

# A Model Study for Release of Plasticizers from Polymer Films Through Vapor Phase

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## Synopsis

A model has been applied to release of plasticizers from polymer films through vapor phase, for which the overall rate of release may be generally determined by evaporation of the plasticizer from the surface of the film, and/or by migration to the surface at below saturation in the polymer. The experimental system employed made use of *n*-butyl formate, diethylphthalate, di-*n*-butylphthalate, and *N,n*-butylbenzenesulfonamide as model molecules in polycaprolactam films, both with the aims of studying undesirable loss of plasticizers, and of simulating a model able to envisage releasing, at a constant rate, of any desired additive, with relatively high solubility and vapor pressure, to the content of packaging films. Experimental measurements were made (at 298–333 K) by investigating in a suitable cell the permeation of plasticizers both at concentrations below and above the saturation limit. Rate of evaporation of plasticizers from the membrane surface above the saturation limit, measured in this cell, were found to coincide satisfactorily with those calculated by application of the mass transfer theory to evaporation from a stationary liquid into a stirred gas, at a known velocity of gas flowing past the surface. From these latter rates and solubilities, the mass transfer coefficients *H* for evaporation could be obtained, as well as from experimental time lags the diffusivities *D<sub>p</sub>* through the polymer membrane. In the light of the theoretical model a correlation was found between activation energies of *H* and evaporation enthalpies of the model molecules.

## INTRODUCTION

Release of any additive from polymer films through vapor phase is a process, which implies conspicuous importance—on the one hand, when additives and plasticizers must be retained in the polymer long enough to maintain their function, and generally when their loss is undesirable (e.g., if packaging films may seriously deteriorate organoleptic properties of foods); on the other hand, when, on the contrary, their release rate may be envisaged as a means of keeping for a certain time a determinate and constant concentration in the gas phase. A comprehensive review, which covers available data on loss of polymer additives, through vapor phase particularly, has been recently published<sup>1</sup> and a general model has been developed, to rationalize the factors which control loss as well as to predict loss times, from the physicochemical properties of the additive and of the polymer.<sup>2-4</sup> The more general attention, however, has been devoted to the problem of additives with very low vapor pressures and solubilities in the polymer. The interest towards the release of plasticizers, or more generally towards additives with relatively high vapor pressures and solubilities, with the particular aims cited above, may be equally recognized. In the present

study, the model recently developed by Billingham and Calvert<sup>2-4</sup> has been applied to release of plasticizers from polymer films through vapor phase, for which the overall rate of release may be generally determined by removing the plasticizers from the surface of the film and/or by migration to the surface at below saturation in the polymer. Measurements were made in polycaprolactam films, by studying in a suitable cell, at various temperatures, the permeation of some model molecules, deposited as liquids on one face of the film, through films initially free from the permeant molecules. The rate of evaporation of pure plasticizers were equally measured in this cell, and compared with those calculated by application of the mass transfer theory to evaporation from a stationary liquid into a stirred gas, at a known velocity of gas flowing past the surface.

## EXPERIMENTAL

### Materials

Polycaprolactam bioriented commercial films  $0.060 \pm 0.004$  mm thick (BX, Snia Viscosa) were first purified through a mild cleaning treatment with sulphonated lauryl alcohol (5 g/L) for 30 min at 60°C, thoroughly rinsed with water, dried in a desiccator under vacuum at room temperature, and finally Soxhlet-extracted with 50% v/v cyclohexane-ethanol to remove completely any plasticizer or additive initially present in the commercial film. Diethylphthalate and di-*n*-butylphthalate were 99% pure products (Janssen Chimica); *n*-butyl formate was a 99.5% pure product (Eastman Kodak). They were used as received, without further purification. *N*, *n*-butylbenzenesulfonamide was prepared from benzenesulfonylchloride and *n*-butylamine, in the presence of aqueous sodium hydroxide, by the method described in the literature.<sup>5</sup> The product was separated from some unreacted *n*-butylamine by fractional distillation under vacuum, and further rectified under high vacuum (bp 184–184.5°C at 0.750 torr). Purity (at least 99.9%) was checked by elemental analysis as well as by gas chromatography. Infrared spectra coincided with those reported.<sup>6</sup>

### Apparatus and Measurements

Two stainless-steel cells, of the same type and size as that previously described<sup>7</sup> were employed parallelly. Constant temperature experimental conditions ( $\pm 0.3$  K) were set up by introducing the whole apparatus in a thermostatted chamber with forced air circulation. On the upper face of the film, the liquid plasticizer ( $50 \mu\text{L}/\text{cm}^2$ ) was uniformly deposited by a standard procedure making use of a microsyringe dispenser. The film was clamped between two suitable elements of the cell (*E* and *C* of Ref. 7, Fig. 1); the lower plate *E* supported the specimen and operated as a collecting chamber of the permeated vapor. A carrier gas (ultrapure helium) flowed past the lower face of the loaded film at a constant velocity of  $0.78 \pm 0.01 \text{ cm} \cdot \text{s}^{-1}$ . Three symmetrical holes in the lower plate *E* let the carrier gas in, and a central hole let it out to the gas chromatographic analysis. The threaded cover was screwed on top of the upper element *C* of the cell. The

part of the cell above the film was simply flushed with helium. Six symmetrical holes were drilled in *C*, with inlet and outlet holes disposed in an alternate position to ensure rapid mixing and let helium from the upper part of the cell flow to the external environment.

A Sigma 10 chromatography data station linked with a Sigma 1 gas chromatograph analyzer (Perkin-Elmer) was employed to collect and elaborate experimental data.

The rate of permeation  $v$  ( $\text{g} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ ) through the vapor phase showed typical trends such as those illustrated in Figures 1–4. As two parallel measurements were carried out at the same time, some additional informations could be obtained by interrupting one of the two series of measurements at a certain stage, while the other was progressing to the end. When this was done at times corresponding to the linearity of  $v$  vs. time in the graphs of Figures 1–4, the recovered membrane was liberated from the liquid and unabsorbed plasticizer, by rapid immersion and washing in cold ( $-20^\circ\text{C}$ ) 50% v/v cyclohexane–ethanol. After removal of the adhering solvent under vacuum in the cold, the film was clamped again in the cell and the rate of evaporation at that time was measured in order to obtain instantaneous values of  $v$  corresponding to films containing incorporated plasticizers at a concentration below the saturation limit in the polymer. This same technique was employed to obtain experimentally the values ( $S_p$ ) of concentration of plasticizer in the polymer corresponding to "saturation," at times corresponding to the constant rates of evaporation ( $v_0$ ) shown by the plateaus in Figures 1–4. In this latter case, after the cold washing, the

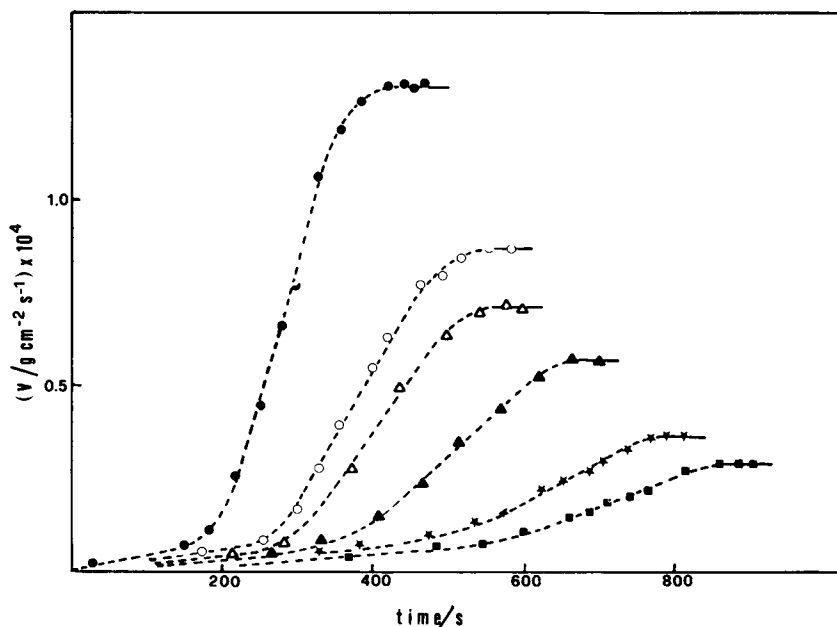


Fig. 1. Rates of evaporation  $v$  ( $\text{g} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ ) of *n*-butyl formate from the surface of bi-oriented polycaprolactam films 0.060 mm thick, measured as a function of time during the process of permeation from the liquid reservoir on the opposite face of the membrane, at various temperatures (K): (●) 333.2; (○) 323.2; (△) 318.2; (▲) 313.2; (★) 303.2; (■) 298.2.

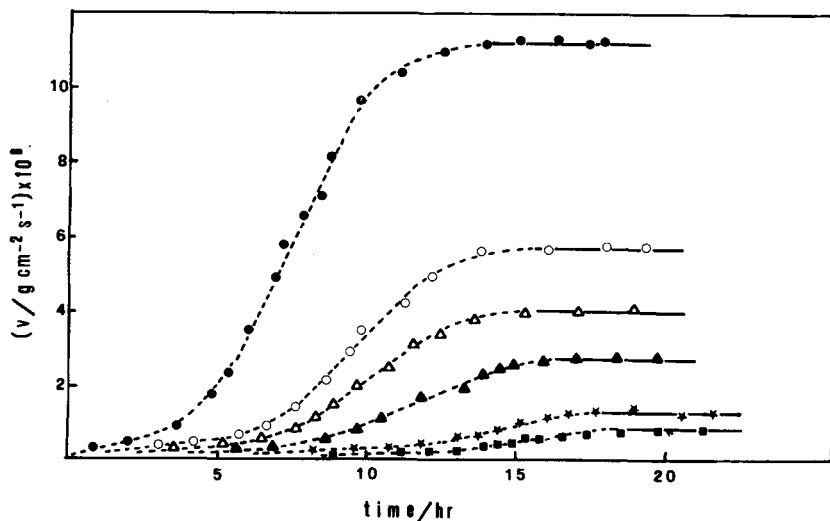


Fig. 2. Rates of evaporation  $v$  ( $\text{g} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ ) of diethylphthalate from the surface of bio-oriented polycaprolactam films 0.060 mm thick, measured as a function of time during the process of permeation from the liquid reservoir on the opposite face of the membrane, at various temperatures (K): (●) 333.2; (○) 323.2; (△) 318.2; (▲) 313.2; (★) 303.2; (■) 298.2.

film was Soxhlet extracted in the same solvent and the concentration  $S_p$  determined gas chromatographically. Experimental values of Figures 1–4 were obtained from a mean of at least four kinetic runs.

Measurements of vapor pressure of *N*, *n*-butylbenzenesulfonamide were carried out making use of the same thermostatted cell employed for permeation and evaporation measurements on films, with the only difference being that a copper wire mesh was used to support *N*, *n*-butylbenzenesul-

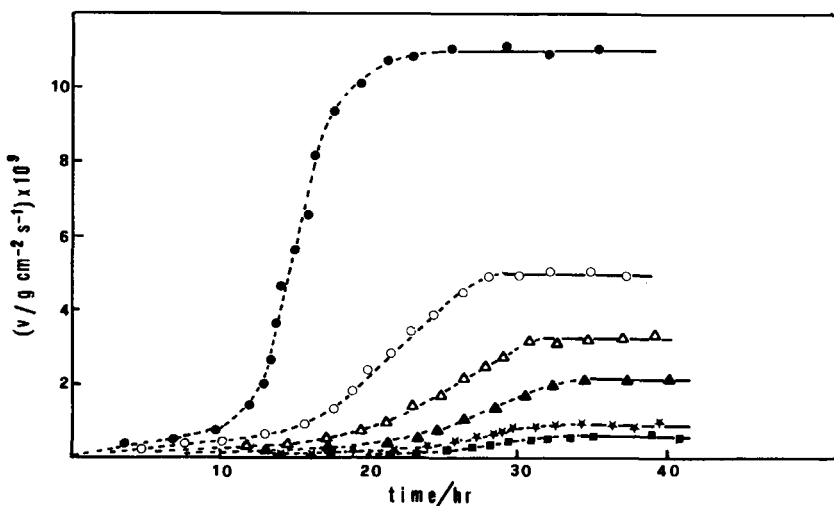


Fig. 3. Rates of evaporation  $v$  ( $\text{g} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ ) of di-*n*-butylphthalate from the surface of bio-oriented polycaprolactam films 0.060 mm thick, measured as a function of time during the process of permeation from the liquid reservoir on the opposite face of the membrane at various temperatures (K): (●) 333.2; (○) 323.2; (△) 318.2; (▲) 313.2; (★) 303.2; (■) 298.2.

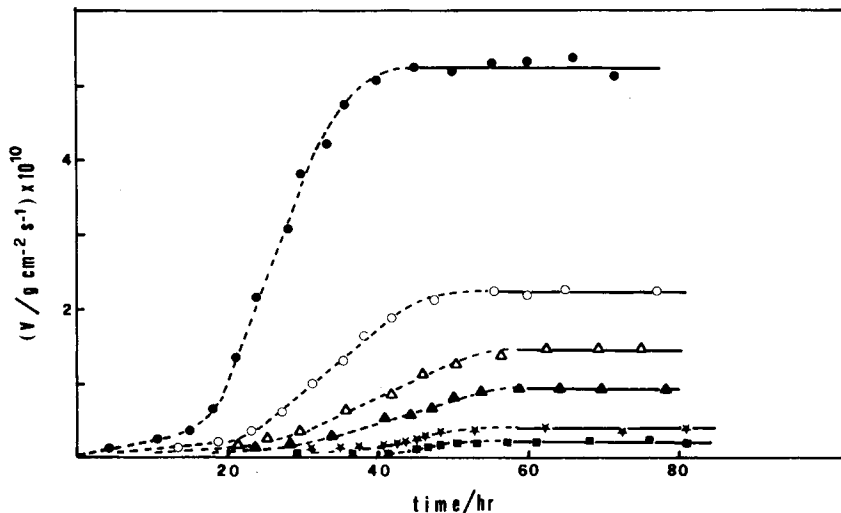


Fig. 4. Rates of evaporation  $v$  ( $\text{g} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ ) of  $N, n$ -butylbenzenesulfonamide from the surface of bioriented polycaprolactam films 0.060 mm thick, measured as a function of time during the process of permeation from the liquid reservoir on the opposite face of the membrane at various temperatures (K): (●) 333.2; (○) 323.2; (△) 318.2; (▲) 313.2; (★) 303.2; (■) 298.2.

fonamide and the lowest possible flow rate of carrier gas was utilized in order to ensure rapidly equilibrium saturation. Detection was made by gas chromatography. Experimental data of vapor pressure  $P^0$  were thus collected in the range 298–463 K, which satisfactorily fitted eq. (1):

$$\log(P^0/\text{mm Hg}) = \frac{-4130 \pm 50}{T} + (8.908 \pm 0.006) \quad (1)$$

(uncertainties are given as probable errors).

## RESULTS AND DISCUSSION

Permeation through the vapor phase of  $n$ -butyl formate, diethylphthalate, di- $n$ -butylphthalate, and  $N, n$ -butylbenzenesulfonamide, as model molecules, was studied as a function of temperature, in the 298.2–333.2 K range on polycaprolactam bioriented commercial films initially freed from any additive and plasticizer. On the upper face of the film, the model molecules were deposited as liquids and permeation of vapors was investigated as a function of time, by using helium as a carrier gas, which flowed past the lower face of the film at a constant flow (velocity  $0.78 \pm 0.01 \text{ cm} \cdot \text{s}^{-1}$ ), in a suitable thermostatted cell. Kinetic runs were carried out parallelly, by making use of two identical cells. Rates of permeation through the vapor phase  $v$  ( $\text{g} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ ), measured gas chromatographically, as a function of time, are reported in Figures 1–4 for the four model molecules investigated, respectively.

It may be easily observed that the behavior of curves of  $v$  as a function of time are qualitatively similar for all the chemical species taken into consideration, but quantitative differences are very important, following the chemical nature of the permeant and evaporating molecules. Qualita-

tively speaking, the curves show three distinct regions: (i) a region where  $v$  values are negligible or very low, (ii) a region where, after a relatively short transition, linearity occurs between  $v$  and time, and finally (iii) a region where, after a new, relatively short transition, stationary values ( $v_0$ ) are obtained. In the latter region, the experimentally determined concentration of the plasticizer molecules in the polymer ( $S_p$ ) remained satisfactorily constant.  $S_p$  and  $v_0$  experimental values, at the different temperatures and for the four molecules studied, are reported in Table I, together with uncertainties expressed as probable errors.

It is reasonable that region (iii) corresponds to the presence of a liquid phase of plasticizer on the lower face of the permeated membrane; then the  $v_0$  values should represent the rate of evaporation of the pure plasticizer. The rate of evaporation of a pure substance from a strip of width  $l$  over which gas flows at velocity  $u$  ( $\text{cm} \cdot \text{s}^{-1}$ ) can be calculated<sup>8</sup> by application of the mass transfer theory to evaporation from a stationary liquid into a stirred gas, as

$$v_0 = 0.33 (u^{1/2}/l^{1/2}) S_g D_g^{2/3} (\rho/\mu)^{1/6} \quad (2)$$

where  $S_g$  ( $\text{g} \cdot \text{cm}^{-3}$ ) represents the concentration in the gas phase,  $D_g$  ( $\text{cm}^2 \cdot \text{s}^{-1}$ ) the diffusion coefficient in the gas phase as well,  $\rho$  the density ( $\text{g} \cdot \text{cm}^{-3}$ ), and  $\mu$  the viscosity ( $\text{g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$ ) of the gas into which evaporation takes place. For the calculation of  $v_0$ , given the known properties,  $\rho^9$  and  $\mu^{10}$  of helium,  $S_g$  and  $D_g$  had to be evaluated. The equilibrium concentration of the plasticizer molecules in the gas phase were obtained for *n*-butyl formate,<sup>11</sup> diethylphthalate,<sup>12</sup> and di-*n*-butylphthalate<sup>13</sup> from tabulated values of the slope and intercept in the linear function of  $\log P_0$ , where  $P_0$  is the vapor pressure, as a function of reciprocal absolute temperature ( $T^{-1}$ ). For *N*, *n*-butylbenzenesulfonamide the same type of function was applied, by employing experimental parameters of eq. (1), determined in the present study. The diffusivity for the transfer of the investigated molecules as vapors in helium was calculated by the following empirical equation of Maxwell, as modified by Gilliland,<sup>14</sup> which has been shown to give satisfactory agreement with experiment

$$D_g = 0.043 T^{1.5} (M_1^{-1} + M_2^{-1})^{1/2} / P (V_1^{1/3} + V_2^{1/3})^2 \quad (3)$$

where  $D_g$  is the diffusivity ( $\text{cm}^2 \cdot \text{s}^{-1}$ ),  $T$  is the absolute temperature,  $M_1$  and  $M_2$  are the molecular weights of the diffusing molecules and helium, respectively,  $V_1$  and  $V_2$  are their molecular volumes, and  $P$  is the total pressure in atmospheres.

The  $v_0$  values calculated by use of eq. (2) are in very good agreement with experimental data: They are reported as continuous solid lines in the plateaux of Figures 1–4. The physical interpretation of  $v_0$  values and of the associated process in region (iii) of kinetic runs is thus well clarified.

For the explanation of experimental behavior in region (ii), as well as in region (iii), the theoretical model of Billingham and Calvert<sup>2,4</sup> is particularly suitable. This model is based on the consideration of two processes occurring: first, removal of the additive from the surface of the polymer by evaporation and, second, migration of the incorporated additive from the bulk of the

TABLE I  
Experimental Rates of Evaporation  $v_0$  and Solubilities  $S_p$  in the Polymer of Molecules I-IV<sup>a</sup>

|   | Temperatures (K) |               |               |               |               |               |
|---|------------------|---------------|---------------|---------------|---------------|---------------|
|   | 298.2            | 303.2         | 313.2         | 318.2         | 323.2         | 333.2         |
| $v_0$ ( $\text{g} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ ) |                  |               |               |               |               |               |
| I   | 0.291 ± 0.006    | 0.367 ± 0.009 | 0.575 ± 0.015 | 0.712 ± 0.028 | 0.876 ± 0.024 | 1.30 ± 0.03   |
| II  | 0.803 ± 0.042    | 1.27 ± 0.05   | 2.75 ± 0.08   | 3.99 ± 0.09   | 5.70 ± 0.26   | 11.2 ± 0.4    |
| III   | 0.558 ± 0.038    | 0.890 ± 0.053 | 2.17 ± 0.08   | 3.33 ± 0.08   | 5.02 ± 0.21   | 11.0 ± 0.4    |
| IV  | 0.205 ± 0.025    | 0.340 ± 0.029 | 0.900 ± 0.065 | 1.43 ± 0.08   | 2.23 ± 0.08   | 5.23 ± 0.34   |
| $S_p$ ( $\text{g} \cdot \text{cm}^{-3}$ )                     |                  |               |               |               |               |               |
| I   | 0.120 ± 0.002    | 0.127 ± 0.003 | 0.143 ± 0.004 | 0.152 ± 0.004 | 0.161 ± 0.005 | 0.178 ± 0.008 |
| II  | 0.150 ± 0.08     | 0.173 ± 0.009 | 0.205 ± 0.012 | 0.224 ± 0.013 | 0.243 ± 0.012 | 0.280 ± 0.014 |
| III   | 0.161 ± 0.08     | 0.176 ± 0.01  | 0.211 ± 0.011 | 0.230 ± 0.012 | 0.250 ± 0.013 | 0.293 ± 0.015 |
| IV  | 0.250 ± 0.015    | 0.276 ± 0.016 | 0.337 ± 0.021 | 0.370 ± 0.022 | 0.404 ± 0.023 | 0.480 ± 0.031 |
| $H$ ( $\text{cm} \cdot \text{s}^{-1}$ )                       |                  |               |               |               |               |               |
| I   | 2.42 ± 0.06      | 2.88 ± 0.09   | 4.01 ± 0.12   | 4.69 ± 0.13   | 5.43 ± 0.15   | 7.30 ± 0.18   |
| II  | 5.35 ± 0.24      | 7.34 ± 0.34   | 13.4 ± 0.6    | 17.8 ± 0.9    | 23.5 ± 1.3    | 40.0 ± 1.8    |
| III   | 3.49 ± 0.21      | 5.06 ± 0.26   | 10.3 ± 0.5    | 14.5 ± 0.6    | 20.1 ± 0.9    | 37.5 ± 2.2    |
| IV  | 0.82 ± 0.06      | 1.23 ± 0.08   | 2.67 ± 0.14   | 3.86 ± 0.24   | 5.51 ± 0.28   | 10.9 ± 0.6    |
| $D_p$ ( $\text{cm}^2 \cdot \text{s}^{-1}$ )                   |                  |               |               |               |               |               |
| I   | 1.22 ± 0.04      | 1.36 ± 0.05   | 1.76 ± 0.06   | 2.14 ± 0.08   | 2.57 ± 0.09   | 3.23 ± 0.12   |
| II  | 1.48 ± 0.06      | 1.66 ± 0.07   | 2.30 ± 0.08   | 2.61 ± 0.07   | 3.02 ± 0.09   | 3.80 ± 0.14   |
| III   | 5.55 ± 0.26      | 7.40 ± 0.31   | 8.33 ± 0.32   | 9.52 ± 0.38   | 12.8 ± 0.5    | 15.1 ± 0.6    |
| IV  | 4.16 ± 0.21      | 4.76 ± 0.23   | 5.95 ± 0.28   | 6.67 ± 0.10   | 8.33 ± 0.35   | 10.7 ± 0.5    |

<sup>a</sup> I = *n*-butyl formate, II = diethylphthalate, III = di-*n*-butylphthalate, IV = *N,n*-butylbenzenesulfonamide; calculated values of mass transfer constants of evaporation  $H$  [eq. (5)] and diffusivities through polymer  $D_p$  (time lag method), relative to polycaprolactam films at various temperatures.

polymer to the surface to replace lost material. For the experimental model studied in the present work, migration takes place either from the liquid deposited on the film, through the film itself in which the plasticizer dissolves, when kinetic runs, such as those of Figures 1–4 are carried out, or from the bulk of the film when various concentrations at below saturation in the polymer are examined and their instantaneous rates of evaporation are measured (interrupted runs, see Experimental). In principle, the overall rate of mass transfer may be determined by the rate of either evaporation from the surface (at saturation concentration of the plasticizer in the film or below it) or migration through the film, or both of these processes. For migration, Fick's law may be retained to be valid, and control by the diffusion coefficient of the permeant molecule through the film results. For evaporation rate, by the model of Billingham and Calvert,<sup>2,4</sup> it may be reasonably expected that  $v$  will be equal to  $HC_s$ , where  $C_s$  ( $\text{g} \cdot \text{cm}^{-3}$ ) is the concentration at the surface and  $H$  is a constant (mass transfer coefficient of evaporation). If the plasticizer is assumed to form an ideal solution in the polymer and the rates of evaporation of both pure and dissolved plasticizers are supposed proportional to their vapor pressures, by this model,<sup>2,4</sup> the rate law may be written as

$$v = HC_s = v_0 C_s/S_p \quad (4)$$

and, consequently,

$$H = v_0/S_p \quad (5)$$

By eq. (5) and experimental  $v_0$  and  $S_p$  values the mass transfer constant of evaporation  $H$  at the various temperatures tested and for the four molecules examined could thus be evaluated (see Table I). Furthermore, a linear function of  $v$  vs. time  $t$  is the consequence of a linear variation of  $C_s$  with time. When the liquid plasticizer is deposited on the upper surface of the film and the kinetic run is started on ( $t = t_0$ ), the concentration on the lower surface is clearly  $C_s = 0$ ; when "saturation" of the plasticizer in the polymer is reached ( $C_s = S_p$ ) and plasticizer is present, in liquid domains or pools in the polymer gel, as a component of the two-phase equilibrium with the saturated polymer, by eq. (4),  $v = v_0$  results. If the variation of  $C_s$  with time is approximatively linear, then from  $v$  values determined experimentally,  $C_s$  at a general time  $t$  may be calculated by linear interpolation, as at  $t = t_0$ ,  $v = 0$ . By eq. (4) the mass transfer constant of evaporation  $H$  could thus also be obtained. These  $H$  values estimated by the latter method agreed fairly well with those reported in Table I and resulting from eq. (5). On the contrary, from instantaneous  $v$  values, determined from interrupted runs, a 15–25% lower value of  $H$  was obtained. This was not unexpected, since the experimental procedure to prepare the film with  $C_s$  below saturation involved, along with removal of unabsorbed plasticizer, also, partially at least, a certain dissolution of adsorbed plasticizer, even by the cold solvent.

By the linear extrapolation of the experimental curves  $v = v(t)$  in region (ii) to  $v = 0$ , the corresponding  $t_0$  values were obtained, and, according to the time-lag method,<sup>15</sup> the diffusion coefficient  $D_p$  ( $\text{cm}^2 \cdot \text{s}^{-1}$ ) through the



polymer film ( $D_p = l_f^2/6t_0$ , where  $l_f$  is the film thickness) could be finally reckoned. The values of  $D_p$  at the various temperatures tested are reported in Table I.

Finally, the influence of temperature may be studied, for the model molecules examined, both on diffusivities  $D_p$  in the polymer phase and on mass transfer constant of evaporation  $H$ . By Arrhenius plots, the activation energies,  $\Delta E_{D_p}$  and  $\Delta E_H$ , respectively were calculated, the values of which are collected in Table II, together with estimated probable errors.

The experimental model taken into consideration has been intentionally formulated in the configuration of a reservoir system given by the liquid deposited on the membrane. Furthermore, for the predominantly crystalline polycaprolactam films used, solute transport in the polymer film should occur by a process involving dissolution of plasticizer molecules in the membrane structure, followed by their diffusion along and between polymer segments. The amorphous regions or the areas of crystal imperfections are most involved by this mechanism. Only one of the model molecules, the sulfonamide, is a realistic and technologically suitable model of plasticization for polycaprolactam. The others have been studied not only because some phthalates have low compatibility with polyamides and, at relatively low temperatures investigated in this work, notwithstanding the difference of solubility parameters, possess a certain plasticizing action,<sup>16</sup> even on polycaprolactam, but because, at least for some of the molecules, a relatively high vapor pressure was needed. For this latter purpose the *n*-butyl formate was selected.

The qualitatively similar behavior of the curves of release through vapor phase suggest that the process involved in region (i) is more or less rapid plasticizer uptake in the surface layers, as plasticizer molecules enter porous areas of the polymer and adhere there, being adsorbed. Then the main process of region (ii) is represented by solute transport via a solution-diffusion mechanism. The low values of activation energies  $\Delta E_{D_p}$  for diffusion through the membrane (see Table II), and their practical independence of the chemical nature of the model molecules imply in fact a simple diffusion process. The order of magnitude of difference in the single  $D_p$  values (see Table I) between that of *n*-butyl formate and those of the others molecules examined appears in line with their molecular dimensions. The influence of vapor pressure is particularly evident in the  $H$  values: the correlation between  $\Delta E_H$  and the evaporation enthalpy  $\Delta H_{ev}$  calculated by vapor pressure data is shown in Figure 5.

TABLE II  
Activation Energies for Diffusivities through Polymer ( $\Delta E_{D_p}$ ) and for Mass Transfer Constants of Evaporation ( $\Delta E_H$ ) Together with Their Uncertainties Expressed as Probable Errors<sup>a</sup>

|                                     | $\Delta E_{D_p}/\text{kcal} \cdot \text{mol}^{-1}$ | $\Delta E_H/\text{kcal} \cdot \text{mol}^{-1}$ |
|-------------------------------------|--|--|
| <i>n</i> -Butyl formate             | 5.7 ± 0.1  | 6.2 ± 0.1                                      |
| Diethylphthalate                    | 5.4 ± 0.1  | 11.3 ± 0.1                                     |
| Di- <i>n</i> -butylphthalate        | 5.4 ± 0.1  | 13.4 ± 0.1                                     |
| <i>N,N</i> -butylbenzenesulfonamide | 5.3 ± 0.1  | 14.6 ± 0.1                                     |

<sup>a</sup> Calculated by Arrhenius plots from data of Table I.

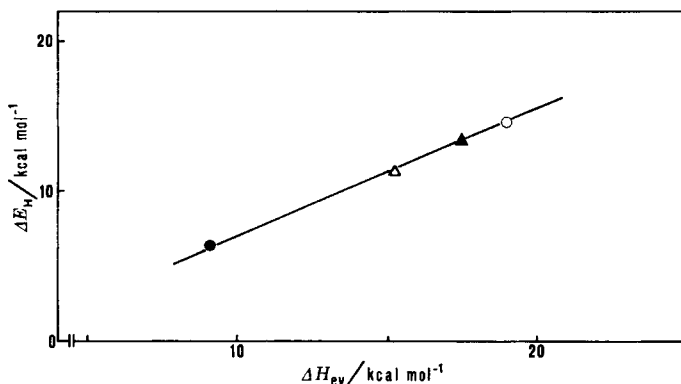


Fig. 5. Activation energies  $\Delta E_H$  ( $\text{kcal}\cdot\text{mol}^{-1}$ ) of mass transfer coefficients of evaporation  $H$  relative to  $n$ -butylformate (●), diethylphthalate ( $\Delta$ ), di- $n$ -butylphthalate ( $\blacktriangle$ ), and  $N$ ,  $n$ -butylbenzenesulfonamide ( $\circ$ ) as a function of the corresponding evaporation enthalpies  $\Delta H_{ev}$  ( $\text{kcal}\cdot\text{mol}^{-1}$ ) of these molecules.

Considering the small number of molecules, and notwithstanding that both  $\Delta E_H$  and  $\Delta H_{ev}$  values are derived from measurements of solubility and vapor pressures, all of which are subject to uncertainties, the good correlation coefficient (0.999) may be considered highly satisfactory.

The experimental model employed in the present study, and its interpretation in terms of parameters<sup>2,4</sup> controlling rate of evaporation, thus appear to show their validity. For the examined molecules, the overall rate clearly gives evidence of being controlled by evaporation, the adimensional value of  $Hl/D_p$  being sufficiently low,<sup>2,4</sup> as a consequence of their relatively high solubilities and vapor pressures, even for the least volatile molecule tested, in addition to the thickness of the film. In any case the relative importances of diffusion or evaporation control to give the rate of release from membranes through the vapor phase may be adequately assessed by this method.

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