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Kinetic model of the evaporation process of benzylbutyl phthalate from plasticized poly(vinyl chloride)

Željko Mrklić [a], Davor Rušić [b], Tonka Kovačić [c],*

[a] *Department of Chemistry, Faculty of Natural Sciences, Mathematics and Education, Nikole Tesle 12, 21000 Split, Croatia*
[b] *Department of Chemical Engineering, Faculty of Chemical Technology, Nikole Tesle 10, 21000 Split, Croatia*
[c] *Department of Organic Chemical Technology, Faculty of Chemical Technology, Nikole Tesle 10, 21000 Split, Croatia*

Abstract

The kinetic model of the physical process of evaporation of plasticizer from plasticized PVC foils was developed from the results of isothermal thermogravimetric investigation of evaporation of benzyl-butyl phthalate in the temperature range 120–150 °C under nitrogen flow. The kinetic parameters were estimated by integral method of analysis. Mathematical modeling of the kinetic of plasticizers evaporation was performed on the basis of function $c = f(T, t)$ and kinetic equation of evaporation $-dc/dt = f(T, c_0, c(t))$. The developed mathematical model was described by the general kinetic equation $-dc/dt = (k_r \exp(k_p T)c_0 + k_q T + k_w)c(t)$. The differential quotients $\delta(-dc/dt)/\delta T = f(T, c_0, c(t)) = f(T, c_0, t)$ and $\delta(-dc/dt)/\delta c_0 = f(T, c(t)) = f(T, c_0, t)$ were performed, and mathematical definition of the changes of the evaporation rate constant with the change of temperature and the change of the initial plasticized concentration were discussed.
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Keywords: Evaporation process; Kinetic model; Plasticized polymer

1. Introduction

The loss of additives in general, and likewise of plasticizers from plasticized polymers, can occur during the process of plasticizing and processing and continue during the product use, which considerably affects the quality of finished articles as well as the durability of the product. The loss of additives, as a physical process [1–6], goes on through two simultaneous processes: the interfacial mass transport between the polymer and the surrounding medium and the transport in the bulk of a polymer to the surface, i.e. the diffusion process. The first process can take place through the processes of evaporation, extraction, and migration.

The rate of evaporation of plasticizer from the polymer surface is defined as the function of temperature and current concentration of the additive in polymer material. If the process of evaporation is slower than the diffusion of additive through the polymer matrix, then the rate of evaporation is a linear function of concentration. In case the process of evaporation is controlled by the additive diffusion through the polymer matrix, this dependence becomes non-linear. The diffusion process is described by Fick's law of diffusion.

The process of evaporation of plasticizer from poly(vinyl chloride) (PVC) surface follows the kinetic laws of the first order reaction; the function $-(dc/dt) = kc(t)^n$ is linear, i.e. $n = 1$ [7,8]. This process, as it is slower than diffusion ($n \neq 1$), determines the kinetics of the plasticizer's weight loss. On the basis of these experimental cognition, obtained through the investigation of evaporation of various types of plasticizers from PVC foils, a kinetic model of physical process of evaporation of plasticizers from plasticized PVC was developed. The aim of this work was considering and mathematical defining of all the factors affecting the kinetics of that process. The analysis of kinetic parameters was done by integral method, on the example of evaporation of benzylbutyl phthalate (BBP) plasticizer.

2. Developing the kinetic model

The model implies that the volatility rate of plasticizer from the plasticized polymer is a function of three variables: temperature, initial concentration, and residual concentra-

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* Corresponding author.
E-mail address: kovacic@ktf-split.hr (T. Kovačić).

tion of plasticizer [8]. The following kinetic model is suggested:

$$-\frac{dc}{dt} = f(T, c_0)c(t)^n \qquad (1)$$

where T is the thermodynamic temperature; c_0, the initial concentration of plasticizer in the plasticized polymer; $c(t)$, the residual concentration of plasticizer; t, the time of evaporation; and n is the kinetic parameter.

If the process of evaporation is realized in the conditions $f(T = \text{constant}, c_0)$, the kinetic model (1) develops into the form:

$$-\frac{dc}{dt} = (k_0 c_0 + q)c(t)^n \qquad (2)$$

where parameters k_0 and q depend on temperature. For the parameter k_0, an exponential analytical form is anticipated:

$$k_0(T) = k_r \exp(-k_p T) \qquad (3)$$

while for the parameter q linear analytical form is anticipated:

$$q(T) = k_q T + k_w \qquad (4)$$

The variable time, t, is introduced into kinetic model (1) when knowing the dependence of the concentration change of plasticizer in the plasticized polymer during the process of evaporation, i.e.

$$c(t) = c_0 \exp(-kt) \qquad (5)$$

In order to achieve a complete description of the evaporation kinetics, the total differential is suggested:

$$\frac{\partial(-dc/dt)}{\partial T \partial(c_0)} = \frac{\partial(-dc/dt)}{\partial T} + \frac{\partial(-dc/dt)}{\partial c_0} \qquad (6)$$

This differential provide an insight into the laws of the change of volatility rate of plasticizer from the plasticized polymer by temperature change and the initial concentration change.

Substituting the functions (3) and (4) into kinetic model (2), volatility rate is obtained depending on temperature and residual concentration of plasticizer, by which the above total differential (6) is mathematically formulated to the full:

$$\frac{\partial(-dc/dt)}{\partial T \partial(c_0)} = \frac{\partial((k_r \exp(k_p T) + k_q T + k_w)c(t)^n)}{\partial T}$$
$$+ \frac{\partial((k_r \exp(k_p T) + k_q T + k_w)c(t)^n)}{\partial c_0} \qquad (7)$$

Substituting the function (5) into (7) the variable t is being introduced.

To estimate the parameters k_0, q, k_r, k_p, k_q, and k_w in the expressions (2)–(5), the procedures of linear and non-linear regression were used [9,10].

3. Experimental

Experimental investigations were carried out on the foils prepared from commercial PVC polymerized in mass (Polikem, Zadar, Croatia) mixed with the 9.9, 19.7, 30.4, and 36.1 wt.% of benzylbutyl phthalate (Bayer, Germany) and with 1 wt.% of thermal stabilizer, modified butyl-stannic mercaptide (BTF-80).

The evaporation of BBP from plasticized PVC foils (PVC/BBP) was studied by the method of isothermal thermogravimetry (Perkin-Elmer TGS with TADS Microprocessor) in the temperature range 120–150 °C, under nitrogen flow of 30 cm^3/min, as described in detail in the previous work [8].

4. The results of verification model and discussion

To verify the suggested model the results of experimental investigations of the evaporation process of BBP plasticizer from PVC/BBP were used, as shown in Table 1 (the accuracy was ±0.0001). It is assumed that for the investigated PVC/BBP foils, 0.1 ± 0.003 mm thick, the value of the kinetic parameter n equals 1. By this, the kinetic model (1) becomes a linear differential equation, which integrates to

$$-\ln\left(\frac{c(t)}{c_0}\right) = f(T, c_0)t \qquad (8)$$

and using the experimental data: $c(t) = c_0 - c$ versus t, were c is the amount of evaporated plasticizer, the kinetic parameter $f(T, c_0)$ was estimated.

Fig. 1 shows an integral method of determining the parameters of kinetic model (1). Calculated results are given in Table 2; the relevant correlation coefficients were 0.9915–0.9998. The linear dependence of data $-\ln(c(t)/c_0) - t$, confirms the accuracy of the assumption that the numerical kinetic parameter n equals 1. Numerical amounts of the parameters $f(T, c_0)$ and n enable the estimate of the parameters k_0, q, k_r, k_p, k_q, and k_w from the kinetic model (2), and functions (3) and (4).

The defining of the relation between the parameter $f(T = \text{constant}, c_0)$ and the initial concentration of BBP plasticizer in PVC/BBP, c_0, at $T = 120$, 130, 140, and 150 °C was carried out on the basis of graphic description of the data in Fig. 2.

Approximate lines indicate the linear function form dependence of $f(T = \text{constant}, c_0)$ parameter on the initial concentration c_0

$$f(T = \text{constant}, c_0) = k_0 c_0 + q \qquad (9)$$

The results of the estimate of parameters k_0 and q by linear regression, as well as the relevant correlation coefficients, R^2, are given in Table 3. The model anticipates the temperature dependence of parameters k_0 and q according to functions (3) and (4).

Table 1
Residual amount of plasticizer in time t

|	Residual amount of BBP, $c_0 - c$/mass fraction											
	10 min	20 min	30 min	40 min	50 min	60 min	70 min	80 min	90 min	100 min	110 min	120 min
$c_0{}^a = 0.099$												
120 °C	0.0990	0.0990	0.0989	0.0989	0.0988	0.0988	0.0988	0.0987	0.0987	0.0987	0.0986	0.0986
130 °C	0.0990	0.0989	0.0989	0.0988	0.0987	0.0986	0.0986	0.0985	0.0984	0.0983	0.0983	0.0982
140 °C	0.0990	0.0988	0.0986	0.0985	0.0983	0.0982	0.0981	0.0979	0.0977	0.0976	0.0975	0.0973
150 °C	0.0990	0.0986	0.0984	0.0981	0.0979	0.0976	0.0974	0.0972	0.0970	0.0969	0.0967	0.0965
$c_0 = 0.197$												
120 °C	0.1969	0.1968	0.1966	0.1965	0.1964	0.1963	0.1962	0.1960	0.1959	0.1958	0.1957	0.1966
130 °C	0.1969	0.1966	0.1963	0.1961	0.1959	0.1956	0.1954	0.1951	0.1949	0.1947	0.1945	0.1943
140 °C	0.1967	0.1962	0.1957	0.1953	0.1949	0.1944	0.1940	0.1936	0.1932	0.1928	0.1924	0.1920
150 °C	0.1963	0.1953	0.1944	0.1966	0.1928	0.1920	0.1911	0.1904	0.1897	0.1890	0.1882	0.1875
$c_0 = 0.304$												
120 °C	0.3039	0.3037	0.3034	0.3030	0.3027	0.3024	0.3021	0.3018	0.3015	0.3012	0.3009	0.3006
130 °C	0.3036	0.3030	0.3025	0.3019	0.3014	0.3008	0.3003	0.2997	0.2992	0.2986	0.2981	0.2976
140 °C	0.3033	0.3023	0.3013	0.3004	0.2994	0.2985	0.2975	0.2966	0.2958	0.2949	0.2940	0.2931
150 °C	0.3024	0.3004	0.2984	0.2965	0.2946	0.2928	0.2910	0.2893	0.2876	0.2859	0.2835	0.2827
$c_0 = 0.361$												
120 °C	0.3607	0.3606	0.3602	0.3598	0.3594	0.3590	0.3587	0.3582	0.3578	0.3575	0.3571	0.3588
130 °C	0.3608	0.3600	0.3592	0.3585	0.3578	0.3571	0.3564	0.3558	0.3550	0.3544	0.3537	0.3531
140 °C	0.3602	0.3587	0.3572	0.3558	0.3544	0.3530	0.3517	0.3504	0.3489	0.3476	0.3463	0.3451
150 °C	0.3589	0.3562	0.3537	0.3514	0.3491	0.3469	0.3447	0.3426	0.3405	0.3384	0.3363	0.3344

[a] Initial amount of BBP.
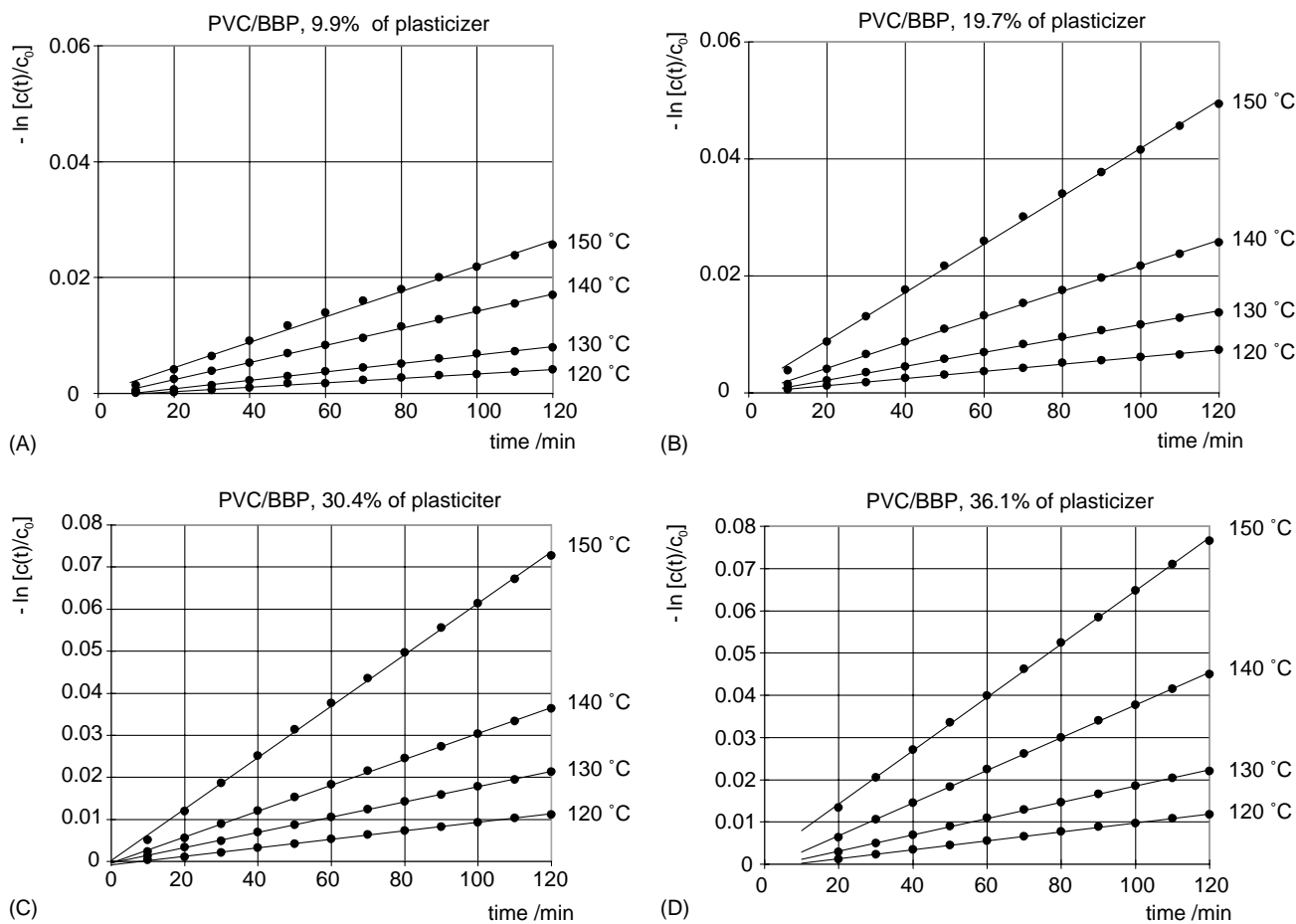
Fig. 1. Estimation of parameters $f(T,c_0)$ and n from the kinetic model (1) by integral method from the Eq. (8), for the initial concentrations of BBP in PVC/BBP: (A) 9.9%, (B) 19.72%, (C) 30.4%, and (D) 36.1%.

Table 2
The values of parameter $f(T,c_0)$

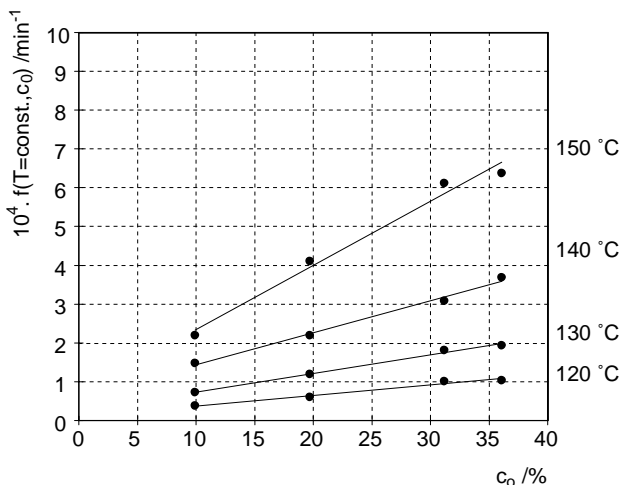| Initial concentration of BBP (c_0 (wt.%))	$10^4 f(T,c_0)$ (min^{-1})			
	120 °C	130 °C	140 °C	150 °C
9.90	0.38	0.73	1.48	2.19
19.7	0.61	1.19	2.19	4.05
30.4	1.01	1.81	3.08	6.12
36.1	1.04	1.94	3.69	6.38

Fig. 2. Dependence of the parameter $f(T,c_0)$ from kinetic model (1), for T = constant (120, 130, 140, and 150 °C), on the initial concentration of BBP in PVC/BBP.

Table 3
The values of the parameters k_0 and q

Temperature(°C)	$10^6 k_0$ (% min)$^{-1}$	$10^5 q$ (min^{-1})	R^2
120	2.72	1.06	0.9791
130	4.83	2.55	0.9940
140	8.95	5.09	0.9908
150	16.70	6.97	0.9832

To estimate the parameters from function (3), the relation between the parameter k_0 and temperature was investigated. The graphic description of these data is given in Fig. 3. Approximate curve indicates the following exponential function:

$$k_0(T) = k_r \exp(k_p T) \tag{10}$$

The estimate results of parameters k_r and k_p, by the method of linear regression (R^2 = 0.9996), are given in Table 4.

Table 4
The values of the parameters k_r, k_p, k_q, and k_w

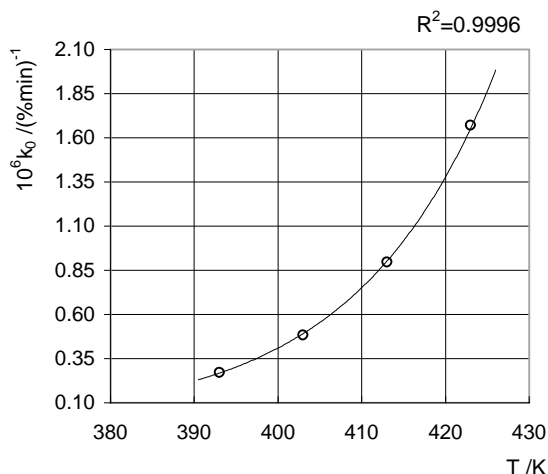| $10^{16} k_r$ (% min)$^{-1}$	$10^2 k_p$ (K^{-1})	$10^6 k_q$ (min K)$^{-1}$	$-10^4 k_w$ (min^{-1})
1.2	6.06	1.95	7.57

Fig. 3. Dependence of the parameter k_0 on temperature.

To estimate the parameters from function (4) the relation between the parameter q and temperature, T is investigated. The dependence of these parameters is graphically shown in Fig. 4.
Approximate line indicates a linear function:

$$q(T) = k_q T + k_w \tag{11}$$

The results of the estimate of parameters k_q and k_w, with R^2 = 0.990, are given in Table 4.

The parameters of function (5) can be determined from the relation of residual concentration, $c(t)$ and pertaining time, t, during the process of evaporation at T = 120, 130, 140, and 150 °C. But, in the case $n = 1$, function (5) represents the integral of the kinetic model (1), i.e. an explicit form of the implicit function (8), i.e.

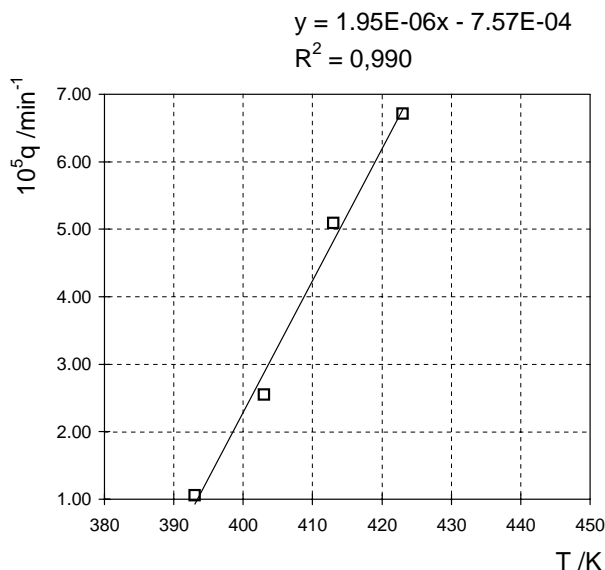$$c(t) = c_0 \exp(-f(T, c_0)t) \tag{12}$$

Fig. 4. Dependence of the parameter q on temperature.

By this, parameter k from function (5) has the same numerical amount as parameter $f(T,c_0)$ shown in Table 2.

The estimated parameters: k_0, q, k_r, k_p, k_q, and k_w, from Table 4, enable the defining of total differential (7), from which the change of volatility rate of plasticizer BBP from BBP/PVC with temperature change, $\partial(-\mathrm{d}c/\mathrm{d}t)/\mathrm{d}T$, and

with the initial concentration change $\partial(-\mathrm{d}c/\mathrm{d}t)/\mathrm{d}c_0$ is observed.

Taking into account the value of the kinetic parameter $n = 1$, the first differential quotient from (6): $\partial(-\mathrm{d}c/\mathrm{d}t)/\partial T = f(T, c_0, c(t))$ or $\partial(-\mathrm{d}c/\mathrm{d}t)/\partial T = f(T, c_0, t)$ (the variable $c(t)$ is substituted with t through
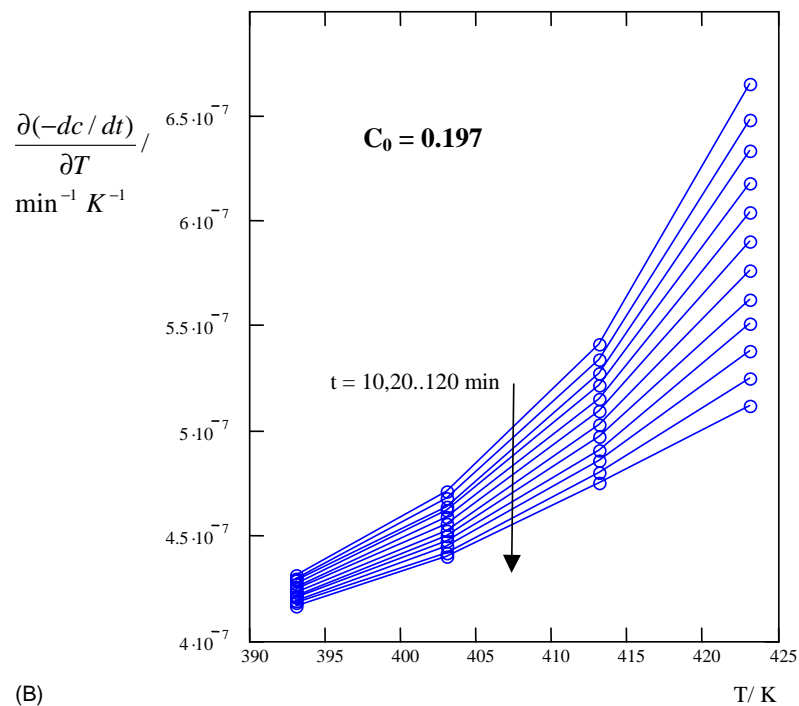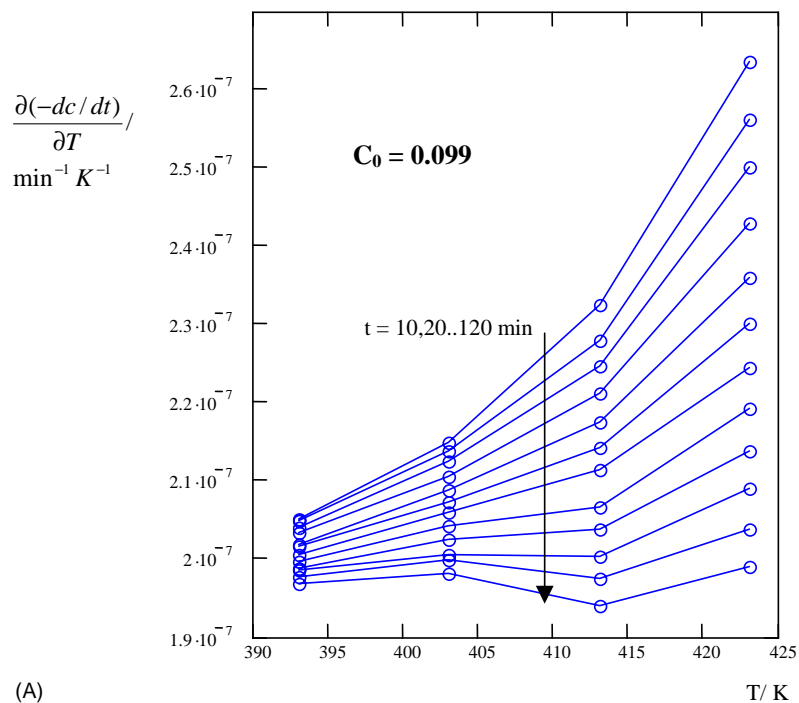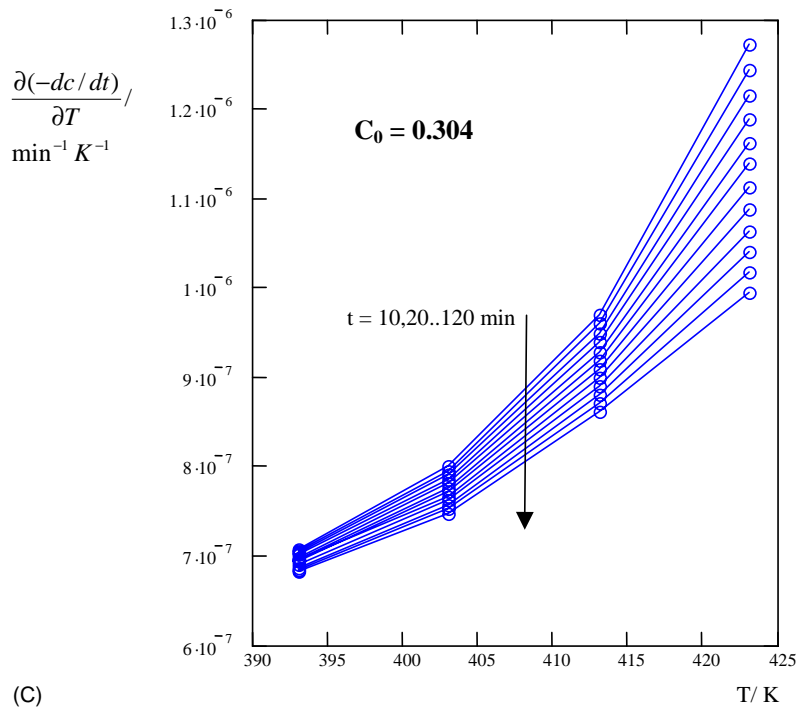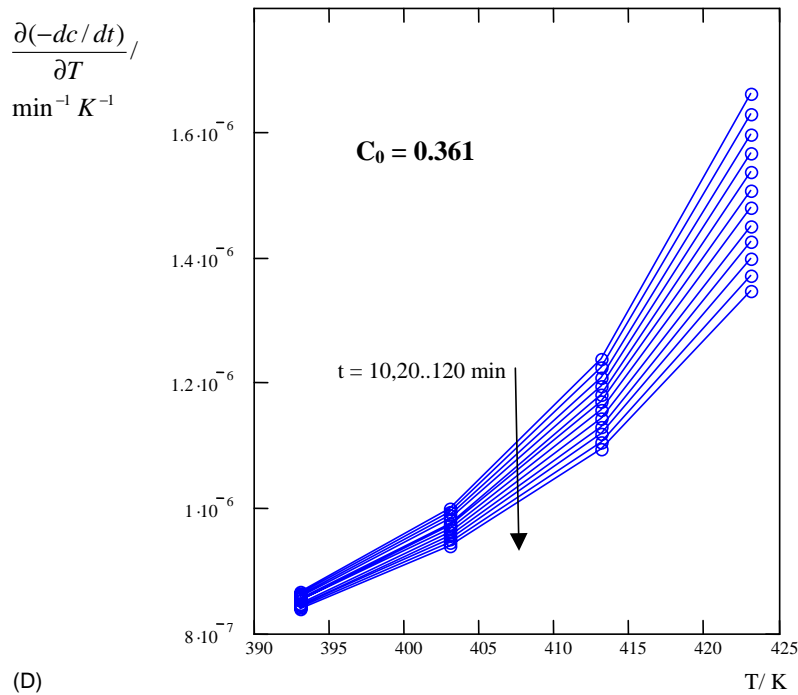

Fig. 5. Dependence of the change of volatility rate of BBP from PVC/BBP on temperature change, for the initial ratio of BBP: (A) 0.099, (B) 0.193, (C) 0.304, and (D) 0.361.

$$\frac{\partial(-dc/dt)}{\partial T}/ \min^{-1} K^{-1}$$

$C_0 = 0.304$

t = 10,20..120 min

(C)

$$\frac{\partial(-dc/dt)}{\partial T}/ \min^{-1} K^{-1}$$

$C_0 = 0.361$

t = 10,20..120 min

(D)

Fig. 5. (*Continued*).

function (5)) becomes a linear function of residual concentration or a exponential function of time. After substitution the numerical amounts of parameters from Table 4 it follows

Differentials (13) indicate that it is possible to investigate the change of volatility rate of plasticizer by temperature change, dependent on residual concentration of plasticizer or dependent on the time of evaporation process.

$$\frac{\partial(-\mathrm{d}c/\mathrm{d}t)}{\partial T} = \frac{\partial((1.2 \times 10^{-16}\exp(0.06T)c_0 + 1.95 \times 10^{-6}T + 7.57 \times 10^{-4})c(t))}{\partial T}$$
$$= (7.2 \times 10^{-18}\exp(0.06T)c_0 + 1.95 \times 10^{-6})c(t) = (7.2 \times 10^{-18}\exp(0.06T)c_0 + 1.95 \times 10^{-6})c_0\exp(-kt) \quad (13)$$

According to differential (13), the data $\delta(\mathrm{d}c/\mathrm{d}t)/\delta T - T$ at $t = 10$, 20–120 min and $c_0 = 0.099, 0.197, 0.304$, a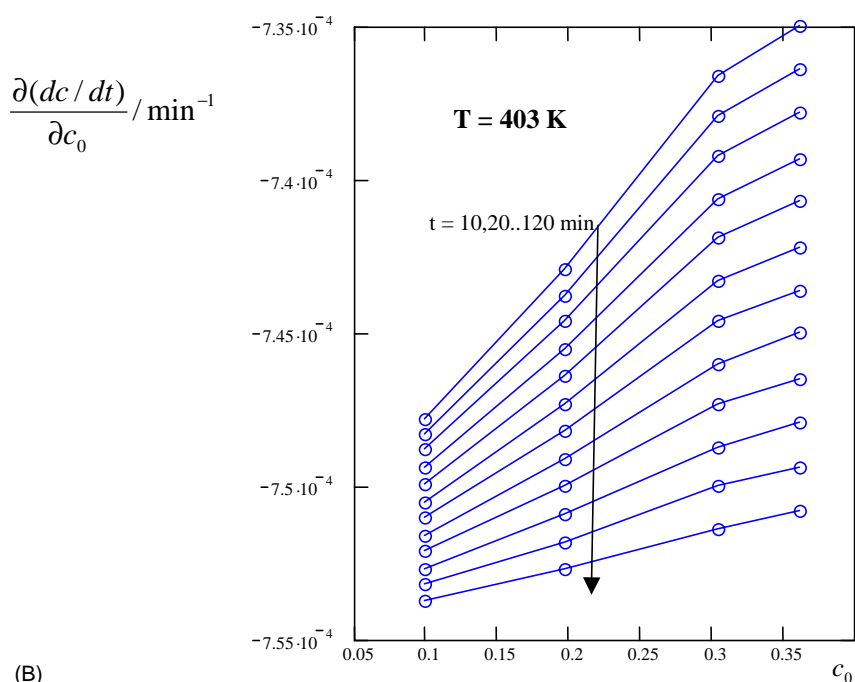nd 0.361, with the appropriate values of parameter k from function (5) (i.e. $f(T,c_0)$ in Table 2) are graphically shown in Fig. 5.

By analogy to the above first differential quotient, the second differential quotient from (6), i.e. $\partial(-\mathrm{d}c/\mathrm{d}t)/\partial c_0 = f(T, c(t))$ or $\partial(-\mathrm{d}c/\mathrm{d}t)/\partial c_0 = f(T, c_0, t)$ is defined as

$$\frac{\partial(-\mathrm{d}c/\mathrm{d}t)}{\partial c_0} = \frac{\partial((1.2 \times 10^{-16} \exp(0.06T)c_0 + 1.95 \times 10^{-6}T + 7.57 \times 10^{-4})c(t))}{\partial c_0}$$

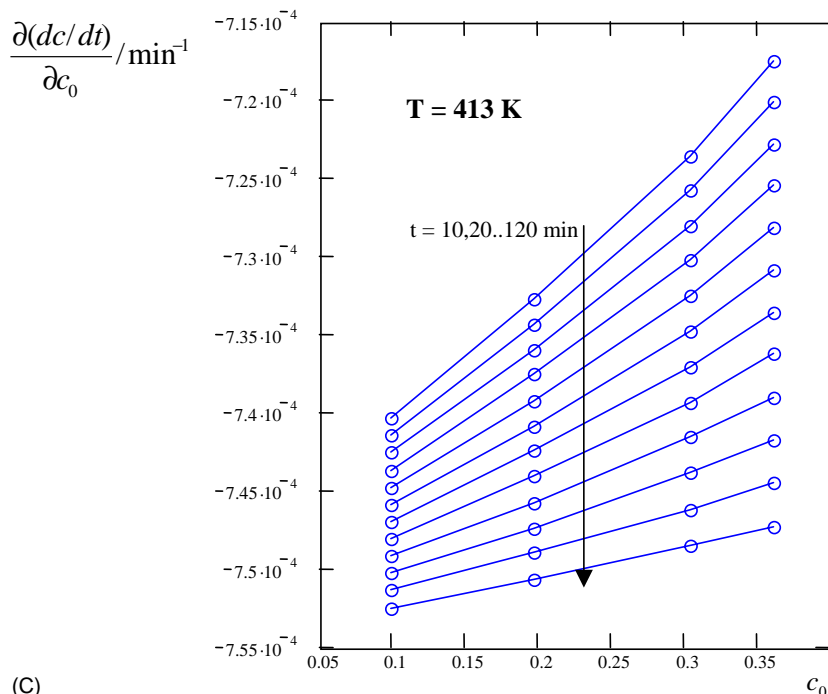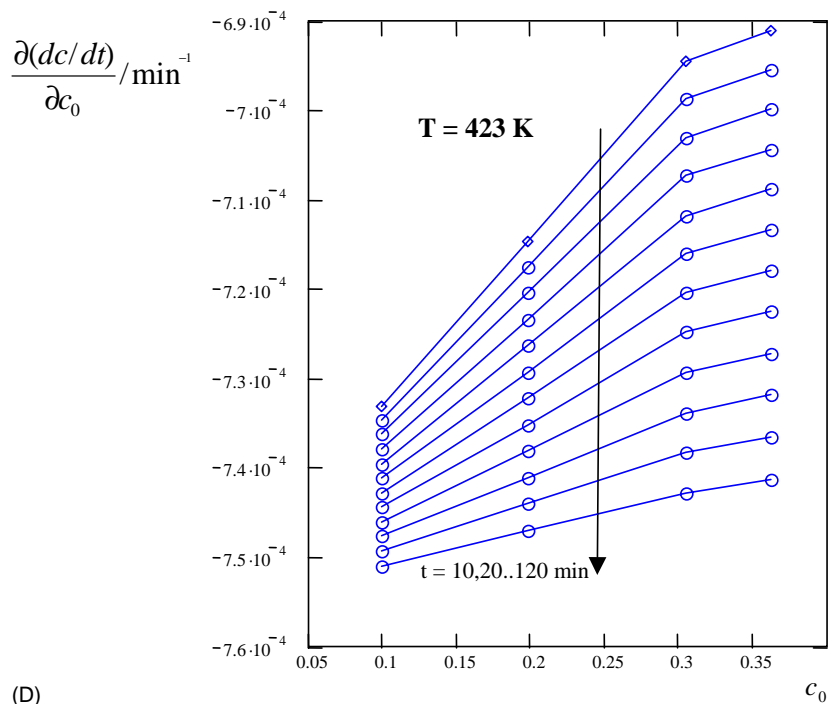$$= (1.2 \times 10^{-16} \exp(0.06T)c(t) = (1.2 \times 10^{-16} \exp(0.06T)c_0 \exp(kt) \qquad (14)$$
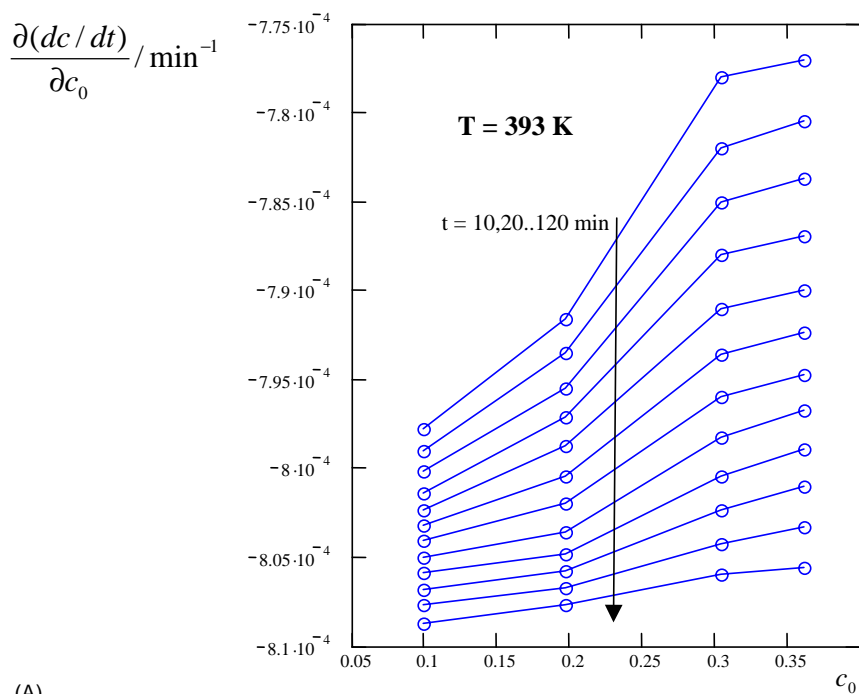
Fig. 6. Dependence of the change of volatility rate of BBP from PVC/BBP on the initial concentration change: (A) 120 °C, (B) 130 °C, (C) 140 °C, and (D) 150 °C.

$$\frac{\partial(dc/dt)}{\partial c_0}/\text{min}^{-1}$$

T = 413 K

t = 10,20..120 min

(C)

$$\frac{\partial(dc/dt)}{\partial c_0}/\text{min}^{-1}$$

T = 423 K

t = 10,20..120 min

(D)

Fig. 6. (*Continued*).

From differential (14) it is evident that the change of volatility rate with the change of the initial concentration depends on temperature and residual concentration (third term of identity). After the substitution of variable $c(t)$ with variable t, through function (5), the variable c_0 appears as well (fourth term of identity). Analyzing the third term, it is possible to state that it also depends on variable c_0. Namely, numerical value of variable $c(t)$ at the beginning

of evaporation process, at $t = 0$, numerically corresponds to the initial concentration of plasticizer in the plastcized polymer, c_0.

The data $\delta(dc/dt)/\delta c_0 - c_0$ at $t = 10$, 20–120 min, with the appropriate values of parameter k from function (5) (i.e. $f(T,c_0)$ in Table 2), for the investigated temperature conditions ($T = 120$, 130, 140, and 150 °C), are graphically shown in Fig. 6.

Consequently, by experimentally investigating volatility process of BBP from PVC/BBP, mathematical formulations which can be applied for describing kinetic occurrences in the system plasticizer–plasticized polymer are verified. The application of the suggested kinetic model on investigated system indicate that the kinetics of the process of BBP loss from plasticized PVC is determined by the evaporation of plasticizer from the surface, being a slower process, and that diffusion does not affect the process of BBP loss from the foils of the investigated thickness. Furthermore, it has been established that, at all initial concentrations, the values $\delta(-dc/dt)/\delta T$ rise with the rise of temperature. This is expected, because the kinetic energy of molecules in the system also rises. Increasing the initial concentration of plasticizer from 9.9 to 36.1%, the span between the curves narrows (Fig. 5). It can be also noticed that the values $\delta(-dc/dt)/\delta T$ are greater at the greater initial concentrations of plasticizer in plasticized polymer. When investigating the concentration effect of plasticizer on the rate of volatility, the values $\delta(-dc/dt)/\delta c_0$ increase with the increase of the initial concentration, and decreases with the increase of the time of heating (Fig. 6).

The established mathematical model of volatility kinetics can be compared with the kinetic model for the evaporation of light-stabilizers from polypropylene, as suggested by Luston et al. [11,12]. This model is acceptable only for the case of linear dependence of volatility rate on residual concentration, i.e. when the process of diffusion does not affect the rate of volatility. If the foils of plasticized polymer are of sufficient thickness, then, due to the impact of diffusion, non-linear relation between volatility rate and residual concentration of plasticizer in plasticized polymer can be expected.

In this work, the suggested model enables the implementation of kinetic analysis of evaporation process even in the case when diffusion processes affect the evaporation of plasticizer from plasticized polymer. Besides, the model gives an insight into the impact of temperature and initial concentration of plasticizer in plasticized polymer on the rate of volatility. This enables the anticipation of temperature condition at which the plasticized polymer can be exposed, with the volatility rate within controlled limits. Likewise, one gets an insight into the choice of the initial concentration of plasticizer for the predetermined change of the volatility rate.

Therefore, the developed mathematical laws of the impact of these two parameters on the rate of volatility, disregarding the inability of determining the conditions of minimal volatility due to the nature of the system, enable the choice of optimal ratio of plasticizer in plasticized polymer for the predetermined temperature conditions.

5. Conclusion

Mathematical model of the kinetics of evaporation of plasticizers was developed on the experimental data of loss of BBP plasticizers from PVC/BBP plasticized polymer. Developing the kinetic function $-dc/dt = f(T, c_0)$, a general kinetic equation of plasticizers volatility was carried out, which enables to control the rate of plasticizers volatility with temperature change and the initial concentration change, for a certain period of evaporation process. The change of volatility rate of plasticizer due to the change of temperature depends on the initial concentration of plasticizer and its residual concentration in plasticized polymer. The change of volatility rate with the change of the plasticizer's initial concentration is approximately the same, without regard to the temperature at which the plasticizer is heated, and it depends on residual concentration of plasticizer in plasticized polymer.

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