. Part A-1*, **4**, 933 (1966).
11. J. Crank and G. S. Park, Eds., *Diffusion in Polymers*, Academic, London, 1968, chap. 1.
12. H. G. Spencer and I. M. Ibrahim, *J. Polym. Sci. Part A-2*, **6**, 2067 (1968).
13. B. H. Zimm, *J. Chem. Phys.*, **21**, 934 (1953).
14. B. H. Zimm and J. L. Lundberg, *J. Phys. Chem.*, **60**, 425 (1956).
15. H. W. Starkweather, *J. Polym. Sci. Polym. Lett. Ed.*, **1**, 133 (1963).
16. J. D. Wellons, J. L. Williams, and V. Stannett, *J. Polym. Sci. Part A-1*, **5**, 1341 (1967).
17. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, New York, 1967, p. 211.
18. H. Tran, M.S. thesis, Department of Chemical Engineering, University of California, Berkeley, 1976.
19. H. Yashuda, C. E. Lamaze, and A. Peterlin, *J. Polym. Sci. Part A-2*, **9**, 1117 (1971).
20. G. J. Tsai, M.S. thesis, Department of Chemical Engineering, National Taiwan University, Taipei, 1979.

Received October 23, 1979

Revised November 30, 1979