Eur. Polym. J. Vol. 21, No. 11, pp. 967–972, 1985
Printed in Great Britain. All rights reserved

0014-3057/85 \$3.00 + 0.00

TRANSFER OF LIQUIDS BETWEEN PLASTICIZED PVC AND ACETIC ACID

MODEL AND EXPERIMENT

A. Manoussaki-Grigorakakis, J. L. Taverdet and J. M. Vergnaud
Laboratory of Materials and Chemical Engineering, U.E.R. of Sciences, University of St Etienne, 23, Dr P. Michelon, Saint-Etienne 42100, France

(*Received* 21 *January* 1985)

Abstract—When plasticized PVC is in contact with acetic acid, there is simultaneous diffusion of the liquid into, and the plasticizer out of the polymer. These transfers are controlled by diffusion in the unsteady state, with concentration-dependent diffusivity for both liquids. The transfer process is complicated for acetic acid, because the amount transferred rises quickly to a maximum with a resulting swelling of polymer, and then decreases to the equilibrium value. A model is used for calculating the amount of the liquids transferred at various times, as well as the profiles of concentration developed through the PVC. Short tests help to give information on the kinetics of these transports.

INTRODUCTION

Polyvinyl chloride (PVC) plays an important role in the packaging industry, and a large part of it is used in this application as soft and plasticized material. Extensively plasticized PVC is accepted for many biomedical applications such as blood bags and other blood-handling devices, in spite of the fact that major components in the plasticizer are not biologically inert [1–4]. Most foodstuffs are packed in PVC [5]. In all these applications, plasticized PVC is in contact with some kind of surrounding medium and the plasticizer may stay in place or migrate with the following results. Because of loss of plasticizer, a considerable change in mechanical properties of the PVC packaging. The surrounding medium is contaminated by the plasticizer and other additives.

The following factors can affect the migration process [6]. (i) The kind of PVC, and the plasticization process. (ii) The nature of the liquid, its compatibility with the plasticizer and polymer. (iii) The nature and amount of plasticizer. (iv) The conditions of the migration process, agitation of liquid, temperature and time.

Experiments for determination of transfer kinetics at room temperature are very time-consuming (25°, 6 months; 45°, 10 days), but studies involving shorter times and higher temperature showed that simulation conditions can only give a very rough idea of the real test, and results did not correlate [7, 8]. A high plasticizer content is responsible for faster transport into the liquid. The migration of phthalate plasticizer from PVC into various liquids has been reported [5]. Several studies were done with liquid foods [9, 10]. Some alcohols were tested [11, 13], and the effect of water content in ethanol was found to affect transfer [14]. The migration was strongly affected by the nature of petroleum oils, and the effect of aromatic content was important [15]. Transfers from PVC into peanut oil [16] and *n*-heptane [17] were also studied, and *n*-heptane was found not to be a perfect simulant for oil [18]. The effect of the external phase on migration has been especially studied [19].

The problem is rather complicated. In a variety of liquids, one must study the simultaneous diffusion of the liquid into, and the previously dispersed plasticizer out of the PVC [20]. Both transfers can be explained by diffusion in the unsteady state, and the coefficients of diffusion are concentration dependent. In view of the complicated concentration dependence of the diffusion coefficient of liquid penetrating PVC, the liquid diffusion is directly coupled to the plasticizer loss. Moreover, another experimental fact was found in the case of simultaneous diffusion of the plasticizer and benzyl alcohol chosen as the liquid: the mass of liquid entering the PVC reached a maximum and then decreased before attaining the equilibrium value [13–18, 20, 21].

Some results are now reported on the simultaneous transfer of acetic acid into, and plasticizer out of plasticized PVC, when the polymer was contacted with the liquid. The effects of temperature and plasticizer content on the transfer process were studied by using long real experiments and short tests followed by calculation. These short tests detailed in earlier papers [22, 23] are of interest for the understanding of the kinetics of transfer, because the concentration of both liquid and plasticizer can be considered as constant during the short experiment. The calculations were done by using an explicit numerical method of finite differences. These calculated results were found to be in agreement with experimental results determined under the same conditions (long real tests).

THEORETICAL

Our prototype problem elucidates the effect of the diffusion of a liquid into a polymer on the simultaneous diffusion of plasticizer out of the polymer into an infinite bath of stirred liquid. Each transfer is regarded as governed by Fick's law [6], in transient conditions. The diffusion coefficients are dependent on the concentration of both liquid and plasticizer. It was assumed in earlier studies that the concentration of plasticizer on PVC surfaces is the same as that in the liquid as soon as PVC slabs are dropped into the liquid [15, 20, 24]. This assumption allows solution of the equation of diffusion, but the concentration is not zero on PVC faces as shown by measurements with attenuated total reflectance [18].

Mathematical treatment for PVC sheets

The equation of diffusion with concentration dependent diffusivity is:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(\mathrm{D}\frac{\partial C}{\partial x}\right). \tag{1}$$

For very short times, the amount of substances transferred at time t as a function of the quantity at equilibrium is expressed by the equation:

$$\frac{M_t}{M_\infty} = 4\left[\frac{\mathrm{D}\cdot t}{\pi\cdot x^2}\right]^{0.5} \tag{2}$$

where x is the sheet thickness, and D is the constant diffusivity at time zero.

The solution cannot be given in a mathematical form for long times by keeping in mind the above assumption.

Numerical treatment

The problem has to be solved with the help of a numerical explicit method with finite differences [23].

Consider the PVC sheet of thickness x as divided into n equal finite slices of thickness Δx by concentration time reference planes (n, for space; i, for time). The liquid balance considered for liquid and plasticizer on the plane n enables one to find the following recurrent equations.

$$C^{\mathrm{l}}_{n,i+1} = \frac{1}{M_{\mathrm{l}}}[C^{\mathrm{l}}_{n-1,i} + (M_{\mathrm{l}} - 2)C^{\mathrm{l}}_{n,i} + C^{\mathrm{l}}_{n+1,i}] \tag{3}$$

with

$$M_{\mathrm{l}} = \frac{(\Delta x)^2}{\Delta t}\cdot\frac{1}{D_{\mathrm{l}}} \tag{4}$$

and

$$D_{\mathrm{l}} = \exp\left(-\frac{A}{C^{\mathrm{p}} + C^{\mathrm{l}}\cdot\alpha} - B\right) \tag{5}$$

$C^{\mathrm{l}}_{n,i+1}$ being the concentration of liquid in PVC at the plane n and time $(i + 1)\ \Delta t$.

For the plasticizer, we have also:

$$C^{\mathrm{p}}_{n,i+1} = \frac{1}{M_{\mathrm{p}}}[C^{\mathrm{p}}_{n-1,i} + (M_{\mathrm{p}} - 2)\cdot C^{\mathrm{p}}_{n,i} + C^{\mathrm{p}}_{n+1,i}] \tag{6}$$

with

$$M_{\mathrm{p}} = \frac{(\Delta x)^2}{\Delta t}\cdot\frac{1}{D_{\mathrm{p}}} \tag{7}$$

and

$$D_{\mathrm{p}} = \exp\left(-\frac{A'}{C^{\mathrm{p}} + C^{\mathrm{l}}\cdot\beta} - B'\right) \tag{8}$$

$C^{\mathrm{p}}_{n,i+1}$ being the local concentration of plasticizer in PVC at the plane n and time $(i + 1)\ \Delta t$.

When the liquid diffuses into the polymer while plasticizer diffuses out, diffusion coefficients are a function of concentrations of liquid and plasticizer [23, 25].

The dimensionless numbers M_{l} and M_{p} must be kept higher than 2, as convergence of equations 3 and 6 is required.

Other equations are used for calculating the liquid concentration on PVC faces.

$$C^{\mathrm{l}}_{\mathrm{face},i+1} = \frac{1}{M_{\mathrm{l}}}\cdot[C^{\mathrm{l}}_{\mathrm{liq},i} + (M_{\mathrm{l}} - 2)\cdot C^{\mathrm{l}}_{\mathrm{face},i} + C^{\mathrm{l}}_{1,i}] \tag{9}$$

$$C^{\mathrm{p}}_{\mathrm{face},i+1} = \frac{1}{M_{\mathrm{p}}}\cdot[C^{\mathrm{p}}_{\mathrm{liq},i} + (M_{\mathrm{p}} - 2)\cdot C^{\mathrm{p}}_{\mathrm{face},i} + C^{\mathrm{p}}_{1,i}] \tag{10}$$

where $C^{\mathrm{l}}_{\mathrm{liq}}$ and $C^{\mathrm{p}}_{\mathrm{liq}}$ are the concentration on PVC when equilibrium is reached; $C^{\mathrm{l}}_{\mathrm{face},i}$ and $C^{\mathrm{p}}_{\mathrm{face},i}$ are the concentration on PVC faces at time $i\ \Delta t$.

The values of the coefficients A, B, A', B', α and β, depend on the working conditions, and must be determined for each liquid.

The total amount M_t of both liquids transferred at time t can be calculated by integrating the profiles of concentration with respect to time obtained with the above equations.

EXPERIMENTAL

Materials

Dioctylphthalate was used as plasticizer and pure acetic acid for the liquid (Rhône-Poulenc). A commercial PVC resin in the form of white powder was used (Lucovyl, Rhône-Poulenc, France). Components of PVC compounds were mixed in a steel mould operated by a press at 150° under a pressure of 50 bars. Discs (18 mm in diameter, 3.4 mm thick) were cut from PVC sheets.

Apparatus for study of transfers

Experiments were carried out with 20 PVC discs in 200 ml acetic acid in a 500 ml closed flask using a controlled rate of stirring. Samples of PVC and liquid were taken at intervals for analysis: so that the liquid–PVC ratio was kept constant, for one PVC disc 10 ml solution was removed.

Each PVC disc was weighed and dissolved in acetone–carbon disulphide mixture, and this solution was injected for analysis by gas chromatography after addition of dioctyl adipate as internal standard. Operating conditions were as follows: gas chromatograph (IGC 16, Intersmat, France). The glass column was 2 m long, and the stationary phase was chromosorb Q 60/80 mesh and 3% OV 17 silicone rubber (Dow Chemical). The column temperature was 270°.

Calculation

Calculation was performed by using a microcomputer (Micral, R2E, France). The values for essential parameters were: number of slices = 10; $\Delta x = 0.033$ cm; $\Delta t = 1800$ sec; $M_{\mathrm{l}} = 4$; $M_{\mathrm{p}} = 17$.

RESULTS

As shown earlier [21–23], the following parameters are of importance: temperature, plasticizer concentration in PVC, stirring of the liquid, and especially nature of the liquid.

Because of the great importance of stirring on both transfers, particularly for short times when transports are partly controlled by boundary layer phenomena in the liquid phase next to PVC faces, all experiments were performed in a well-stirred vessel (Reynold's number 3000).

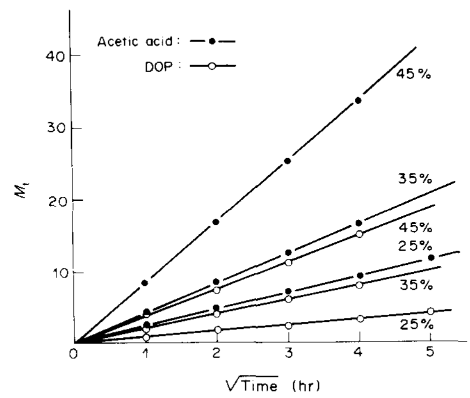

Fig. 1. Short test, amount of plasticizer and acetic acid transferred vs $(\text{time})^{1/2}$ for different initial plasticizer concentrations in PVC at 30°.

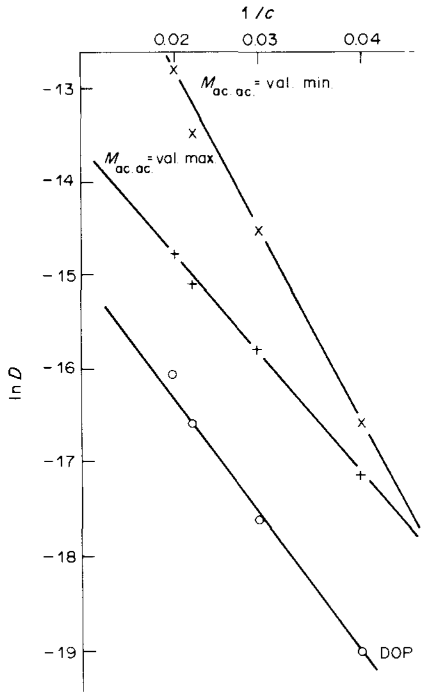

Fig. 2. Logarithm of diffusivity vs (concentration of plasticizer in $\text{PVC})^{-1}$.

PVC samples with different plasticizer concentration were used for studying the kinetics of both transfers.

Short tests for determining diffusivities

As shown in Fig. 2, the amount of liquid transferred up to time t is directly proportional to $(\text{time})^{1/2}$, and diffusivities can be obtained from the slope of these straight lines. Results for four initial concentrations of plasticizer in PVC are plotted in Fig. 1 for transfer of plasticizer and that of liquid.

The diffusivity in the logarithm form for both liquids is shown in Fig. 2 to be proportional to (plasticizer concentration in $\text{PVC})^{-1}$. The values of diffusivities obtained for those liquids are cited in Table 1 for 30, 40 and 50°C.

The diffusivity of the liquid is considerably higher than that of the plasticizer. Moreover, the total concentration of both plasticizer and liquid has to be taken into account, and notably in the denominator of equation (5) and (8) relating diffusivity to the local concentration of liquids.

The following expressions for the diffusivity were set up, with two coefficients α and β depending on the operational conditions of temperature and local plasticizer concentration as shown in Table 2.

$$D^{l} = \exp\left(-\frac{117.35}{C^{p} + C^{l}\cdot\alpha} - 12.41\right) \tag{5'}$$

$$D^{p} = \exp\left(-\frac{132.78}{C^{p} + C^{l}\cdot\beta} - 13.65\right) \tag{8'}$$

Although the liquid and plasticizer are in PVC at the same time, they do not play exactly the same role in rate transfer, as coefficients α and β are not equal to 1. We do not have a satisfactory explanation at present for this fact. It is obvious that these two liquids have quite different physical properties, notably viscosity, molecular size and diffusivity.

Long real experiments

The amounts of liquid transferrred into the plasticizer out of PVC discs, are shown in Fig. 3 (25% plasticizer), as a function of time, and for other initial plasticizer concentrations (35–45%). In this Figure, we can appreciate transfers for both liquids. Experimental values can be compared with those calculated by applying our model.

Experimental results are in close agreement with those calculated for plasticizer over the whole range of the transfer process, and for all the PVC samples of different initial plasticizer concentrations.

The problem for acetic acid is difficult. Although good agreement between theoretical and experimental results is obtained for a short time, up to the maximum value reached by the amount of liquid transferred, quite different results are shown for longer times. In fact, unlike calculation, experiments show that the amount of liquid transferred into PVC reaches a maximum after a steep rise and then decreases rather slowly before attaining the equilibrium value. This fact is not new as recently demonstrated in other cases with a variety of liquids [2, 6, 13]; it occurs very often when the rate of transfer

Table 1. Diffusivities related to liquid for different plasticizer concentrations in PVC and temperature

Temperature	30°			40°			50°		
% Plasticizer	25	35	45	25	35	45	25	35	45
$D_l \times 10^8$ (cm²/sec)	3.7	14	27.7	7.8	17.3	27.4	12.1	18.9	48.7
$D_p \times 10^8$ (cm²/sec)	0.58	2	6.3	0.7	3.4	8.2	1.7	5.3	16.5

Table 2. Variation of α and β with temperature and % DOP

Temperature	30°			40	50°
% Plasticizer	25	35	45	35	35
α	0.7	0.5	0.2	0.9	1.0
β	0.7	0.8	0.6	1.0	1.2

is notably higher for the liquid than for the plasticizer, when considerable swelling is observed.

Studies on the above-mentioned problem are in progress, and we hope to be able to improve our model, so that it gives calculated values in agreement with experimental when a maximum is obtained.

The profiles of both liquids (plasticizer and acetic acid) developed through PVC samples can easily be calculated by applying our model and using data concerned with diffusion coefficients obtained in short tests. The shape of the profiles are illustrated in Figs 4–6 for initial plasticizer concentrations of 25–35 and 45%. These profiles are determined over the whole transfer process for the plasticizer, and only up to the maximum value for the liquid. Two interesting points can be mentioned about the concentration of both liquids on PVC faces. (i) Concentrations of the plasticizer are not zero on PVC faces, as proved previously [18] with the help of attenuated total reflection. (ii) The concentration of acetic acid on PVC faces is not the same as that in the liquid phase, because of the presence of PVC and plasticizer. (iii) As soon as the process starts, concentrations of the plasticizer and acetic acid on PVC surfaces tend rapidly to the value at equilibrium. These last values are also the same as those obtained inside PVC at equilibrium.

However, if the profiles of concentration of plasticizer through PVC mass are well described, our model is not suitable for determining the profiles of concentration of acetic acid for times longer than 150 hr for 25% DOP, 100 hr for 35% DOP and 30 hr for 45% DOP. This is due to the fact that the model does not take into account the right situation for acetic acid transport with the maximum shown in Fig. 3.

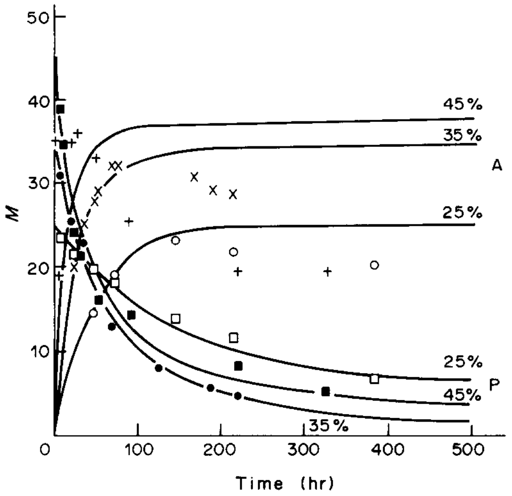

Fig. 3. Long real test, amount of liquids transferred vs time. P = plasticizer; A = acetic acid. A: (+) 45% DOP; (×) 35% DOP; (○) 25% DOP. P: (■) 45% DOP; (●) 35% DOP; (□) 25% DOP.

CONCLUSIONS

In this paper, concerned with the effect of contacting plasticized PVC with acetic acid, simultaneous diffusion of the liquid into, and plasticizer out of the PVC has been observed. Both transfers are controlled by diffusion in a non-steady state, and diffusivities are concentration dependent. In both the equations expression diffusivities for the liquid and plasticizer, concentrations of the liquid and plasticizer do not play exactly the same role; no explanation is yet available.

A model previously described has been shown to give calculated results in good agreement with experimental for the amount of plasticizer leaving PVC. The model is useful to find the amount of liquid transferred into PVC, when this amount is rising to the maximum value. It also gives information of interest on the profiles of concentration of both liquids developed throughout the PVC sample.

The work is continuing, in order to improve the model so that it leads to correct calculated values, especially for the liquid when a maximum has been reached.

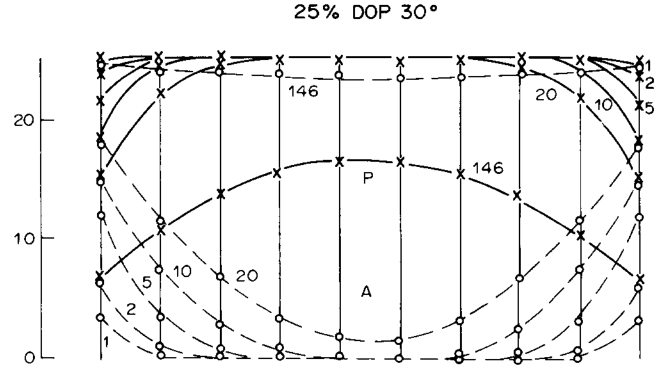

Fig. 4. Profiles of concentration developed through polymer thickness. P: 25% plasticizer; A: acetic acid.

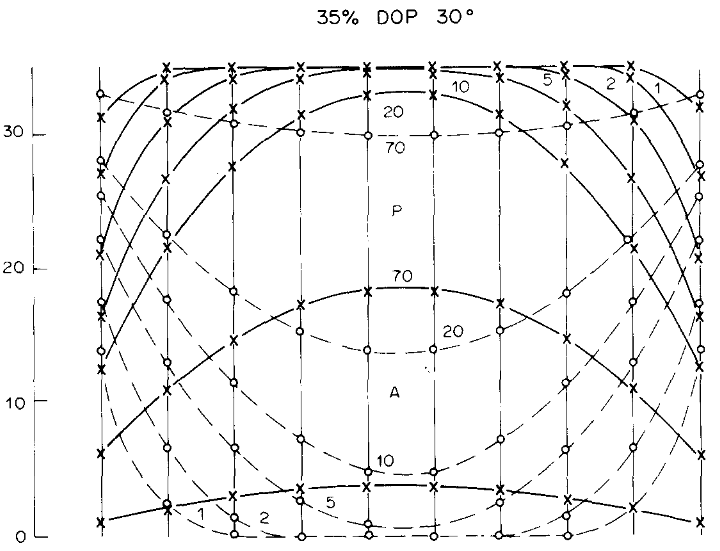

Fig. 5. Profiles of concentration developed through polymer thickness. P: 35% plasticizer; A: acetic acid.

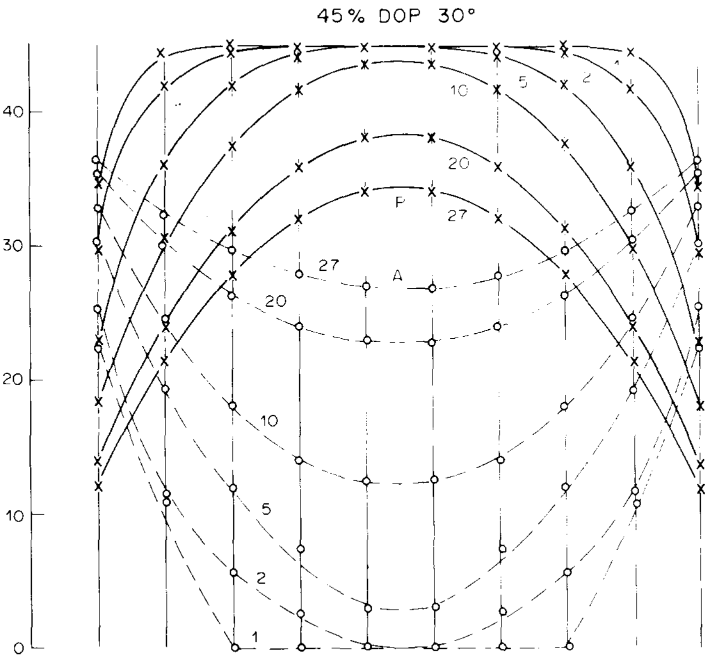

Fig. 6. Profiles of concentration developed through polymer thickness. P: 45% plasticizer; A: acetic acid.

REFERENCES

1. D. P. Rall, *Conference on Phthalates*, Washington, D.C., 9 June (1981).
2. R. W. Baker, *Toxicology* **9,** 319 (1978).
3. M. Morioka, T. Aoyama and H. Karasowa, *Chem. Pharmac. Bull.* **25,** 1791 (1977).
4. T. J. B. Gray, K. R. Butterworth, I. F. Gaunt, P. Grasso and S. D. Gangoli, *Fd Cosmet. Toxic.* **15,** 389 (1977).
5. G. Haesen and A. Schwarze, *Migration Phenomena in Food Packaging*. Commission of the European Communities, Petten (1978).
6. J. M. Vergnaud, *Polym. Plast. Technol. Engng* **20,** 1 (1983).
7. H. Woggon, W. J. Uhde, K. Romminger and H. Hoppe, *Nahrung* **18,** 671 (1974).
8. W. Hofman and H. Ostromow, *Kautsech. Gummi. Kunstst.* **25,** 145 (1972).
9. S. G. Gilbert, *J. Fd Sci.* **41,** 955 (1976).
10. W. J. Koros and H. B. Hoffenberg, April 5–6 (1979).
11. E. M. Kampouris, F. Regas, S. Rokotas, S. Polychronakis and A. Pantazoglou, *Polymer* **16,** 840 (1975).
12. D. Messadi and J. M. Vergnaud, *J. appl. Polym. Sci.* **26,** 667 (1981).
13. D. Messadi and J. M. Vergnaud, *J. appl. Polym. Sci.* **26,** 2315 (1981).

14. D. Messadi and J. M. Vergnaud, *J. appl. Polym. Sci.* **27,** 3945 (1982).
15. E. M. Kampouris, *Eur. Polym. J.* **2,** 705 (1975).
16. J. L. Taverdet and J. M. Vergnaud, *Third International Flavor Conference*. American Chemical Society, Athens, July 7 (1981).
17. D. Messadi and J. M. Vergnaud, *J. chem. Phys.* **77,** 935 (1980).
18. J. L. Taverdet and J. M. Vergnaud, *Third International Flavor Conference*. American Chemical Society, Corfu, July 16 (1983).
19. R. C. Reid, K. R. Sidman, A. D. Schwope and E. T. Derek, *Ind. Engng Chem. Prod. Res. Dev.* **19,** 580 (1980).
20. H. L. Frisch, *J. appl. Polym. Sci.* **16,** 1651 (1978).
21. J. L. Taverdet, D. Messadi and J. M. Vergnaud, *I & EC Prod. Res. Devl.* Vol. 22 (1983).
22. J. L. Taverdet and J. M. Vergnaud, *Congress of the American Chemical Society*, Division of the Organic Coatings & Plastic Chemicals, Kansas City, September 13 (1982).
23. J. L. Taverdet and J. M. Vergnaud, *J. appl. Polym. Sci.* **29,** 3391 (1984).
24. J. Crank, *The Mathematics of Diffusion*. Clarendon, Oxford (1976).
25. F. B. Rudolph, *J. Polym. Sci. Phys. Ed.* **17,** 1709 (1979).