

Moisture permeation through polymer films

SIR,—Based on Fick's law of diffusion and Henry's law, the movement of a gaseous permeant through a film may be expressed as (Kumins, 1965):

$$\frac{W}{A\Delta p} = \frac{P}{t} \quad \dots \quad (1)$$

where W is the weight of permeant passing through the film in g/hr, A is the area of the film in cm², Δp is the pressure gradient across the film in mm Hg, P is the permeability coefficient in g/hr/cm/mm Hg, and t is the film thickness in cm. In a previous paper concerned with the transmission of water vapour through polymer films (Banker, Gore & Swarbrick, 1966), the term $\frac{W}{A\Delta p}$ was referred to as R_{wvt} , the rate of water vapour transmission, with units of g/hr/cm²/mm Hg. Substitution of this term into equation 1 leads to:

$$P = R_{wvt} \cdot t \quad \dots \quad (2)$$

According to equation 2, the product of R_{wvt} and t will be constant if the film system is behaving in accordance with Fick's and Henry's laws. Graphically, a plot of R_{wvt} vs t will result in a hyperbola; when plotted on a log-log basis, a straight line with a slope of -1 will result. This ideal system is shown in Fig. 1A, 1B, line II. Moisture permeation data giving plots of $\log R_{wvt}$ vs $\log t$ with a slope of less than -1 (line I, Fig. 1A, 1B) indicates that the effect of increasing film thickness is not as predicted by Fick's and Henry's laws. In this case, moisture is permeating the film at a rate faster than would be expected. Conversely, data resulting in log-log slopes of greater than -1 (line III, Fig. 1A, 1B) are indicative of systems transmitting moisture at a rate below that predicted by equation 2 as the film thickness is increased.

If permeation is proceeding in accordance with equation 2, then P will be independent of t . Figure 1C shows the relation obtained when the data used in Fig. 1A and 1B is plotted in this manner. With the accelerated transmission of system I, P exhibits a positive deviation with increasing thickness. A negative deviation is shown by system III. Only in the case of system II, which is ideal, is P truly independent of t .

It is reasonable to suppose that, in these theoretical examples, the polymer films exemplified by system I have an affinity for moisture which is not taken account of by Fick's or Henry's laws. Likewise system III, where the data imply an active repulsion between water molecules and the film. In both cases, the closer the log-log slopes are to -1 , the more ideal is the film.

In a previous investigation on the water vapour transmission properties of three polymer film systems (Banker & others, 1966), linear log-log relations typical of system I were observed. With hydroxypropyl cellulose films and mixed Methocel:Ethocel films, both relatively hydrophilic systems, the slopes ranged from -0.389 to -0.468 . With the more lipophilic butyl methacrylate films the slopes ranged from -0.672 to -0.701 . The present authors have found a similar log-log relation with cast films of cellulose acetate hydrogen phthalate (CAP, Eastman Organic Chemicals, No. 4642) plasticized with diethyl phthalate. The results are presented in Table 1. In all cases the slope values are less than -1 and are of the same magnitude as the other cellulosic films studied previously.

Taken as a whole, these results indicate that the greater the affinity of moisture for the polymer film system, the greater will the water transmission data deviate

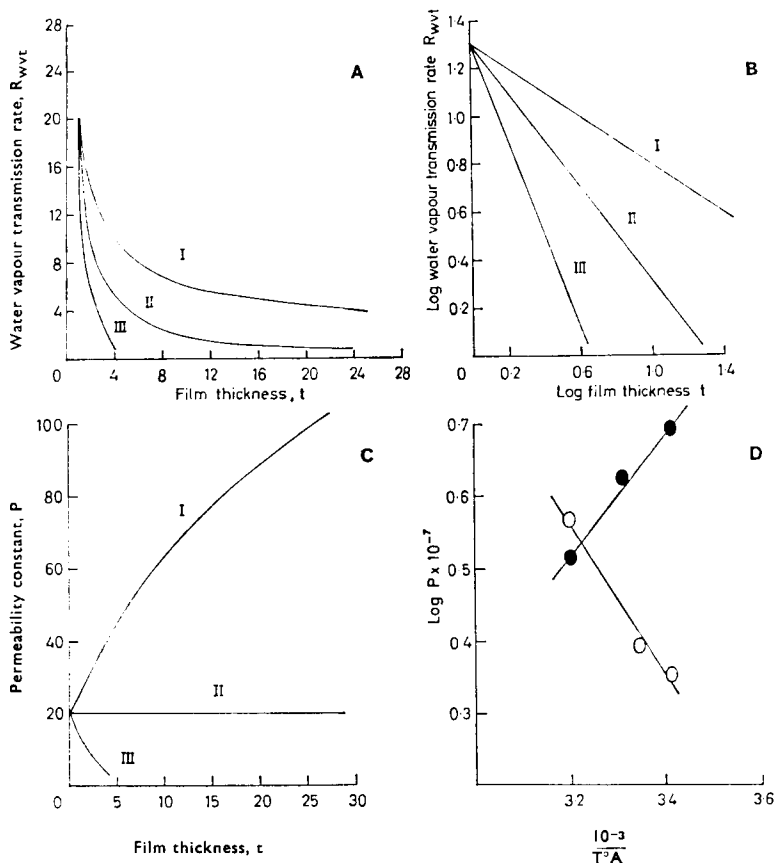


FIG. 1. Water vapour transmission through ideal and nonideal polymer films.

A. Effect of film thickness on rate of water vapour transmission. System I shows positive deviation (accelerated permeation) from equation 1; system II is ideal, conforming to equation 1; system III shows negative deviation (retarded permeation) from equation 1.

B. Data in A plotted on log-log basis. Slopes are -0.5 , -1.0 , and -2.0 for systems I, II, and III, respectively.

C. Effect of film thickness on permeability coefficient. Based on data used in A.

D. Variation of log permeability coefficient with temperature at a film thickness of 0.0064 cm and a vapour pressure difference of 17.5 mm Hg. Key: *n*-butyl methacrylate, ○; cellulose acetate hydrogen phthalate, ●. Film casting solution: *n*-butyl methacrylate 100.0 g; diethyl phthalate 2.5 g; methylene chloride and acetone equal parts to 1000 ml.

from ideality. This affinity of permeant for film will be a function of the hydrophilic nature of the film system, in particular the availability for hydrogen bonding. To test this latter hypothesis, we have also studied the effect of temperature on the permeability properties of CAP and *n*-butyl methacrylate [BMA, DuPont Elvacite (formerly Lucite) 2044] polymer films plasticized with diethyl phthalate. Typical results are shown in Fig. 1D. In the more ideal BMA films the permeability coefficient, increases with temperature in the expected normal manner. The slope of $\log P$ vs $1/T$ has a value of -1.08×10^3 . In direct contrast, the permeability coefficient for CAP decreases

TABLE 1. STATISTICAL CONSTANTS FOR RELATION BETWEEN LOG WATER VAPOUR TRANSMISSION RATES AND LOG FILM THICKNESS OF CELLULOSE ACETATE HYDROGEN PHTHALATE FILMS*

Temperature °C	Vapour pressure mm Hg	Correlation coefficient	Slope of line	Ordinate intercept log
20	17.5	0.96	-0.388	-3.779
20	13.2	0.94	-0.396	-3.788
25	23.6	0.99	-0.430	-3.698
30	31.8	0.97	-0.479	-3.645
30	23.9	0.98	-0.466	-3.732
30	10.3	0.96	-0.505	-3.466
40	55.3	0.99	-0.361	-3.925
40	41.6	0.97	-0.315	-4.044
40	17.4	0.98	-0.399	-3.902

* Film casting solution: Cellulose acetate hydrogen phthalate .. 50.0 g
 Acetone, to 400.0 ml
 Diethyl phthalate 12.5 g
 Methylene chloride, to 1000.0 ml

as the temperature is raised, the slope in Fig. 1D having a value of $+0.75 \times 10^3$. This anomalous behaviour, also observed with other cellulosic films (Patel, Patel & Lemberger, 1964), would seem to be related to a breaking of hydrogen bonds between permeant and film, causing in effect dehydration of the film and a reduction in permeation. This view is supported by the effect of temperature on dehydration of ether linkages in nonionic surfactants (Greenwald & Brown, 1954; Schick, 1962) resulting in a cloud point, the anomalous aqueous solubility of methylcellulose, and the dehydration of starch (Knyaginichev, Chernyak & Lyapunova, 1966). With BMA films there is little opportunity for hydrogen bond formation, the log R_{wvt} vs log t slope is closer to -1 and hence the normal temperature effect on permeation is observed.

Division of Pharmaceutics,
 School of Pharmacy,
 University of Connecticut,
 Storrs, Connecticut 06268, U.S.A.

JAMES SWARBRICK
 ANTON H. AMANN

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Determination of methylimidazoleacetic acids in human urine by gas chromatography (Correction)

SIR,—In the addendum to a Letter to the Editor (*J. Pharm. Pharmac.*, 1968, **20**, 659-661) a typographical error has arisen which affects the gas chromatogram. Line 3 of the addendum should begin "0.05M acetate buffer, . . ." and not "0.5M acetate buffer, . . .".

Department of Pharmacology,
 University of Dundee, Dundee, Scotland.

A. S. KELVIN

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