MATEC Web of Conferences **3**, 01029 (2013)
DOI: 10.1051/matecconf/20130301029

# Specific migration of IRGASTAB 17 MOK and DBP from rigid and plasticized poly(vinyl chloride) into organic liquids

A. Amara[1], C. Zeddam[2], and N. Belhaneche-Bensemra[2]

[1]Laboratory of Chemical Engineering, Department of Industrial Chemistry, Faculty of Engineering, University Saad Dahleb Blida, road Soumaa BP 270 Blida, Algeria
[2]Laboratory of Science and Environmental Technology, Department of Environmental Engineering, National Polytechnic School, PO Box 182, El-Harrach, Algeria

**Abstract.** The aim of this paper is the determination of the specific migration of a plasticizer and an organotin heat stabilizer (IRGASTAB 17 MOK) from plasticized and rigid PVC into organic liquids, hexane and ethanol simulating fatty food. The migration test conditions were 10 days at 40°C and 2 hours at 70°C. FTIR and UV-Visible at 490 nm spectroscopy and gas chromatography were used to investigate the migration phenomena. The influence of various parameters such as temperature time of contact and the nature of food simulant were considered. The results show that plasticizer accelerates the heat stabilizer migration. On the other hand that gas chromatography could be substituted by FTIR spectroscopy to investigate the DBP migration phenomena. It is a simple, low cost and rapid method which can be used.

## 1 Introduction

Gadgets and toys for children and babies are made of plasticized and rigid PVC. The suppleness article is due to the phthalates addition such as DBP, DEHP. 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]. In contact with liquid media (saliva, fatty foods) these additives may migrate from these items and cause toxicity problems. Indeed, phthalate plasticizers are suspected of be carcinogenic. The toxicity of organotin compounds is associed with impurities, such as the dialkyl and tetra alkyl-tin; they affect the cerebral and renal systems. Furthermore, the tin can compete with the calcium in the bone [3, 4].

The aim of the present paper is to carry out a kinetic study of the specific migration of an organotin heat stabilizer and DBP from rigid and plasticized PVC films into food simulants at 40 °C and 70 °C by gas chromatography, FTIR spectroscopy and UV-Visible at 490 nm.

## 2 Experimental

### 2.1 Products

Commercial grade PVC from Sheintech, dibutyl phtalate PALATINOLAH-L (DBP), DEHP (intern standard) from Prolabo and the heat stabilizer IRGASTAB 17 M0K (dioctyl tin bis 2-ethyl hexyl thioglycolate), a yellowish liquid with % of tin: 15,3 ± 0,5 and % of monooctyl tin: 28,8% ± 3 from Ciba Geigy were used. The chemical structure of IRGASTAB 17 M0K and DBP are shown in Figure1. Tetrahydrofuran, ethanol and hexane were purchased from Prolabo.

### 2.2 PVC films preparation and migration tests

Rigid formulations $FR_x$ containing (x wt %: 0.75; 1.5; 2.5; 3.5 and 4.5) of IRGASTAB 17 M0K were considered. Plasticized films contain 50 % of DBP and x % of IRGASTAB 17 M0K (x wt %: 0.75; 1.5; 2.5; 3.5 and 4.5). 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 hours, then the films were dried at 50°C in a thermostatically controlled chamber for 2 hours. Square films (2 x 2 $cm^2$) with 120 µm of thickness were cut and used. The weights of the films were 0.0540 ± 0.0041 g.

Migration tests were carried out by immersing 10 films and/or $FR_x$ in 100 mL ethanol and/or hexane. Testing conditions (time, temperature) were chosen according to EU Directives 82/711/EEC and 85/572 EEC [5]. Test temperatures and times were two weeks at 40°C and 2 hours at 70°C. A square film and 10 ml of liquid were taken off at regular intervals. Films and $FR_x$ were analyzed by 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 organotin heat stabilizer and DBP. IRsolution software was used for spectra processing data. Before analysis, the films were wiped and dried at 50°C in a thermostatically controlled chamber for 24 hours to desorb the liquid simulators. In ethanol and hexane, heat stabilizer migration was detected by the Shimadzu UV-160 spectrophotometer at 490 nm of the red complex by reacting the organotin and dithizone [6, 7]. DBP was detected by chromatograph using Shimadzu GC 17A (Debit vector gas $N_2$: 24 L/min, 80kPa column SE 30, T column = 250°C $T_{(detector\ FID)}$ = 320°C, $T_{inj}$=300°C).

## 3. Results and discussion

### 3.1 DBP Migration: FTIR and CPG investigation

FTIR spectra of IRGASTAB 17 M0K, DBP, virgin PVC, $FR_x$ and films given in figure 1 show C=O ,C-O, C-S and C-Sn functions vibration [8]. Interactions plastic/liquid are manifested by the double migration of PVC additives to liquid and liquid in the polymer matrix [9, 10].

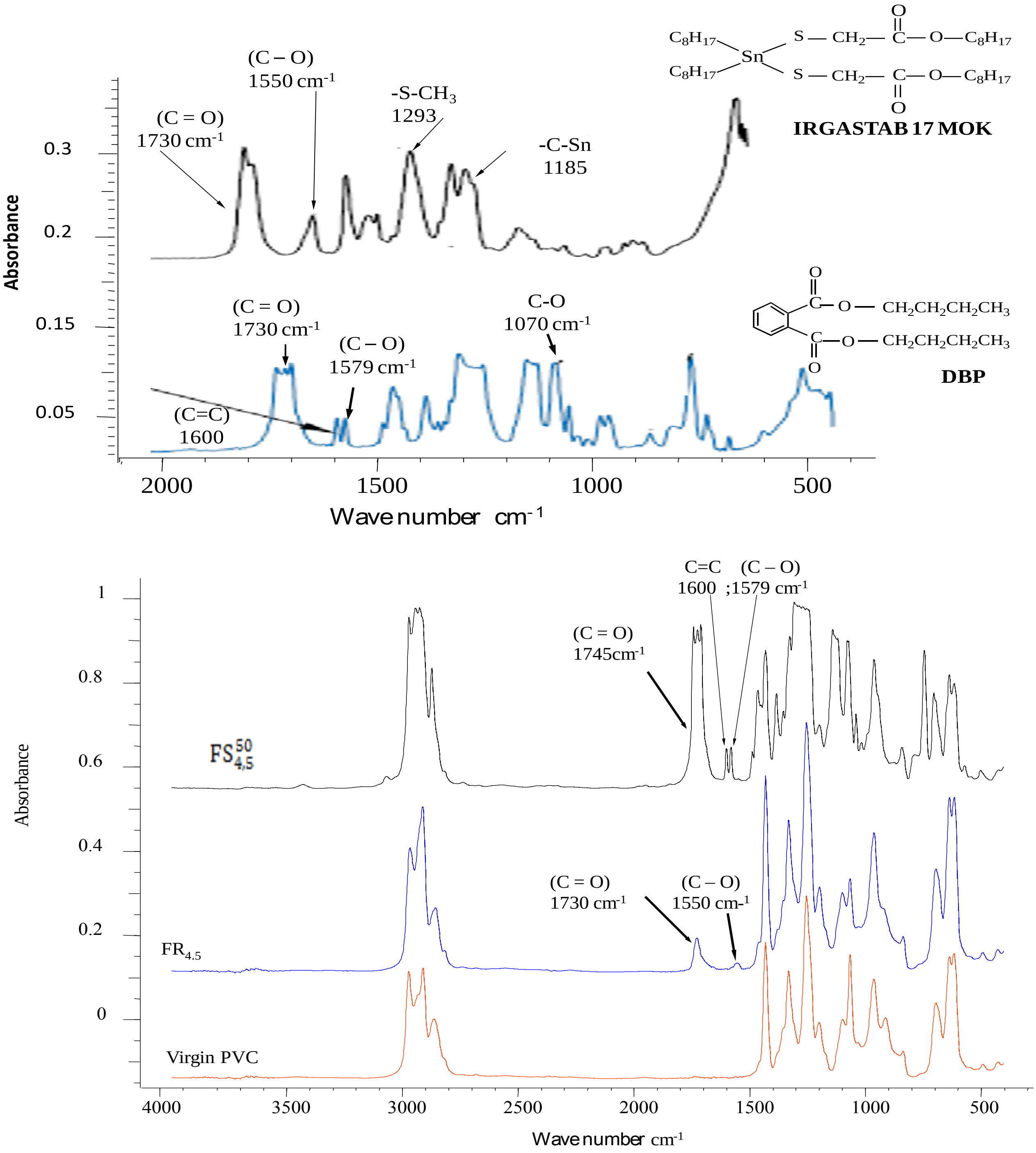

**Figure 1.** IRTF Spectrum rigid ($FR_{4.5}$) and plasticized PVC films.

Then modification of common and specific absorption bands area of additives after migration testing can be correlated to a phenomenon of plasticizer migration. Therefore, DBP migration would be observed by the regression specific band at 1579 $cm^{-1}$ (figure 2).

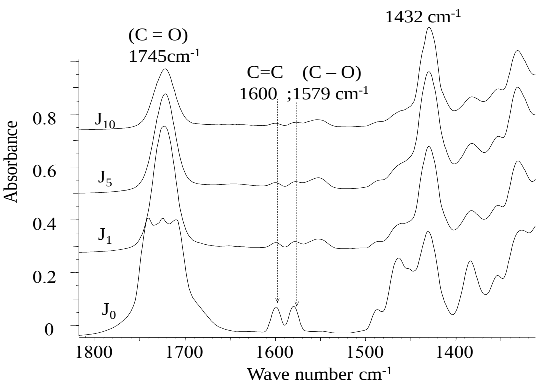

**Figure 2.** FTIR spectrum of plasticized PVC films in ethanol at 40°C.

A quantitative estimation of this additive migration was carried out. For that purpose the area's ratios $A_{1579}/A_{1432}$ 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 [8]. On the other hand, the migration kinetic of DBP was followed in ethanol and hexane by observing the increase GC chromatographic peak at 2.34 mn. The obtained rates of migration ($M_t/M_0$) are given in Figure 3, where $M_t$ and $M_0$ were migrated and initial DBP amounts, respectively.

It can be observed that the additive migration is related to the temperature. As it is mentioned in the literature, the migration is more important at higher temperatures [11-14]. It is obvious that the mobility of the migrant molecules increases with enhancement temperature, since the highest migration is obtained at 70 °C.

Indeed, in ethanol the gas chromatography and IRTF spectroscopy show that DBP migration exceeds 80 %. At 40°C, with the same analytical techniques, the results show that only 33.29 % and 60.85 % of DBP were lost, respectively.

To observe the effect of the liquid composition on the DBP diffusion from plasticized films , migration tests were carried out in hexane and ethanol for 10 days at 40 °C. Figure 4 shows that DBP migration rates detected by GC in ethanol and hexane are quite similar.

However, by FTIR we observe that DBP migration is more important in ethanol than hexane. It seems the ethanol and hexane penetrated the PVC films. The sorption of volatile solvents by polymeric films was already mentioned in literature [9, 10]. The presence of ethanol in the films could be observed by FTIR the development of the OH band in the films spectrum after migration tests at 40 or 70 °C (figure 5), so it is easy to control the desorption of ethanol by films drying.

With hexane, it is difficult to distinguish its characteristic bands since they overlap with PVC. Therefore, the real migration of DBP would be hidden in hexane.

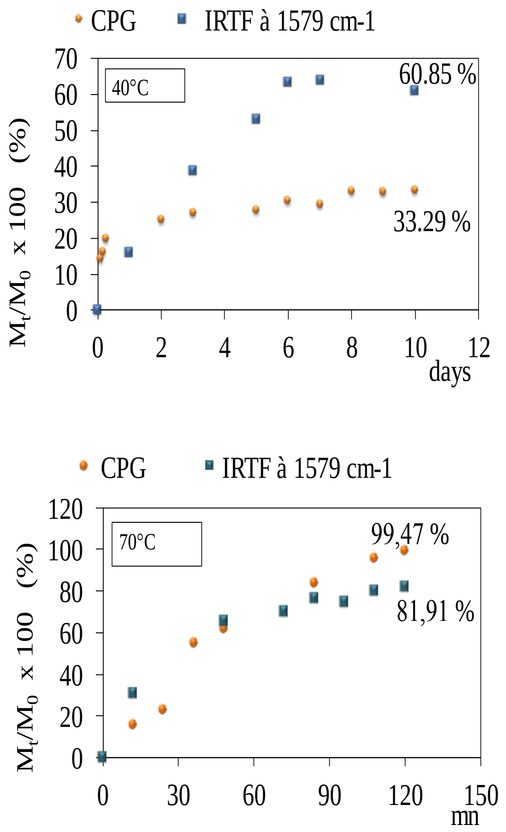

**Figure 3.** Migration kinetic of DBP in ethanol with for 2 hours at 70°C and 10 days at 40°C.

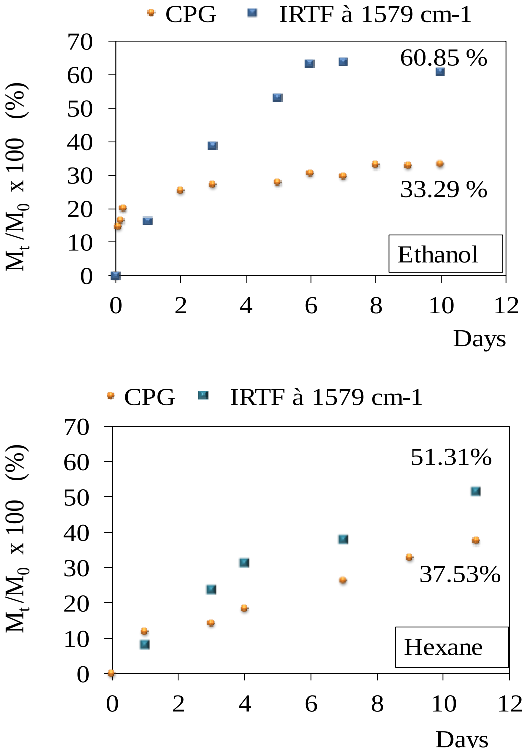

**Figure 4.** Migration kinetic of DBP in ethanol and hexane with for 10 days at 40°C.

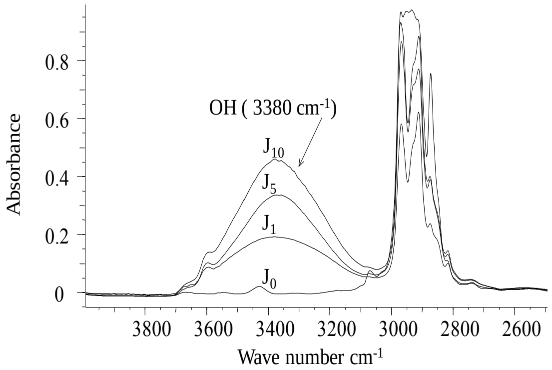

**Figure 5.** FTIR spectrum of in ethanol for 10 days at 40°C

### 3.2 IRGASTAB 17 MOK migration: UV-Visible at 490 nm investigation

The specific migration of heat stabilizer IRGASTAB 17 MOK was carried out in hexane at 40 °C with the plasticized films and rigid $FR_x$ (x: 0.75; 1.5; 2.5; 3.5 and 4.5). As shown in Figure 6 migration rates (%) obtained increase with IRGASTAB 17 MOK concentration in rigid and plasticized films according to literature data [9, 11-14].

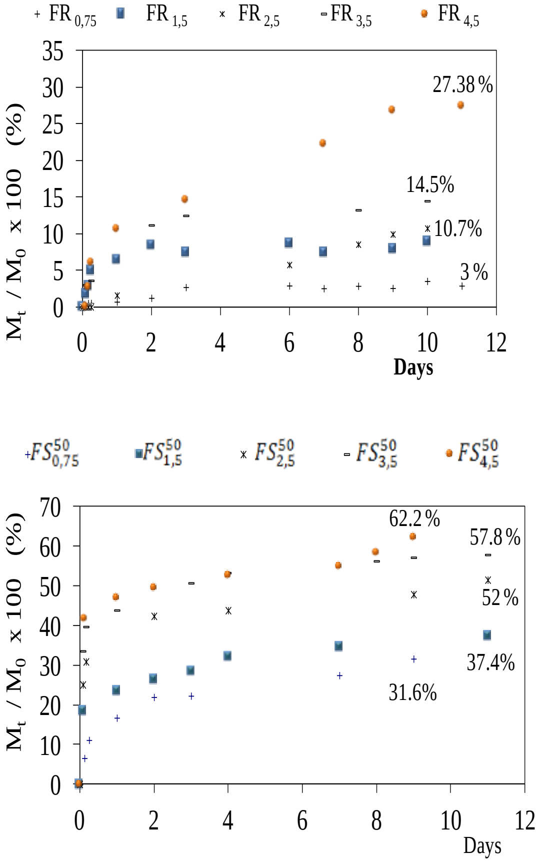

**Figure 6.** Migration kinetic of IRGASTAB 17MOK in hexane with $FR_x$ rigid and plasticized at 40°C.

The presence of the plasticizer in films accelerates heat stabilizer migration [9, 11, 12, 14], obtained rates migration were 2.25 times higher than rigid films $FR_{4.5}$.

For heat stabilizer concentrations between (x: 1.5; 2.5 and 3.5%), plasticized films rates diffusion were 4 times greater than rigid films $FR_x$.

## 4. Conclusion

The study of DBP migration was carried by GC and FTIR spectroscopy in ethanol and hexane at 40 °C and 70 °C with . Rates migration obtained at 70 °C are higher than 40°C in ethanol. IRTF spectroscopy could substitute gas chromatography. The results obtained by gas chromatography are quite similar. In hexane and ethanol at 40 °C and they are lower than FTIR spectroscopy. Increasing temperature, heat stabilizer concentration and the presence of the plasticizer in the films accelerate migration.

Gas chromatography could be substituted by FTIR spectroscopy to investigate the DBP migration phenomena. It is a simple, low cost and rapid method which can be used.

## References

1. R.J. Crawford, *Plastics Engineering*, Press, 2nd ed., Pergamon, Belfast, 1987
2. J. Bost, *Matières Plastiques*, Chimie- Applications, Tech&Doc-Lavoisier, 1985
3. M. Bisson, J.G Bureau, G.;Gay, S. Joachim, G. La Croix, J.P. Lefevre, M.P Strub, S. Tissot, *INERIS-Fiche de données toxicologiques et environnementales des substances chimiques, oxyde de tributyle étain* 2005, Version N°2-1
4. S. Hill, B. Shaw and Clin, A.Wu. Chim. Acta **304** 1 (2001)
5. N.H. Stoffers , R. Brandsch, E. L. Bradley, I. Cooper, M. Dekker, A. Störmer, R. Franz, Food Additives and Contaminants **22** 173 (2005)
6. V. Alexeev, *Analyse qualitative*, MIR, Moscou, 1980
7. G. Charlot, *Dosages absorptiométriques des éléments minéraux*, Masson, Paris, 1978
8. G. Socrates, *Infrared characteristic group frequencies*, Wiley publication, New York, 1980
9. M. Vergnaud, *Liquid transport processes in polymeric materials, Modeling and Industrial applications*, Prentice Hall, Englewood Cliffs, New Jersey, 1992
10. C. Sammon, J. Yarwood, N. Everall, Polymer **41** 2521 (2000)
11. C. Zeddam and N. Belhaneche-Bensemra, J. Polymeric Materials **59** 318 (2010)
12. N. Belhaneche-Bensemra, C. Zeddam, S Ouahmed, Macromol. Symp. 180 (2002)
13. A. Feigenbaum, *Evaluation de la migration des matériaux plastiques au contact des aliments par des méthodes alternatives, L'emballage des denrées alimentaires de grandes consommations*, Technique & Documentation Lavoisier, Paris, 1998
14. M.O. Boussoum, D. Atek, N. Belhaneche-Bensemra, Polym. Degrad. Stab 579 (2006)