The Effect of Phase Separation on the Structure and Permeability of Gelatin–Dextran Films

K. L. PETRAK, *Kodak Ltd., Headstone Drive, Harrow,*
Middlesex HA14TY, United Kingdom

Synopsis

The effect of polymer–polymer phase separation on the transport properties of gelatin–dextran films has been studied. In the gelatin–dextran–water system, the phase separation and gel formation do not occur due to the presence of a nonsolvent, but depend entirely on the temperature and the total polymer concentration. It has been found that the permeability of polymer blend films to aqueous solutes can be varied not only by changing the volume ratio of the phases, but also by varying the size of the individual domains of the two phases in the films. Under the conditions of restricted demixing (e.g., after gel formation), the course of the phase separation process can be changed by varying the length of time allowed for unrestricted separation. The two most important parameters affecting the result are the total polymer concentration in the casting solution, and the temperature regime. An exponential dependence of the permeation coefficient on the volume fraction of the solvent in the film is shown.

INTRODUCTION

Significant progress in membrane separation technology was possible after the development of selective membranes of relatively high flux, such as the porous, asymmetric membranes of Loeb and Sourirajan.[1] Although a number of techniques now exist for the preparation of porous membranes,[2-4] the phase-inversion method[1,5] probably remains the most studied and used approach. The heterogeneity of the film prepared by the phase-inversion process is the consequence of a polymer–liquid phase separation in a solvent–nonsolvent–polymer mixture on the removal of the solvent.

The typical morphological features of porous membranes (skin, sponge structure, cavity formation) as related to the conditions during phase separation have been discussed by Smolders.[6] It is generally believed that, in the solvent–nonsolvent membrane forming systems, the liquid–liquid phase separation is responsible for the formation of the porous sublayer. The skin is formed as a result of increased polymer concentration due to solvent loss.

By analogy, it can be expected that under certain conditions, the phase separation in a polymer–polymer–solvent ternary mixture could lead to the formation of porous films. The control of the scale of phase separation in such systems should then allow us to change the morphology, and thus also the properties, of the resulting membranes.

For this study we selected the gelatin–dextran–water system in which the phase separation and gel formation do not occur due to the presence of a nonsolvent, but depend entirely on the temperature and the total polymer concentration. The effect of polymer–polymer phase separation on the structure and the per-
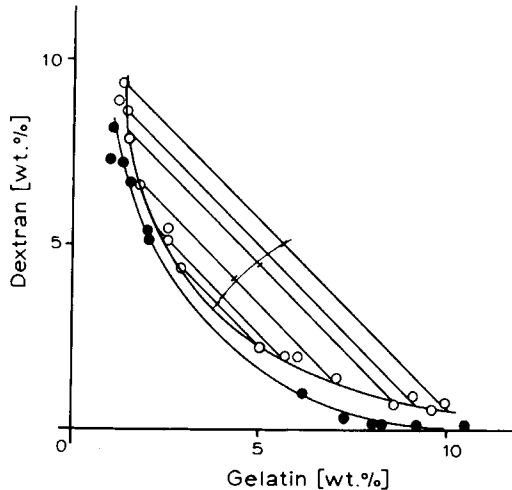
Fig. 1. Phase diagram of the gelatin–dextran–water ternary mixture at 40°C: (O) dextran mol wt 5×10^5; (●) dextran mol wt 2×10^6; gelatin mol wt 2×10^5.

meability of gelatin–dextran membranes has been studied. The results are presented in this paper.

EXPERIMENTAL

Materials Used. A blend of photographic bone gelatin was used. The intrinsic viscosity of the blend was measured in $2M$ aq KCNS at 25°C, and the molecular weight was calculated using the equation of Williams et al.[7] $[\eta] = 2.9 \times 10^{-4} [M_W]^{0.62}$; $M_W = 2.1 \times 10^5$. Dextrans of various average molecular weight were obtained from Sigma Chemical Co. Gelatin was crosslinked with bisepoxy hardener, Araldite DY022 (Ciba Geigy). Methyl Orange (Eastman Kodak Co.) was purified by repeated crystallization from methanol to constant molar absorptivity ($a = 1.9 \times 10^4$ dm^3·mol^{-1}·cm^{-1}).

The phase diagram for the gelatin–dextran–water ternary system was constructed as follows: gelatin–dextran–water mixtures of various composition were allowed to separate into two phases at 40 ± 0.1°C. After 3 days at this temperature, the volumes of the two phases were measured, and each phase was analyzed (a) by thermogravimetry for the total polymer content and (b) by elemental analysis for the relative content of gelatin and dextran. The resulting binary mixture-type phase diagram (% gelatin vs. % dextran) is given in Figure 1.

The membranes were prepared by casting from the corresponding solutions containing gelatin, dextran and hardener in water (cf. Table I). The initial temperature of the solutions was 45°C. The solutions were cast at room temperature onto rigid poly(methyl methacrylate) plates and the gelled wet films were first dried at room temperature for 24 h in a forced air circulation drying cabinet, and then at 45°C for several days. The dry films were cut to give membranes of the size required for the measurements.

The *transport properties* of the membranes were studied using a diffusion cell described schematically in Figure 2. The increase in the optical density with time at $\lambda = 420$ nm in compartment B (volume 25 mL) of the cell was measured

TABLE I
The Composition of the Casting Solutions

Expt no	Gelatin (wt %)[a]	Dextran (wt %)	Dextran (mol wt)	Total polymer concn (wt %)
1A	5.6	5.6	5×10^5	11.2
B	3.85	3.85		7.7
C	2.95	2.95		5.9
D	2.4	2.4		4.8
E	2.0	2.0		4.0
F	1.75	1.75		3.5
2B	3.85	3.85	2×10^6	7.7
C	2.95	2.95		5.9
D	2.4	2.4		4.8
E	2.0	2.0		4.0
3A	5.6	5.6	$>5 \times 10^6$	11.2
B	3.85	3.85		7.7
C	2.95	2.95		5.9
D	2.4	2.4		4.8
E	2.0	2.0		4.0
F	1.7	1.7		3.4
4A	5.6	5.6	1×10^4	11.2
B	3.85	3.85		7.7
C	2.95	2.95		5.9
5A	10.0	—	—	10.0
B	5.6	—		5.6
C	3.8	—		3.8
E	2.4	—		2.4
6A	7.1	3.6	5×10^5	10.7
B	7.9	2.6		10.5
C	8.3	2.1		10.4
7A	7.1	3.6	$>5 \times 10^6$	10.7
B	7.9	2.6		10.5
C	8.3	2.1		10.4
D	8.6	1.7		10.3
E	8.8	1.5		10.3
F	9.0	1.3		10.3
8A	3.85	3.25	5×10^5	7.1
B	5.75	5.75		11.5
C	4.40	4.00		8.4

[a] With 2 wt % hardener; gelatin mol wt 2.1×10^5 (cf. Experimental).

using the Brinkmann Dipping Probe Colorimeter Model PC/600D equipped with a 2-cm stainless steel probe tip. The compartment A was filled with 25 mL of 10^{-3} mol·dm^{-3} aqueous solution of methyl orange dye. The effective nominal area of the membrane was 1 cm^2. The measurements were carried out at room temperature (21 ± 2°C); the rate of stirring was kept constant at approximately 200 rpm.

Before the measurement, the membranes were soaked in deionized water for at least 30 min before being mounted in the diffusion cell. After this time the membranes can be considered fully swollen (cf. swelling measurements below). The dry and wet thicknesses of the membranes were also measured with a micrometer.

The swelling behavior of the membranes was investigated using the swello-
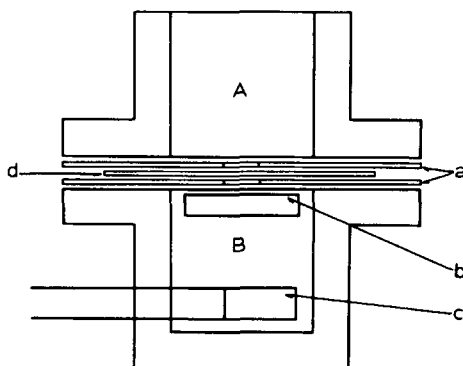
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Fig. 2. Diffusion cell: (a) metal plates; (b) magnetic stirrer; (c) probe tip; (d) membrane.

meter described in Ref. 8.   The data on swelling in deionized water are given in
Table II.
   Microscope Investigation.   The polymer films were stained with a protein
specific acid wool dye (dye concn 2.5×10^{-2} wt % in water) and examined in
transmitted light on Leitz Dialux 20 EB optical microscope at 320X magnification
[cf. Fig. 3(a)–(f)].

RESULTS AND DISCUSSION

   Two high polymers are usually compatible with one another only if their free
energy of interaction is favorable, i.e., negative.   Since the mixing of a pair of
polymers in the great majority of cases is endothermic, *incompatibility of*

TABLE II
The Swelling Behavior of Gelatin–Dextran Films

Expt no	Dry thickness (μm)	Swelling ratio q^a	$t_{50\%}$ (s)
1A	150	1.7	68
B	100	1.9	70
C	50	2.7	22
D	60	3.0	30
E	50	3.8	35
F	40	4.4	35
2B	80	1.9	30
C	35	3.3	18
D	50	4.0	30
E	55	4.2	70
3C	50	4.1	43
D	60	5.0	68
E	40	5.9	52
4A	65	5.1	>100
B	60	5.9	>100
C	55	5.7	>100
5A–E	65	2.7	66

[a] q = wet thickness/dry thickness; $t_{50\%}$ = the time (s) needed for reaching 50% of the maximum
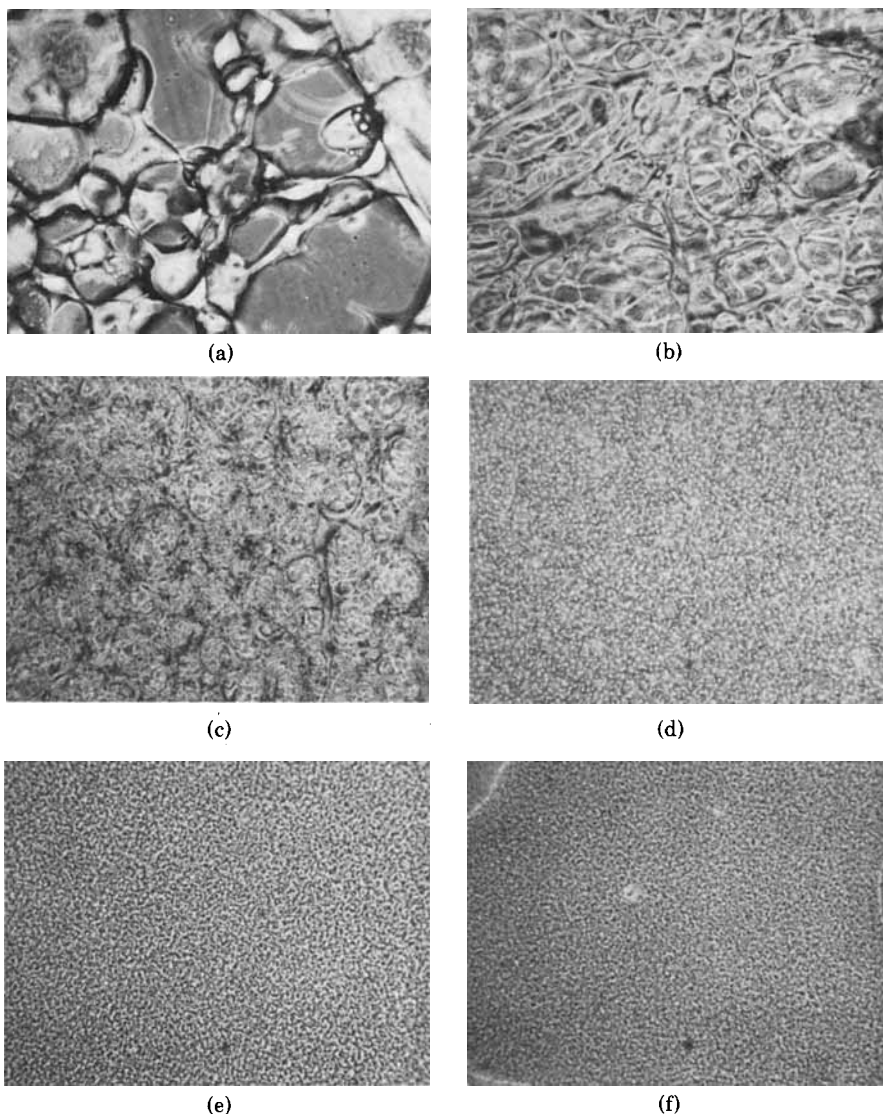swelling.

Fig. 3. The transmitted light microscope pictures of gelatin–dextran films. The gelatin/dextran wt ratio = 1; the total polymer concentration in the casting solution (wt %): (a) 11.2; (b) 7.7; (c) 5.9; (d) 4.8; (e) 4.0; (f) 3.5 (dextran mol wt = 5×10^5, gelatin mol wt = 2.1×10^5).

chemically dissimilar polymers is observed to be the rule and compatibility is the exception (Flory).[9] However, no matter how incompatible two polymers may be, *it is always possible to make a very dilute solution containing both polymers*, as long as a solvent that dissolves both polymers exists (Krause).[10] The conditions of equilibrium between various phases of a system are well illustrated by a phase diagram. Figure 1 shows such a diagram for a system gelatin (abscissa)–dextran (ordinate)–water under isothermal conditions (40°C). Although a number of polymer–polymer–water systems has been described in the literature,[10,11] data on the gelatin–dextran–water system are scanty.[12] It can
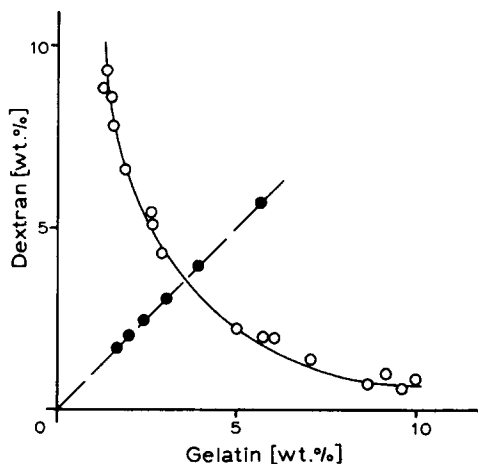
Fig. 4. The position of six gelatin–dextran–water (●) mixtures (cf. Fig. 3) on the corresponding phase diagram.

be seen from Figure 1 that under the experimental conditions used, and, for the polymers of molecular weights used in the experiment, mixtures with the total polymer concentration higher than about 7 wt % become incompatible. It must be pointed out here that the above three-component phase diagram is necessarily a simplification of what is really a multicomponent system due to the polymer polydispersity. It is quite likely that phase separation from a mixture containing a polydisperse polymer leads to fractionation of this polymer.[11]

The thermodynamic criterion of phase separation is that $\partial^2 G/\partial X_i^2 > 0$, where G is the molar free energy of mixing and X_i is the mole fraction of component i.[13] The outcome of the phase separation process depends on the molecular weight of the polymers, the difference in the chemical structure of the polymers, the temperature, etc. The time needed for the phases to separate varies considerably for the different systems and, in addition to being dependent on the above parameters, is also influenced by the difference in density between the two phases and their viscosities. The kinetic aspect of phase separation is significant since different morphologies are believed to form under different conditions.[14,15]

All the above general comments relate to the situation where the *demixing of the two phases is not severely restricted.* Our experiment deals with a special case where the growth and coalescence of droplets is interrupted and the mixture is "frozen" at some stage of the phase separation process. Depending on the overall composition of the mixture and the time allowed for the phase separation to take place, both the volumes of the two phases and the size of the individual domains can be controlled. Consequently, the *morphology* and the properties of the system can be varied.

The condition of restricted demixing can be easily introduced by using a polymer that gels rapidly when the temperature of the mixture is lowered. At this stage we have not attempted to carry out an exact study of the rate processes taking place in such a system. Instead, we examined the effect of phase sepa-
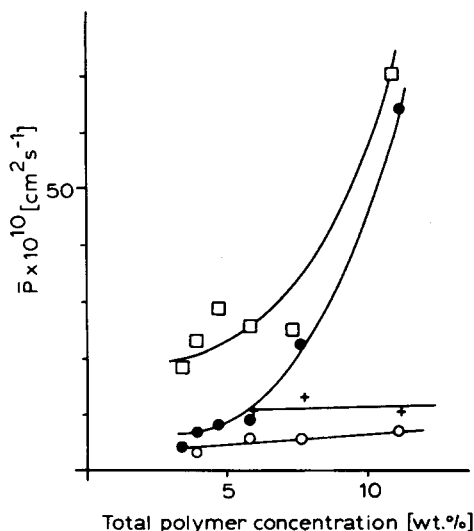
Fig. 5. Permeability of various gelatin–dextran films vs. the total polymer concentration in the casting solutions; (○) gelatin only; (+) gelatin–dextran (mol wt 1×10^4); (●) gelatin–dextran (mol wt $\times 10^5$); (□) gelatin–dextran (mol wt $> 5 \times 10^6$ (cf. Tables I and III); gelatin/dextran weight ratio = 1.

ration under restricted demixing on the transport properties of polymer films.

Figure 4 shows the composition of six gelatin–dextran–water mixtures with respect to the phase diagram. In all cases, the weight ratio of gelatin to dextran is 1. Figures 3(a)–(f) show the transmitted light optical microscope pictures of six films prepared from these mixtures. It can be seen that as the total polymer concentration of the casting solution is increased, the phase separation gives films with "coarser" texture. The difference in the phase separation above and below the critical point composition for this system can clearly be seen [cf. Fig. 3(a)–(c) vs. 3(d)–(f)] (cf. Ref. 16). Phase interconnectivity is evident for polymer films cast from the more conentrated solutions [Fig. 3(a)–(c)]. The obvious difference in morphology of the two sets of films [i.e., 3(a)–(c) and 3(d)–(f)] is a likely consequence of the order in which two events take place: for mixtures 3(a)–(c), the phase separation begins before the gel is formed; for mixtures 3(d)–(f), it is likely that the gel formation precedes phase separation. A quantitative description of these processes will require further experimentation.

We measured the permeability of these six films to methyl orange in water.

Zelman et al.[17,18] concluded that a completely unambiguous characterization of the membrane transport coefficients is impossible. In order to make possible a comparison between the behavior of various polymer films we maintained the solute concentration $\overline{C}_A$, approximately constant during the experiment, with the $\overline{C}_B/\overline{C}_A = 0.016$ at the end of each experiment ($\overline{C}_B$ is the solute concentration in the B compartment of the diffusion cell). The transmembrane hydrostatic pressure was kept constant.

In general, the permeation coefficient P is defined as the flux under unit concentration gradient: $J = P(\Delta C/l)$, where ΔC can be expressed in terms of
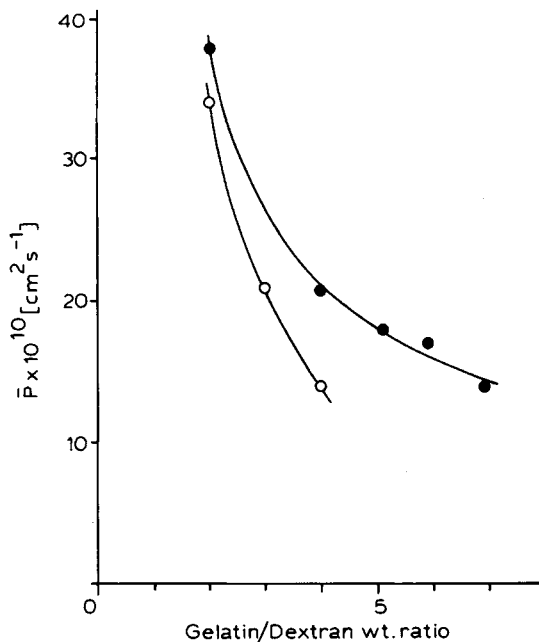
Fig. 6. The effect of the gelatin/dextran wt ratio on the permeability of the films; (O) dextran mol wt 5 × 10^{5}; (●) dextran mol wt > 5 × 10^{6} (cf. Tables I and III, experiments nos. 6 and 7.)

the measurable quantities of our experiment giving the equation

$$P = 2.5 \times 10^{-2} \, \Delta Dl/a \, \Delta Ct \tag{1}$$

where a is the molar absorptivity of the solute, ΔD is the optical density difference, and l is the membrane thickness (cm); taking t (s) as the time needed for 3.95×10^{-7} mol of the solute to permeate through the membrane ($\Delta D = 0.30$), the average permeation coefficient $\overline{P}$ is defined here as

$$\overline{P} = 3.95 \times 10^{-4} \, l/t \tag{2}$$

and is obtained in units of $cm^2 \cdot s^{-1}$.

The permeability of the six polymer films is presented graphically in Figure 5. About a 10-fold difference in the permeation coefficient can be observed on varying the total polymer concentration in the starting casting solution.

The effect of the casting solution concentration on the permeability of films consisting of hardened gelatin only is negligible (cf. Fig. 5). An addition of a low molecular weight dextran to the casting solution increases only slightly the permeability of the resulting polymer film, and the permeability is not affected by the starting concentration of the casting solution (cf. Fig. 5). The observed increase in the permeability of the gelatin–dextran films is thus seen to be a consequence of polymer–polymer phase separation. The trend is further confirmed by the results of experiments with higher molecular weight dextrans (cf. Figs. 5 and 6).

It is a property of phase diagrams such as that in Figure 1 that any total composition represented by points on the same tie line will give phase systems with the same phase compositions, but with different volumes of the two phases.[11]

TABLE III
Permeability of Various Gelatin–Dextran Films

Expt no.	$\bar{P}$ (cm$^2 \cdot$s^{-1}) $\times$ 10^{10}
1A	64
B	22
C	9.4
D	8.3
E	7.0
F	4.8
2B	21
C	11
D	8.3
E	7.7
3A	70
B	23
C	25
D	29
E	23
F	19
4A	11
B	13
C	10
5A	6.7
B	5.3
C	5.4
E	3.7
6A	34
B	21
C	14
7A	38
B	22
C	21
D	18
E	17
F	14
8A	35
B	27
C	21

Table III shows the results for compositions that fall approximately on the same tie line. It can be seen that as the volume of the dextran-rich phase decreases the permeability of the films also decreases.

At the critical point of the phase diagram the compositions and the volumes of the two phases theoretically become equal.[11] Our extrapolated values of the critical point composition for the gelatin–dextran (mol wt 5 $\times$ 10^5) in water are gelatin 3.85 wt. % and dextran 3.25 wt %. When the volumes of the two phases are identical, the maximum degree of phase separation resulting in the maximum permeability of the films can be expected (cf. Table III). Near the critical point composition, however, the control of the phase separation process becomes more difficult.

The above data demonstrate that the transport properties of polymer blend films depend both on their chemical composition and on morphology. On polymer–polymer phase separation, both the total volumes of the two phases
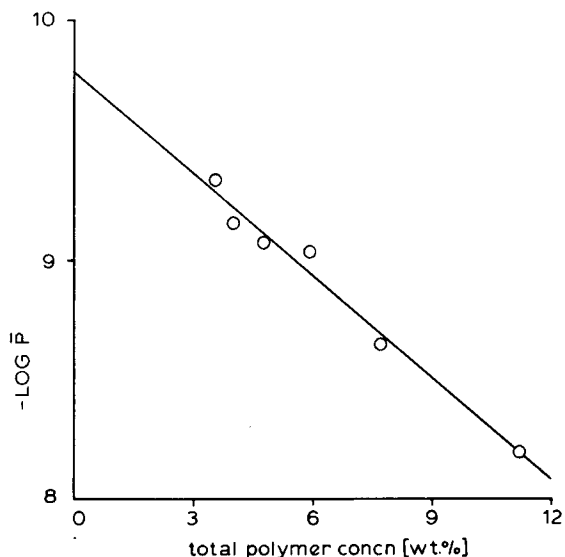
Fig. 7. The plot of $(-\log \overline{P})$ against the total polymer concentration in the casting solution (the best straight line fit by the linear least-squares analysis; the correlation coefficient = -0.992).

and the size of the individual domains of the phases have an effect on the final properties of the films.

Wendt et al.[19,20] and others[21-23] showed that, except for cases of internal concentration polarization or for very unusual pore size distributions, a simple exponential function provides a close approximation to actual solute flux in porous membranes. According to Yasuda et al.,[22] the free volume of a hydrated swollen membrane is given mainly by the volume fraction of the solvent, ϕ, and the diffusion coefficient D of an electrolyte in a membrane is given by the expression $\log D = \log D_w - k\phi^{-1}$, where D_w is the diffusion coefficient of the electrolyte in water and k is a proportionality constant.

The data shown in Figure 5 and Table III clearly indicate an exponential increase in the permeability of phase-separated gelatin–dextran films with increasing total polymer concentration, while the gelatin–dextran weight ratio is maintained constant and equals unity. No such dependence of permeability on the polymer concentration is seen for homogeneous membranes (e.g., gelatin/low molecular weight dextran). The plot of $(-\log P)$ against the total polymer concentration gives a straight line (cf. Fig. 7) (the correlation coefficient = -0.992).

The gelatin–dextran phase separated membranes thus behave as typical porous membranes. Although this is an indirect evidence, we can say tentatively that phase-separated gelatin–dextran membranes are porous, and the porosity increases as the total concentration of the polymers in the casting solution increases (while the weight ratio of the polymers is kept constant).

CONCLUSIONS

The permeability of polymer blend films to aqueous solutes can be varied not only by changing the volume ratio of the phases, but also by varying the size of

the individual domains of the two phases in the films. Under the conditions of restricted demixing (e.g., after gel formation), the progress of the phase separation process can be changed by varying the length of time allowed for unrestricted separation. The two most important parameters affecting the result are the total polymer concentration in the casting solution and the temperature regime.

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