

Food and Packaging Interactions: Use of Methyl Red as a Probe for PVC Swelling by Fatty Acid Esters

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SYNOPSIS

A study of the interaction of fatty foods with rigid PVC packages was undertaken, using fatty acid esters $\text{CH}_3(\text{CH}_2)_{n-2}\text{COOR}$ ($8 \leq n \leq 18$; R = Me, Et) as food simulants. Determination at 50°C of weight uptaken by PVC and of depth of penetration of the simulant into the material allowed us to define the time required to reach a thermodynamic equilibrium and the amount of liquid sorbed. Sorption at equilibrium decreased when chain length increased. When the simulant was tinted by methyl red, the dye adsorbed by the material was located exclusively in the diffusion layer. In contrast to sorption of the simulant, the absorbance of the dye in PVC went through a maximum for $n = 14$. Its spectrum depended on the extent of swelling of the polymer. In materials swollen by short-chain esters, the dye preferred a nonplanar conformation, stabilized through intermolecular solvation by fatty acid esters. When solvation and swelling were weak ($n = 16, 18$), the dye adopted a planar conformation, driven by intramolecular chelation, with a higher λ_{max} and a large extinction coefficient. Methyl red thus appeared as a probe for the study of interactions with slight swelling. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Plastic packages may give rise to contamination of foodstuffs through migration of their low molecular weight constituents (residual monomers, additives, etc.).¹ To ensure whether materials can be used safely for food packaging, it is essential to control these migration processes.² In Official control procedures, model foods—called food simulants—are preferred to real foodstuffs for practical reasons.

European legislation for food packaging is based on a comparison of the simulated worst-case exposure of consumers with the acceptable daily intake of the migrants.³ The highest migrations, which correspond to this worst case, are usually met with fatty foodstuffs, which strongly interact with the lipophilic polymers used for food packaging.¹ Current Official fatty food simulants are triglycerides (olive oil, sunflower oil, corn oil, and synthetic mixtures

of triglycerides).^{2,4} Their use is a source of difficulties in packaging industries and in enforcement laboratories, for two main reasons: (1) Many Official control procedures involve a 10 day contact and, in case of overall migration—the total amount of substance having migrated, a tedious workup, which is too long for routine controls. (2) Detection and quantification of migrants in triglycerides can be very difficult, especially if they cannot be separated on the basis of their volatility⁵ or their solubility.⁶ For these reasons, volatile solvents have been proposed as alternative fatty food simulants: With such media, the tests can be accelerated and the detection limits are much lower than in fats.^{7–14} However, there is still the need for criteria to select a given simulant suitable for use with a given polymer.

A main point for the definition of the aggressivity of a simulant is its ability to penetrate into the material. We have shown that the depth of penetration of methyl palmitate—i.e., the thickness of its diffusion layer—into rigid poly(vinyl chloride) (PVC) could be measured via microscopic observation of sectioned slices of the material.¹⁵ This method en-

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abled penetration determinations with a much better resolution (down to 2 μm) than did other current methods. An indirect determination of penetration has also been proposed, based on a correlation with a very simple colorimetric technique. Methyl red, initially dissolved in the simulant, was vehiculated into the material when the fatty acid ester penetrated, and its absorbance could be correlated to the penetration. In this article, we show that the visible spectrum of methyl red is very sensitive to the extent of swelling of the polymer by fatty esters.

EXPERIMENTAL

The PVC samples studied were prepared by Dorlyl, Le Havre. They were transparent and had the same composition as that of rigid PVC bottles for mineral water. Three kinds of PVC materials were studied: plate (1 mm thickness), foil (0.38 mm thickness), and bottle (0.5 mm thickness). Methyl red, ethyl esters, and methyl esters were supplied by Aldrich (purity > 99%). Dichloromethane, diethyl ether, and ethanol were supplied by Prolabo (Paris).

Conditions of Contact

Each PVC sample (1 \times 0.5 cm) was cut and immersed in the simulant (4 mL) in a screw-stopped flask. Whenever dyes were added to the simulant, their concentrations were indicated in the text. The flasks were then maintained at 50°C in a water bath for the appropriate time.

Weight Uptake and Spectrophotometric Measurements

After immersion, the samples were wiped, washed briefly with ethanol, and dried. Weight uptake was evaluated on a Mettler AE200 balance for the tinted and the reference samples.

The spectra of the colored samples were recorded with a Kontron Uvikon 941 or with a Perkin-Elmer Lambda spectrophotometer, the PVC sample being held between two quartz plates, mounted on a spring cell holder (Hellma). To account for the slight yellowing of PVC, appearing during contact, a sample which had been immersed under the same conditions, but without dye, was used as the reference.

Sectioning and Depth of Penetration Measurements

Detailed information on the sectioning technique was reported in a preceding paper.¹⁵ For each simulant, the reference and the tinted samples were microtomed at room temperature to slices of 5 μm thickness. The depth of the diffusion layer was measured by image analysis using a Biocom 200 instrument. Each depth value was measured 10 times independently.

Spectrum of Methyl Red in PVC

A PVC sample was immersed in a solution of methyl red (0.03 g L⁻¹) for 2 days. The sample was removed and dried under vacuum (14 mmHg) for 2 days.

Influence of Acid, Bases, and Ethyl Acetate on the Spectrum of Methyl Red in Dichloromethane

A solution of methyl red (5 \times 10⁻⁵ mol L⁻¹) in dichloromethane was bubbled with anhydrous hydrogen chloride for 10 s directly in the UV cell (1 = 1 cm). Alternatively, 4-dimethylaminopyridine (5 mg) was added to the cell. The spectra were recorded immediately. To study the influence of solvation of methyl red by ethyl acetate, solutions were prepared as indicated in the text.

RESULTS

The replacement of triglycerides by alternative fatty simulants, such as aqueous ethanol or isooctane, involves drastic changes of both the polarity and the size of these model foodstuffs. Since each of these factors can influence interaction between food and packaging, we decided first to investigate the behavior of alkyl fatty acid esters, which are similar to triglycerides through their functional groups, but whose molecular weight is closer to the volatile compounds. The influence of chain length was studied through methyl fatty (C₈-C₁₈) esters; the influence of the steric hindrance on the alcoholic part of the ester group was investigated with ethyl (C₈-C₁₆) fatty acid esters.

Three parameters related to the penetration of fatty acid esters were monitored against time:

- The percentage of weight uptake $\Delta m/m$ (%).¹⁶
- The depth of penetration measured by microscopic observation.¹⁵⁻¹⁷

- The optical density of the material tinted through the use of methyl red dissolved in the simulant.¹⁵

In official test methods,^{2,4} one of the most important set of conditions of testing is for 10 days at 40°C. Kinetic curves of sorption show whether these conditions correspond to a thermodynamic equilibrium between simulant and PVC. To approach as quickly as possible this equilibrium, we studied relatively thin foils (0.38–0.5 mm) and used 50°C as the temperature of contact.

Penetration of Methyl and Ethyl Fatty Acid Esters Monitored by Measurements of Weight Uptake

After immersion in methyl octanoate, even for very short times, the foils visually appeared to be swollen. With the longer chain fatty acid esters ($n \geq 14$), no modification of the appearance of the samples was apparent. The results on weight uptake of the methyl and ethyl esters $\text{H}_3\text{C}(\text{CH}_2)_{n-2}\text{COOR}$ ($R = \text{Me}$ or Et) are shown on Figures 1 and 2: for different chain lengths of fatty acid esters as a function of time of contact (Fig. 1) and as a function of n for 6.7 days of contact (Fig. 2). After this time, the systems (PVC–simulant) reached the thermodynamic equilibrium with the shorter-chain fatty acids ($n \leq 14$) (Fig. 1).

Weight-uptake measurements were not accurate: Short-chain fatty acid esters penetrated quickly into rigid PVC, but they also evaporated rapidly when the sample was removed from the simulant, so that the weight of the simulant absorbed by the plastic could not be determined repeatably. The measurements for methyl and ethyl octanoate and decanoate

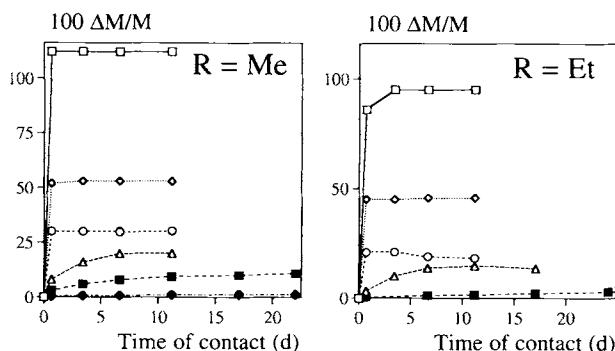


Figure 1 Weight uptake of rigid PVC in contact with $\text{CH}_3(\text{CH}_2)_{n-2}\text{COOR}$ at 50°C as a function of time. (\square) $n = 8$; (\diamond) $n = 10$; (\circ) $n = 12$; (\triangle) $n = 14$; (\blacksquare) $n = 16$; (\blacklozenge) $n = 1$. Each value is the average of two determinations.

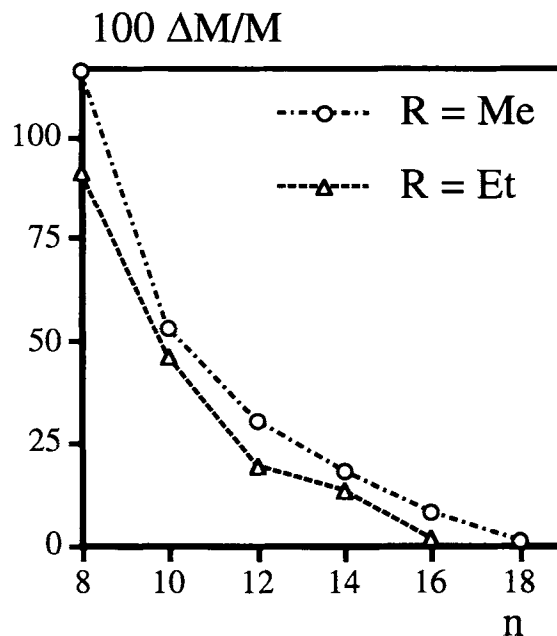


Figure 2 Weight uptake of rigid PVC foils (thickness = 0.38 mm) in contact with $\text{CH}_3(\text{CH}_2)_{n-2}\text{COOR}$ for 6.7 days at 50°C as a function of n : (\circ) $R = \text{methyl}$; (\triangle) $R = \text{ethyl}$.

(Fig. 1) were therefore not accurate. No attempt was made to improve this accuracy. With longer-chain esters, the penetration was much slower and smaller. It was even difficult to differentiate between the behavior of methyl hexadecanoate and methyl octadecanoate. Nevertheless, the overall trend in the influence of the carbon number n appears very well in Figure 2: Short-chain fatty acid esters penetrate much faster than do the longer-chain ones; a methyl ester penetrates faster than does the ethyl ester of the same fatty acid.

Penetration of Methyl and Ethyl Fatty Acid Esters Monitored by Depth of Penetration Measurements

The depth of penetration measured by microtomy showed a similar trend to weight uptake: For a given time of contact, it strongly decreased when the number of carbon atoms n of the fatty acid moiety of $\text{CH}_3(\text{CH}_2)_{n-2}\text{COOR}$ increased (Fig. 3). With short-chain fatty acid esters ($n = 8$ and $n = 10$), penetration was complete within a few hours, and swollen samples were so soft that their sectioning and the measurement of the depth of penetration were difficult. A value $e = 1000 \mu\text{m}$ was assigned to each of these esters. The penetra-

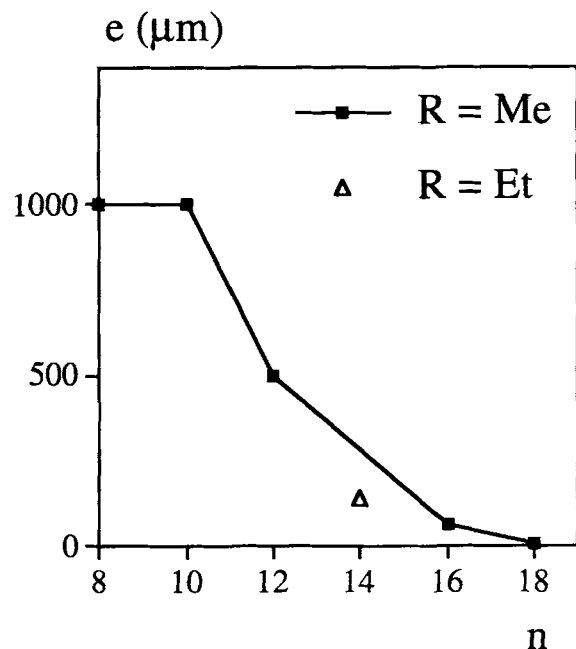


Figure 3 Depth of penetration e of $\text{CH}_3(\text{CH}_2)_{n-2}\text{COOR}$ into rigid PVC sheets (thickness 1 mm) after 6 days at 50°C . Samples with $n = 8$ and $n = 10$ were strongly swollen.

tion was much slower with longer-chain esters. The data in Figure 3 are shown for 1 mm foils, to emphasize the large difference between short- and long-chain esters.

Penetration of Fatty Acid Esters Followed Through Measurement of Absorbance of Methyl Red

PVC foils (thickness 0.38 mm) were immersed in solutions of methyl red (0.03 g L^{-1}) in each simulant. The initial solutions of methyl red in fatty acid esters $\text{CH}_3(\text{CH}_2)_{n-2}\text{COOR}$ all had the same spectrum ($\lambda_{\text{max}} = 478 \text{ nm}$, $\epsilon = 40400 \text{ L mol}^{-1} \text{ cm}^{-1}$). Absorbance of PVC foils was measured after different contact times; for each simulant, the absorbance increased with time of contact and reached a plateau (Fig. 4). However, in contrast to weight uptake and to the depth of penetration measurements, the plots of absorbance against n showed a maximum at $n = 14$ for methyl esters and at $n = 12$ for ethyl esters (Fig. 5).

In the visible spectrum, the maximum wavelength of the dye in PVC depended on the fatty acid ester used as a simulant and gradually shifted from 490 to 500 nm (Table I) when n increased from $n = 8$ to $n = 18$. Since the spectrum of the dye in swollen PVC appeared to depend on the

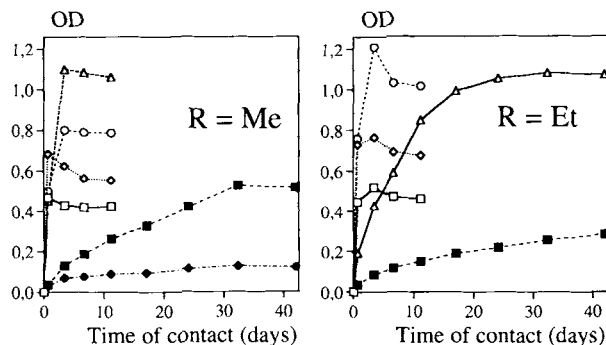


Figure 4 Dependence of absorbance of PVC sheets (thickness = 0.38 mm) upon time of contact at 50°C with $\text{CH}_3(\text{CH}_2)_{n-2}\text{COOR}$ containing methyl red (0.03 g L^{-1}): (\square) $n = 8$; (\diamond) $n = 10$; (\circ) $n = 12$; (Δ) $n = 14$; (\blacksquare) $n = 16$; (\blacklozenge) $n = 18$. Each value is the average of at least three determinations

swelling liquid, we also prepared a sample of tinted PVC where the solvent (diethyl ether) had been removed under a vacuum. This sample had $\lambda_{\text{max}} = 499 \text{ nm}$ (Table I). The following experiments were undertaken to understand the behavior of the dye in PVC.

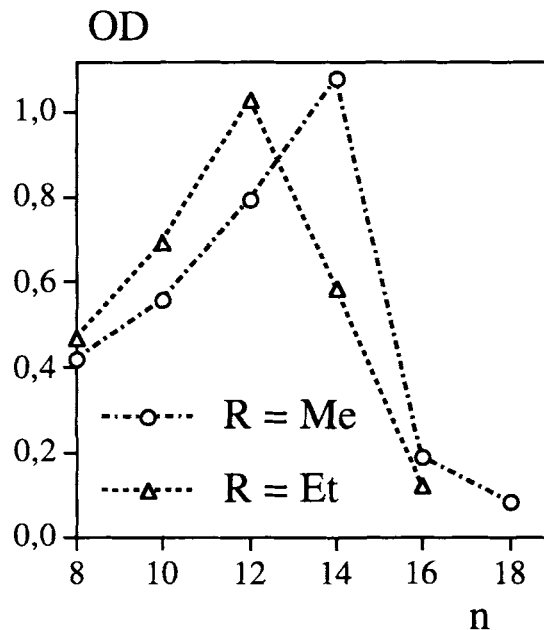


Figure 5 Optical density of tinted PVC (thickness = 0.38 mm) after contact (6.7 days at 50°C) with $\text{CH}_3(\text{CH}_2)_{n-2}\text{COOR}$ containing methyl red ($c = 0.03 \text{ g L}^{-1}$) as a function of n .

Table I λ_{\max} of Methyl Red in PVC After Contact with Tinted $\text{CH}_3(\text{CH}_2)_{n-2}\text{COOR}$

Fatty Acid Ester (<i>n</i>)	λ_{\max} (nm)	
	R = Me	R = Et
8	490	493
10	493	495
12	495	498
14	496	499
16	499	499
18	499	
18 : 1	500	

Influence of the Partition Coefficient of the Dye Between PVC and Simulant on Its Spectroscopic Behavior

The bell-shaped curves relating absorbance of PVC to *n* (Fig. 5) could be explained by the simultaneous occurrence of two antagonistic effects: the result of penetration of the simulant decreasing with *n* associated to a partition coefficient of the dye increasing with *n*. This hypothesis was ruled out for the following reasons:

Samples 0.5 mm thick, were immersed at 50°C in solutions of methyl red (0.03 g L^{-1}) in methyl alcanoates (*n* = 8–16) until equilibrium was reached. After immersion, these PVC samples all had absorbance OD_i values (Table II). When each tinted sample was incubated again with the same alcanoate, but without dye added, methyl red migrated out of the samples into the simulant. The absorbance of PVC was measured from time to time. The final absorbance OD_f corresponded to the reextraction of most (>74%) of the dye by the simulant. The percentage of dye migrated was given by the ratio $[100(OD_i - OD_f)]/OD_i$. The absorbances of all the

solutions were similar, indicating that similar amounts of dye were present in PVC before reextraction (Table II).

Partition coefficient considerations could not explain the differences in the spectra of PVC samples after contact with the esters of different chain lengths. Even when these PVC samples contained the same amount of methyl red, their absorbances were very different. The extinction coefficients of the dye in PVC thus appeared to depend on *n*. Since the spectra in solution did not depend on *n*, this behavior reflected an interaction of the fatty acid esters with rigid PVC.

Possible Influence of Hydrogen Chloride Which Might Be Formed in PVC on the Spectroscopic Behavior of Methyl Red

Since methyl red is widely used as an acid/base indicator, we thought that its spectroscopic behavior in PVC might be caused by hydrogen chloride formed by degradation reactions of the polymer. This could be ruled out by comparison of the spectrum of the dye under its neutral, its protonated, and its deprotonated form. The spectra of these species were recorded in solution in dichloromethane—selected because, like PVC, it is a chlorinated aprotic molecule. Methyl red had a $\lambda_{\max} = 488 \text{ nm}$ (neutral form) in dichloromethane, which shifted to 540 nm (acid form) in the presence of anhydrous hydrogen chloride or to 410 nm (basic form) in the presence of anhydrous 4-dimethylaminopyridine. These spectroscopic modifications associated to protonation and deprotonation of the dye were much larger than those observed in PVC. In all experiments described in Figures 1–5, the dye is always under its neutral form.

Table II Absorbance of Completely Penetrated PVC Samples (0.5 mm) Before and After a Second Incubation in Virgin Simulant at 50°C

<i>n</i> (no. C in Methyl Alcanoate)	First Contact (Tinted Simulant)		Second Incubation (Virgin Simulant)			
	Time (Days)	Absorbance of PVC After Contact (OD_i)	Time (Days)	Absorbance of PVC After Contact (OD_f)	Percentage of Dye Released ^a	Absorbance of Solution After Incubation
8	0.24	0.48	0.27	0.08	84	0.41
10	0.8	0.87	0.27	0.14	84	0.42
12	0.8	0.98	5.46	0.08	92	0.38
14	13.5	1.22	28.3	0.32	74	0.40

Table III Spectra of Methyl Red in Dichloromethane in Presence of Various Amounts of Ethyl Acetate

Solvent: % of Ethyl Acetate in Dichloromethane (v/v)	λ_{\max} of Methyl Red ($c = 3.2 \cdot 10^{-5}$ mol L $^{-1}$)	ϵ (L mol $^{-1}$)
0	488	44,000
10	487	45,200
30	485	44,200
50	484	41,750
80	482	37,320
100	478	37,000

Influence of Solvation by Fatty Acid Esters on the Spectroscopic Behavior of Methyl Red in PVC

The behavior of methyl red in PVC was attributed to solvent effects varying with the concentration of fatty acid ester in the material and, hence, with the extent of swelling. This was supported by recording spectra of methyl red in dichloromethane with different concentrations of ethyl acetate. These two solvents were selected since they were expected to develop dipolar interactions similar to those of PVC and of the fatty acid esters respectively (Table III).

When the concentration of ethyl acetate in dichloromethane increased from 0 to 100%, the spectrum of methyl red exhibited a hypsochromic shift from 488 to 479 nm and a slight decrease in the extinction coefficient from 44,000 to 37,000 (Table III). These changes in the spectrum of methyl red in dichloromethane are similar to results shown in Table I for PVC.

Spectroscopic properties of amphiphilic azo dyes in polymers have been explained on the basis of electron delocalization.¹⁸ In the case of methyl red, protonation favors planar zwitterionic structures,

with delocalization from the nitrogen atom to the carboxyl group.¹⁹

In nonhydrogen donating media like PVC (Table I) or dichloromethane (Table III), intramolecular hydrogen bonding between the carboxyl group and the diazo group compensates the steric repulsion between these two functional groups and favors a planar structure of the dye. In solution, in presence of a hydrogen bond acceptor like ethyl acetate,²⁰ this chelation is in competition with intermolecular hydrogen bonding. This intermolecular hydrogen bond involves a nonplanar conformation of the dye with reduced electron delocalization resulting both in a hypsochromic shift and in a drop in the extinction coefficient. An increase in the concentration of ethyl acetate favors intermolecular hydrogen bonding, which explains the observed spectroscopic changes.

Penetration of Methyl Oleate and Tricaprylin

The influence of additional functional groups of the ester was investigated by putting PVC in contact with solutions of methyl red in methyl oleate and

Table IV Comparison of the Penetration of Methyl Stearate, Methyl Oleate, and Tricaprylin in Rigid PVC After 10 Days at 50°C

	Plate (6.2 Days)		Bottle (32 Days)		Foil (11.2 Days)	
	OD ^a	e (μm)	OD ^b	e (μm)	OD ^b	$\Delta M/M$ (%)
Me stearate ($n = 18$)	0.264	5	0.11	60	0.07	1.1
Me oleate ($n = 18$)	1.128	33	0.37	220	0.21	4.5
Tricaprylin (Tri C8)	1.350	51				

^a Methyl red: 0.24 g L $^{-1}$.

^b 0.03 g L $^{-1}$.

in glycerol trioctanoate (tricaprylin). The results (Table IV) indicated that their penetration was much more important than that of methyl stearate whatever the criteria used: weight uptake, depth of penetration, or absorbance of the material tinted with methyl red in the simulant.

DISCUSSION AND CONCLUSION

Swelling of PVC by Fatty Acid Esters

The penetration of the fatty esters (Figs. 2–4) decreased with increasing n ($n = 8$ to $n = 18$), which was consistent with the general knowledge on interactions of plastics with solvents.^{16,21} An increase of the size of the chain in a homologous series has two opposite effects: Solubility in the polymer increases, but diffusivity decreases.²¹ Cohesive energy differences between fatty esters and polymers determined their compatibility.²² The presence of other functional groups had a strong effect on sorption. The double bond of methyl oleate and the three ester functions of trioleate render these molecules more polar than methyl stearate and strongly favor their penetration in a polar polymer like PVC (Table IV). This result is especially important since glycerol trioctanoate is one of the main constituents of miglyol, a fatty simulant recently introduced by the Food and Drug Administration.⁴ Similar effects have been pointed out to describe the sorption of triglycerides by polymers.^{22,23} The presence of a double bond was shown to enhance the sorption of fatty esters by polar poly(ethylene terephthalate); with apolar polyolefins, the opposite behavior was observed.²² There was also a slight effect of sterical hindrance of the alcoholic part of the ester, and ethyl esters penetrated slightly slower than did methyl esters.

With short-chain fatty acid esters, PVC was strongly swollen, became soft, and lost its physical properties; these esters are slightly volatile, but could not be used as fatty food simulants. They destructed the polymer and behaved like extractants. Esters with $n \geq 14$ penetrated much more slowly, without any apparent swelling; they are more realistic as fatty food simulants.

Spectroscopic Changes of Methyl Red in PVC and in Dichloromethane, in Presence of Esters

During contact, the dye is drawn into PVC by the simulant and is located exclusively in the diffusion layer.¹⁵ In PVC ($490 < \lambda_{\max} < 500$ nm), only the neutral form of the dye is involved. The variation

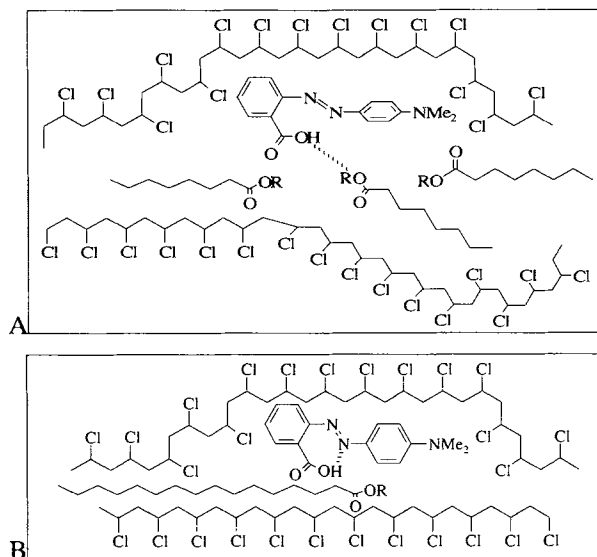


Figure 6 Solvation of methyl red in PVC: (A) PVC swollen by a fatty acid ester $\lambda_{\max} < 490$ nm; (B) intact PVC $\lambda_{\max} = 500$ nm.

of λ_{\max} with n can be interpreted on the basis of different conformations of the dye depending on its extent of solvation by esters (Fig. 6). With short-chain fatty acid esters ($n = 8, 10$), the polymer is swollen, the dye is strongly solvated [Fig. 6(A)], and λ_{\max} tends toward values measured in solution in the simulant or in ethyl acetate ($\lambda_{\max} = 478$ nm) (Table III). The longer the chain of fatty acid esters, the smaller is the swelling and the solvation. With long-chain esters, there are only a few ester molecules which can interact with the carboxyl group of the dye, which then prefers a planar conjugation [Fig. 6(B)]. This results in larger extinction coefficients of the dye. This increase seems to be much steeper in PVC (Fig. 5) than in solutions (Table III), probably because the conformational equilibria:

planar form (intramolecular chelation) \rightleftharpoons

twisted form (intermolecular chelation)

are frozen in the polymer.

For fatty acid esters with $n \leq 14$ (Fig. 4), the absorbance increased rapidly for short period of times and then slightly decreased before reaching a plateau. At the same time, there is a 1–3 nm hypsochromic shift of the spectrum after the initial period. Our observations regarding the behavior of methyl red suggest that a reorganization of the polymeric network takes place after a few hours of

contact. Such behavior has been reported for solvent absorption by plasticized PVC: The weight of immersed polymer samples goes through a maximum before reaching a plateau.^{16,24}

It is noteworthy that the response of the methyl red increased for long-chain esters, whereas weight uptake and penetration depth methods were getting very insensitive. The behavior of methyl tetradecanoate, hexadecanoate, and octadecanoate could be very well distinguished by the colorimetric method. Methyl red thus appears as a useful probe for exploring very slight swelling processes and for studying food and packaging interactions.

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