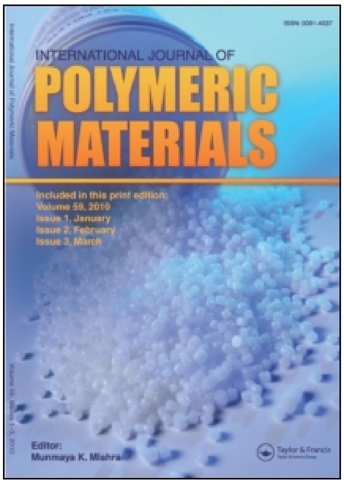

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Zeddam, C. and Belhaneche-Bensemra, N.(2010) 'Kinetic Study of the Specific Migration of an Organotin Heat Stabilizer from Rigid Poly(vinyl chloride) into Food Simulants by FTIR Spectroscopy', International Journal of Polymeric Materials, 59: 5, 318 — 329

To link to this Article: DOI: 10.1080/00914030903478867

URL: http://dx.doi.org/10.1080/00914030903478867

International Journal of Polymeric Materials, 59:318–329, 2010
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ISSN: 0091-4037 print/1563-535X online
DOI: 10.1080/00914030903478867

Kinetic Study of the Specific Migration of an Organotin Heat Stabilizer from Rigid Poly(vinyl chloride) into Food Simulants by FTIR Spectroscopy

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The aim of this paper is the determination of the specific migration of an organotin heat stabilizer (Irgastab 17 MOK) from rigid poly(vinyl chloride) (PVC) into food simulants. For that purpose, two fatty simulants were used: hexane and ethanol. The test conditions were 15 d at 4 and 40°C and 3 h at 70°C. The rate of the mass loss of the films was followed as a function of time. FTIR spectroscopy was used to investigate the migration phenomena and to estimate the diffusion coefficients and the activation energy of diffusion by using mathematical models. The influence of various parameters such as temperature, time of contact and the nature of food simulant was considered. The results show that FTIR spectroscopy is a simple, low cost and rapid method which can be used to investigate the migration phenomena.

Keywords food simulant, migration, organotin stabilizer

Received 26 September 2009; in final form 6 October 2009.
The authors acknowledge Mrs A. Amara and B. Ouhalima for their collaboration and help for performing some of the FTIR work in the Industrial Chemical Department of University Saad Dahleb of Blida.

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INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the most widely used polymeric materials in the plastics industry. It is approved for use as films and gaskets for bottle-corks in general contact applications. It is well-known that PVC suffers from poor thermal stability. It undergoes severe degradation via zip elimination of HCl at relatively low temperatures. To increase the heat stability of PVC, different metal soaps like Pb, Cd, Ca and Zn carboxylates and some di- and mono-alkyltin compounds are used [1,2]. Furthermore, various additives such as plasticizers (phthalic and phosphoric acids) and lubricants are generally incorporated. The addition of such substances is necessary for processing and for achieving the desired chemical and mechanical properties. For example, plasticizers are added to give it elasticity [3]. They provide a good transparency to rigid and flexible films for food packaging and pharmaceutical applications. However, despite their high compatibility with PVC, these low molecular weight additives possess a high mobility and, in contrast to the macromolecules, are capable of migration from the packaging material into the packed product [4–8]. Some of the migrants may affect quality of the packed product as exhibited by sensorily determinable changes (odor and/or taste) or by toxicological symptoms from ingestion [9]. According to the EC regulation, the detection and the quantification of contaminants migrating from the polymers are essential for the safety assessment of food contact plastic packaging materials.

In fact, until now, migration of plasticizers into food and their simulants has been the subject of many investigations [10–18] but few studies were carried out on the migration of other additives [19–21]. The most used method for the experimental study of migration phenomena is gas chromatography (GC) [5–18] which is costly and time-consuming. Hence, it is desirable to identify simple, low-cost and rapid techniques to study these phenomena.

The aim of the present paper is to carry out a kinetic study of the specific migration of an organotin heat stabilizer from rigid PVC films into food simulants by FTIR spectroscopy. The toxicity of organotin compounds is associated with impurities, such as the dialkyl- and tetra-alkyl-tin; they affect at the cerebral and renal systems. Furthermore, the tin can compete with the calcium in the bone [22,23].

For that purpose, two liquid simulants of food (hexane and ethanol) were used and three temperatures (4, 40 and 70°C) were considered. The rate of the mass variation of the films was followed as a function of time. FTIR spectroscopy was used to investigate the migration phenomena and to estimate the diffusion coefficients by using mathematical models. The activation energy of diffusion was also estimated.

MODELING APPROACHES

Mathematical modeling of migration processes may be carried out at different levels of description. It concerns small or large molecules, into, through or from a packaging material and may be described by the second Fick's law [24]:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial X^2} \tag{1}$$

where C is the additive concentration in the plastic at time t and distance X.

The solutions for a large number of diffusion problems were provided by Crank [24]. The amount of migrant is given by the following convergent series:

$$\frac{M_t - M_\infty}{M_\infty} = \frac{8}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{(2n+1)^2} \times \exp\left[-\frac{D(2n+1)^2\pi^2}{L^2}t\right] \tag{2}$$

where, M_t: Amount of substance transferred; M_∞: Amount of substance at equilibrium; D: diffusion coefficient or diffusivity of the substance; L: sheet thickness.

For long times, only the first term is significant and Eq. (2) becomes:

$$\frac{M_t - M_\infty}{M_\infty} = \frac{8}{\pi^2}\exp\left[-\frac{D\pi^2}{L^2}t\right] \tag{3}$$

For short times, when $M_t/M_\infty < 0.6$:

$$\frac{M_t}{M_\infty} = \frac{4}{L}\left(\frac{D}{\pi}\right)^{\frac{1}{2}} \times \sqrt{t} \tag{4}$$

Diffusion coefficients are estimated graphically by plotting Log $[M_t - M_\infty/M_\infty]$ and M_t/M_∞ as a function of time and square root of time, respectively.

Then, for long times:

$$f(t) = Log\frac{M_t - M_\infty}{M_\infty} = Log\frac{8}{\pi^2} - \frac{D \cdot \pi^2}{L^2} \cdot t;$$

The slope of the curve is

$$S = \frac{D \cdot \pi^2}{L^2} \tag{5}$$

And for short times:

$$\frac{M_t}{M_\infty} = f(\sqrt{t});$$

The slope of the curve is

$$S^2 = \frac{16}{L^2\pi} \times D \tag{6}$$

Many works on food packaging gave useful informations' about the assumptions under which appropriate equations apply [25–30].

Temperature, migrant concentration and the nature of the food simulator are parameters which affect the diffusivity. The dependency of the diffusion coefficient (denoted by Dp in this model) on temperature is described by the Arrhenius equation [27]:

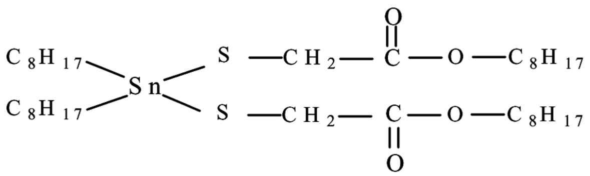
$$Dp = D_0 \exp -(E/RT) \tag{7}$$

where D_0 is the hypothetical diffusion coefficient at very high temperature, E is the activation energy of diffusion (J/mol), R the gas constant (J/mol K) and T the temperature (K). D_0 and E can still only be obtained by fitting with experimental data.

EXPERIMENTAL

Materials

Commercial grade PVC from Sheintech and the heat stabilizer Irgastab 17 MOK (dioctyl tin bis (2-ethylhexylthioglycolate), a yellowish liquid with 15,3 ± 0,5 % of tin and 28,8% ± 3 % of monooctyl tin) from Ciba Geigy were used as received. The chemical structure of Irgastab 17 MOK is the following:



Tetrahydrofuran, ethanol and hexane were purchased from Prolabo and used as received.

PVC Films Preparation

A formulation containing 4.5 wt% of Irgastab 17 MOK was considered. The PVC films were prepared by dissolving completely the compounds in tetrahydrofuran. The solution was transferred into a petri dish and the solvent was evaporated at room temperature during 24 h, then the films were dried at 50°C in a thermostatically controlled chamber for 2 h. Square films (2 × 2 cm) with 120 μm of thickness were cut and used.

Migration Testing

For analytical feasibility reasons, migration tests were carried out by using two fatty food simulants: 96% ethanol and hexane. Testing conditions were chosen according to EU Directives 82/711/EEC and 85/572 EEC [31]. Test temperatures and times were two weeks at 4°C, 40°C and 3 h at 70°C. Concerning the tests carried out at the two first temperatures, fifteen rigid PVC films were immersed in 150 ml of each food simulant. A square film and 10 ml of food simulant were taken off at regular intervals. For the test carried out at 70°C, 10 rigid PVC films were immersed in 100 ml. A square film and 10 ml of food simulant were taken off at regular intervals. Before analysis, the films were wiped and dried at 50°C in a thermostatically controlled chamber for 24 h to desorb the liquid simulators. The weights of the films were 0.0540 ± 0.0041 g. The mass variation was calculated according to the following relation:

$$\sigma(\%) = \frac{m_t - m_0}{m_0} \times 100 \tag{8}$$

where m_0: initial mass before immersion and m_t = mass of the film at the time t after wiping and drying.

Fourier Transform Infrared Spectroscopy Analysis

The IR spectra of the PVC films were taken using a Shimadzu FTIR 8000 PC infrared spectrophotometer with 40 scans per sample and a resolution of 2 cm^{-1}. The KBr pellets were used for the organotin heat stabilizer. IR solution software was used for spectra processing data.

RESULTS AND DISCUSSION

Rate of Mass Variation

The whole PVC films were weighed before and after migration tests. Therefore, the mass loss gives informations' about the phenomena occurring between the samples and the liquid simulants. An increase means that the liquid simulant penetrated the PVC films while a decrease means that the additive migrated into the simulant. In our case, the PVC films were wiped and dried at 50°C before analysis to desorb the liquid simulants. So, the gravimetric data measure essentially the migration out of the PVC matrix. Figure 1 illustrates the mass variations as a function of time for the two food simulants used at 4, 40, and 70°C. It can be noted that the mass has decreased in both simulants and for all the considered temperatures. This means that the migration of Irgastab 17 MOK occurred in both considered simulants. The highest rates of mass loss were observed at 40°C. At equilibrium, Figure 1 shows that in hexane, 0.65%, 4.63%, and 2.27% of mass loss were obtained at 4, 40, and 70°C, respectively. While, in ethanol, the rates were 0.13%, 3.19%, and 1.37%, respectively, for the same temperature order.

We observe also the highest rates of mass loss in the hexane for the three temperatures; it might be attributed to the better solubility of Irgastab 17 MOK in hexane. Indeed, several works showed that the migration increases with the temperature [19–21]. It is to be noted that the obtained results are

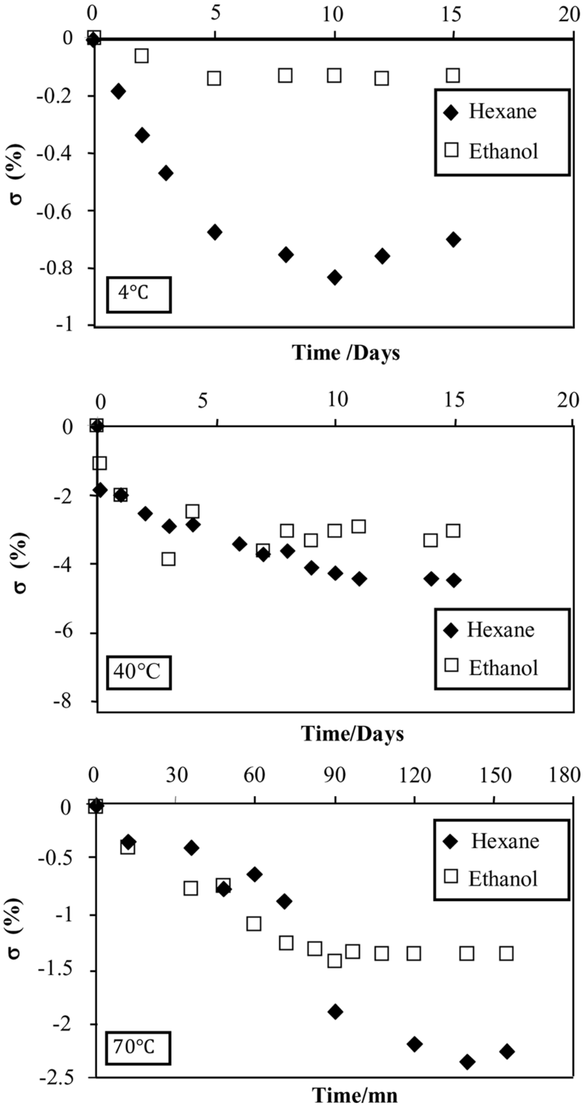


Figure 1: Effect of the temperature and nature of the food simulant on the rate of mass variation for rigid PVC.

due to the effects of temperature rather than the effects of glass transition temperature (T_g) as rigid PVC exhibits a T_g of about 80°C [3].

FTIR Investigation

Preliminary Characterization of the PVC Films before Migration Testing

FTIR spectra of Irgastab 17 MOK, virgin PVC and PVC with Irgastab 17 MOK are given in Figure 2. The spectrum of the organotin heat stabilizer shows C=O group vibration at 1730 cm^{-1} and COO^- vibrations at 1380 and 1540 cm^{-1}. The C–S group absorbs at 1293 and 2854 cm^{-1} while the C–Sn group absorbs at 1184 cm^{-1} [32].

The comparison of the three spectra of Figure 2 shows the presence of the bands at 1550, 1732 and 2854 cm^{-1} due to the organotin stabilizer in the spectrum of PVC containing this stabilizer. Then, a modification of the intensity of these bands after migration testing can be correlated to a phenomenon of organotin migration. The presence of a band at 1065 cm^{-1} is to be noted. It is due to the residual THF used as solvent for films casting.

FTIR Investigation of the PVC Films after Migration Testing

The comparison of PVC films spectra before and after all migration testing shows a decrease of the carbonyl band at 1732 cm^{-1} with time. This was attributed to the Irgastab 17 MOK migration in the considered liquid simulants. A quantitative estimation of this additive migration was carried out. For that purpose, the areas ratios A_{1732}/A_{1432} were calculated as a function of time. The band at 1432 cm^{-1} is due to the vibration of CH_2 of PVC and was taken as a reference band [32].

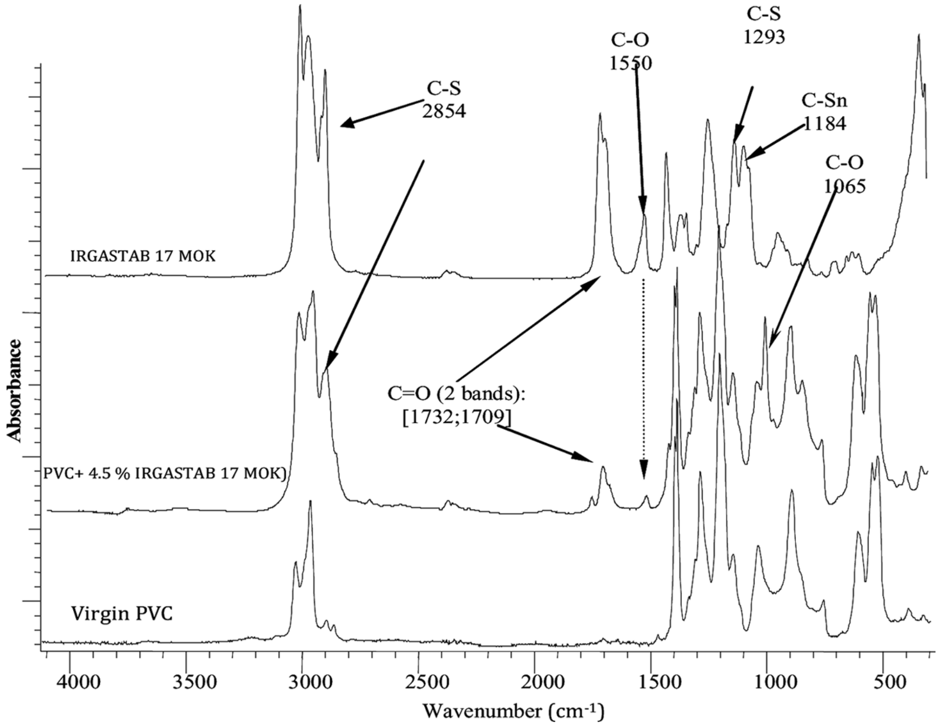


Figure 2: FTIR spectra of rigid PVC films and organotin stabilizer Irgastab 17 MOK.

The migrant levels (M_t) of Irgastab 17 MOK were calculated by using a calibration curve. The obtained rates of migration (Mt/M_0) are given in Figure 3, where M_t and M_0 are migrated and initial amount of the Irgastab 17 MOK, respectively. It can be observed that the additive migration is related to the nature of the food simulant and the temperature.

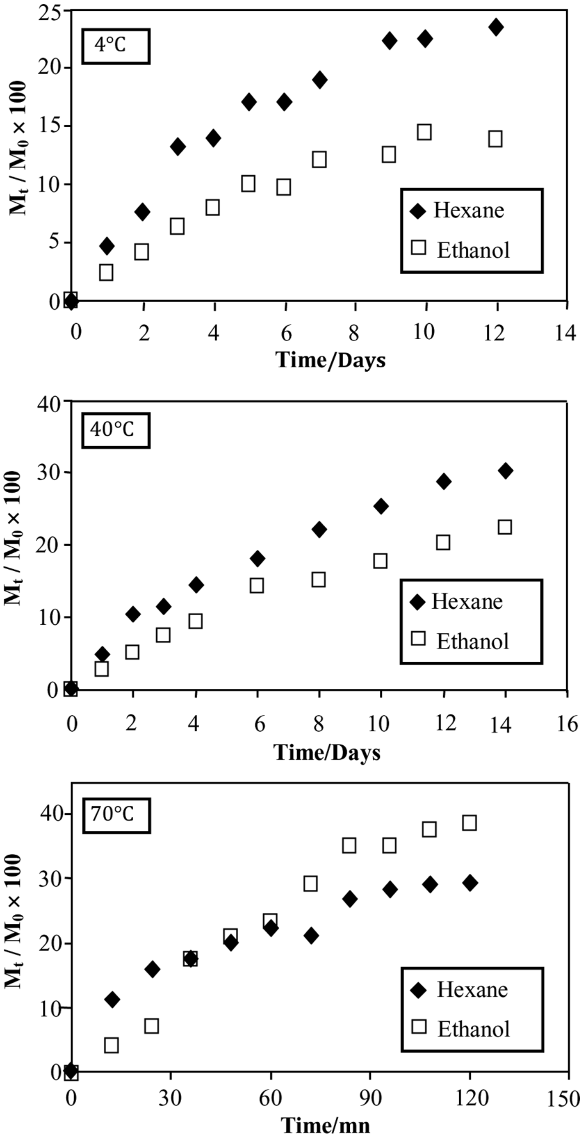
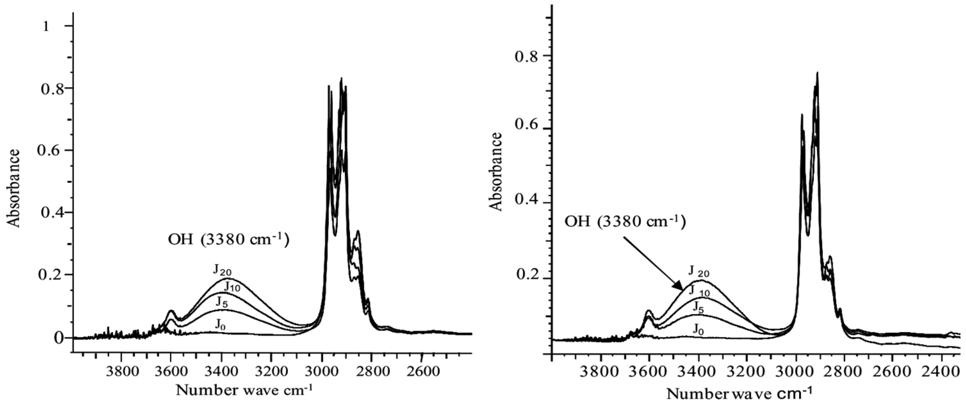


Figure 3: Effect of the nature of food simulant and the temperature on the migration of Irgastab 17 MOK.



(a) (b)

Figure 4: FTIR spectrum of rigid PVC films in ethanol at: a) 40°C; b) 70°C.

As is mentioned in the literature, the migration is more important at higher temperatures [19,21]. It is obvious that the mobility of the migrant molecules increases with increasing temperature, since the highest migration is obtained at 70°C. In fact, the diffusion is favored in hexane at 4 and 40°C. This is due to the better solubility of Irgastab 17 MOK in hexane. At 70°C, the migration in hexane is higher than in ethanol up to 30 min. An inversion occurred for times higher than 60 min. It seems the ethanol penetrated the PVC films and this penetration favored the migration of the heat stabilizer.

In fact, the increase of the intensity of the hydroxyl bands at 3380 and 3600 cm^{-1} can be noted (Figure 4a, b). As the PVC films were wiped and dried before analysis, these bands are due to the residual ethanol which is not completely eliminated by drying. Therefore, this feature confirms the penetration of ethanol in the PVC films and then the real mass loss of the films would be masked. In fact, the sorption of volatile solvents by polymeric films was already mentioned in the literature. The diffusion of methanol, ethyl acetate,

Table 1: Values of coefficient of diffusion of Irgastab 17 MOK at various temperatures in hexane and ethanol.

Mathematical models	**Hexane**	**Ethanol**
Fick		
For T = 4°C and 40°C	$D_{4^\circ C} = 3.09E\text{-}11$	$D_{4^\circ C} = 3.33E\text{-}11$
$D = \frac{SL^2}{\pi^2}$	$D_{40^\circ C} = 3.43E\text{-}11$	$D_{40^\circ C} = 3.53E\text{-}11$
For T = 70°C	$D_{70^\circ C} = 3.36E\text{-}09$	$D_{70^\circ C} = 4.84E\text{-}09$
$D = \frac{\pi S^2 L^2}{16}$		
Arrhenius		
$D_p = D_0 \exp - (E/RT)$	$D_{4^\circ C} = 1.26E\text{-}11$	$D_{4^\circ C} = 6.76E\text{-}11$
	$D_{40^\circ C} = 1.69E\text{-}10$	$D_{40^\circ C} = 6.38E\text{-}10$
	$D_{70^\circ C} = 1E\text{-}9$	$D_{70^\circ C} = 4.06E\text{-}09$

Table 2: Values of D_0 and activation energy of diffusion E in hexane and ethanol.

Parameters	Hexane	Ethanol
D_0 (cm^2/s)	0.095	0.38
E (KJ)	50.931	55.072

ethanol and water into polymers and their effects on the polymer structure have been examined [33,34]. Sammon et al. [33] have used FTIR–ATR method to obtain both kinetic and structural information during liquid sorption into polymers. They have observed that the sorption of methanol into the polymer is accompanied by swelling and follows non-Fickian or anomalous kinetics.

Determination of the Diffusion Coefficients

The experimental diffusion coefficients D_{exp} were evaluated according to Eqs. (5) and (6) and compared to the theoretical values given by Eq. (7). Table 1 gives the diffusion coefficients D_0 and D determined from experimental data for the three considered temperatures (4, 40, and 70°C).

The comparison of the obtained diffusion coefficients shows the effect of temperature on the diffusion phenomena in both simulants. The diffusion coefficient increases with temperature. Therefore, the higher coefficients correspond to 70°C in ethanol and hexane. At this temperature, the Arrhenius model gives lower values of coefficients than Fick's model.

The activation energy of diffusion E was estimated from the curve of log D_{exp} as a function of the inverse of the temperature. E/R is the slope of the representative curve and D_0 is the value at origin Y-axis. Table 2 shows the activation energy of diffusion E determined from experimental data. It can be noted that the activation energy of diffusion of Irgastab 17 MOK is relatively lower in hexane ($E = 50.931$ KJ) in comparison with ethanol ($E = 55.072$ KJ).

CONCLUSIONS

Based on the results of this study, it is concluded that interactions between rigid PVC and food simulants occurred. The issues to be noted are the following:

- The mass of the films during food simulants contact decreased with time, indicating the migration of the stabilizer in the two food simulants considered.
- The penetration of ethanol into the PVC films was observed by FTIR. It favored the mobility of the stabilizer and then its migration.

- The migration phenomenon is influenced by the nature of food simulant, the temperature and the time of contact. The migration is more important at high temperatures. At 4°C and 40°C, hexane appear as the simulant where the additive diffusion is better than ethanol.
- The obtained diffusion coefficients increased with temperature.
- The activation energy of diffusion was relatively higher in ethanol in comparison with hexane.
- Finally, it can be stated that, in comparison with GC, the FTIR spectroscopy is a simple, low-cost and rapid method which can be used to investigate the migration phenomena.

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