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A shrinking core model for the alkaline hydrolysis of PET assisted by tributylhexadecylphosphonium bromide

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ABSTRACT

The kinetics of the alkaline hydrolysis of PET in an aqueous slurry assisted by tributylhexadecylphosphonium bromide as suitable phase transfer catalyst was studied at temperatures ranging from 60 to 80 °C. The results were adequately described by an unreacted shrinking core model that was first order with respect to sodium hydroxide concentration, quaternary salt concentration, and particle surface area and, hence, to the remaining particle mass raised to the 2/3 power. Temperature effects for both catalytic and non-catalytic steps were modelled with an Arrhenius equation resulting in activation energy values of 61–63 kJ mol^{-1}, thereby suggesting a similar mechanism for the alkaline hydrolysis with or without phase transfer catalyst. Hence, the notable enhancement in reaction rate observed when using the selected quaternary salt was mainly attributed to an increase in the concentration of the reactive hydroxide anion in the liquid–solid boundary layer.

1. Introduction

Plastics are the main sources of non-biodegradable solid wastes, disposal of which is a major problem, although they make up only 6–7% by weight of the total solid waste. Furthermore, they occupy large amounts of space thus reducing the capacity of landfill areas and causing environmental pollution. Although incineration of waste polymers including PET aiming at the recovery of energy is currently the most effective strategy to reduce the volume of organic plastics, this method should be considered as ecologically unacceptable. In contrast chemical recycling is more appropriate according the principles of Sustainable Development. In this way the environment is not surcharged and there is no need for extra resources (monomers) for polymer production [1]. Over the last several decades, the process of recycling polymer waste has attracted the attention of many scientists working on this issue. Polymer recycling is very important for at least two main reasons: firstly, to reduce the ever increasing volumes of polymer waste coming from many sources (from daily life packaging materials and disposables) and secondly, to generate value-added materials from low cost sources by converting them into valuable materials similar, to some extent, to virgin materials.

Poly(ethylene terephthalate) (PET) is a thermoplastic saturated polyester produced by reacting monoethylene glycol (EG) with terephthalic acid (TPA) (or dimethyl terephthalate), which is widely used for manufacturing mainly textiles and bottles for packaging. PET is one of the polymers with the most growing market with an estimated expansion rate of 4–8% [2], so that the recycling of this material is an interesting field. PET indeed occupies the top of the list of polymers to be recycled due to its easy recycling by different ways, which, in accordance, give variable products that can be introduced as starting ingredients for the synthesis of virgin PET and many other polymers [3,4]. In this case the term 'depolymerisation' is used. PET can be chemically recycled or depolymerised by glycolysis, methanolysis, hydrolysis, aminolysis or ammonolysis [5]. Nowadays there is a growing interest in hydrolysis for the chemical recycling of PET, since it is the only method that leads to terephthalic acid and ethylene glycol. This recycling process meets the criteria of simplicity, low energy consumption, relatively low environmental impact, and recovery of materials that can be readily assimilated into the polymerisation technology. Hydrolysis can be carried out under (a) alkaline, (b) acid and (c) neutral conditions [6].

A recent study [7] has shown that certain quaternary salts (QX) acting as efficient phase transfer catalysts (PTCs) can markedly accelerate the reaction rate of the process under alkaline conditions, allowing the reaction to be carried out under milder conditions, especially in terms of temperature (lower than 100 °C). The role of these agents is to efficiently transport the hydroxide

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Nomenclature

c	integration parameter
C_{NaOH}	concentration of sodium hydroxide (mol m^{-3})
$C_{PET,0}$	initial concentration of PET repeating units (mol m^{-3})
C_{PET}	concentration of PET repeating units (mol m^{-3})
C_{QX}	concentration of the quaternary salt (mol m^{-3})
DSC	differential scanning calorimetry
$Ea_{(NO\text{-}QX)}$	activation energy of the non-catalytic reaction (kJ mol^{-1})
$Ea_{(QX)}$	activation energy of the QX-catalysed reaction (kJ mol^{-1})
EG	monoethylene glycol
k	pseudo-first order reaction rate constant (h^{-1})
$k_{APP.}$	apparent rate constant (m h^{-1})
$k_{NO\text{-}QX,0}$	pre-exponential factor of the $k_{NO\text{-}QX}$ rate constant (m h^{-1})
$k_{NO\text{-}QX}$	intrinsic non-catalytic depolymerisation rate constant (m h^{-1})
$k_{QX,0}$	pre-exponential factor of the k_{QX} rate constant (m^4 mol^{-1} h^{-1})
k_{QX}	intrinsic catalysed depolymerisation rate constant (m^4 mol^{-1} h^{-1})
M	NaOH:PET initial molar ratio
Na_2-TPA	disodium terephthalate
NMR	nuclear magnetic resonance
N_{PET}	number of moles of PET repeating unit (mol)
PET	poly(ethylene terephthalate)
PTC	phase transfer catalyst
Q^+	tributylhexadecylphosphonium cation
QOH	tributylhexadecylphosphonium hydroxide
QX	quaternary salt (tributylhexadecylphosphonium bromide)
$-r_{PET}$	overall reaction rate of PET alkaline hydrolysis (mol m^2 h^{-1})
R	radius of the unreacted PET particles (m)
R_0	initial radius of PET particles (m)
t	time (h)
T	temperature (°C, except in Arrhenius plots, K)
TPA	terephthalic acid
$W_{PET,0}$	initial weight (kg)
W_{PET}	weight of unconverted PET particles at a specific reaction time (kg)
X	fractional conversion of PET at a specific reaction time
z	integration parameter

Greek symbols

ρ_{PET}	molar density of PET (mol m^{-3})
υ	stoichiometric coefficient of NaOH in the reaction

anion from the aqueous phase to the organic phase (external surface of solid PET particles), thereby increasing the conversion. The most active quaternary salt was found to be tributylhexadecylphosphonium bromide. Other remarkably active quaternary salts have been reported elsewhere [8,9].

The phase transfer-catalysed hydrolysis of PET under alkaline conditions is a heterogeneous liquid (PTC)–liquid (aqueous alkali)–solid (PET particles) reaction. Taking into account that PET particles are virtually insoluble in the aqueous sodium hydroxide solution, the solid particles are nonporous and the depolymerised products are readily soluble, the relatively simple shrinking core model should capture the essence of the reaction mechanism [10,11]. Accordingly, the objective of this study reported herein is to develop an approximate model for the reaction kinetics of the alkaline hydrolysis in the presence of a soluble quaternary salt (tributylhexadecylphosphonium bromide).

2. Experimental

Uncoloured virgin PET granules (Aldrich Chemical Co.) with a mean particle size of 2×10^{-3} m were used. Granules were previously cut with a cryogenic rotary cutter (Retsch ZM 2000) to reduce the particle radius to 2.5×10^{-4} m. The experimental set-up for reaction experiments consisted of a 3×10^{-4}-m^3 capacity stainless steel batch reactor (Autoclave Engineers) [12]. The tank was equipped with a cooling coil, a thermometer pocket, a disk turbine impeller, an electric heating mantle, a digital temperature control system and a manometer. A nitrogen purge was used to create an inert atmosphere inside the vessel.

PET particles, aqueous sodium hydroxide solution, and the quaternary phosphonium salt (tributylhexadecylphosphonium bromide, supplied by the Aldrich Chemical Co.) were charged into the reactor at room temperature and then heated to the selected temperature. The selected operating conditions for alkaline hydrolytic experiments were stirring rate 6.7 Hz, particle radius 2.5×10^{-4} m, inert atmosphere 200×10^3 Pa N_2, temperature 60–80 °C, NaOH concentration 1666.7 mol m^{-3}, PET concentration 292.1 mol m^{-3}, and QX concentration 0–73 mol m^{-3}. The mixture was allowed to react for 1.5 (catalytic experiments) and 4 h (non-catalytic experiments). After the required time interval for reaction was reached, the vessel was quickly removed from the heating mantle and immersed in an ice bath so as to interrupt the progress of hydrolysis. Details of the experimental procedure for separation and quantitative analysis of the reaction products are given elsewhere [7], and schematically depicted in Fig. 1. Briefly, the reaction mixture was first filtrated to separate unconverted solid PET particles. Next, excess hydrochloric acid (1×10^4 mol m^{-3}) was added into the filtrate in order to provoke the precipitation of the terephthalic acid. After acidification the remaining liquid was essentially composed of ethylene glycol, the quaternary salt and water.

3. Results and discussion

PET particles were hydrolysed with sodium hydroxide in the presence of tributylhexadecylphosphonium bromide as phase transfer catalyst to yield the disodium salt (Na_2-TPA) and ethylene glycol according to the following liquid–solid chemical reaction:

$$\mathrm{PET(s) + 2NaOH(l) \xrightarrow{QX} Na_2\text{-}TPA(l) + EG(l)} \qquad (1)$$

Fig. 2 shows the influence of QX concentration (18, 36.5 and 73 mol m^{-3}) and reaction temperature (60, 70 and 80 °C) on PET conversion. For 1×10^{-2} kg of PET particles depolymerised in 1.5×10^{-4} m^3 of a 6.7% aqueous sodium hydroxide solution (NaOH:PET:QX molar ratio = 22.8:4:1 for $C_{QX} = 73$ mol m^{-3}) it was found, as expected, that conversion was promoted with increasing catalyst concentration and temperature. For example, at 80 °C about 95% conversion could be attained only after 1.5 h with a QX concentration as low as 73 mol m^{-3} (C_{QX}:$C_{PET,0}$ = 0.25). It was observed that the reaction also proceeded in the absence of phase transfer catalyst. Hence, 23% conversion was achieved for the non-catalysed reaction although the time required for complete hydrolysis would be about 10 h. In contrast, Kosmidis et al. [13] found a very low PET conversion (<2%) at this temperature. This difference could be probably attributed to different factors such as a lower NaOH

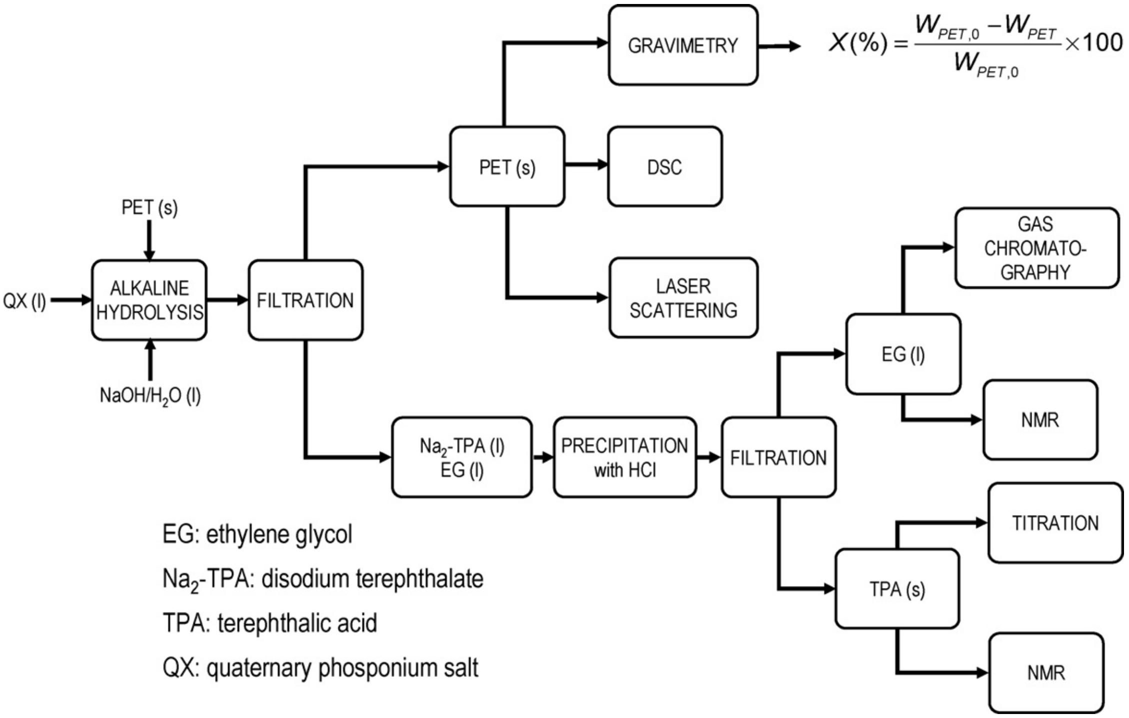

Fig. 1. Schematic diagram of the reaction and analytical procedure for the alkaline hydrolysis of PET.

concentration (5 wt%) and a larger size of the PET particles (about 1×10^{-3} m).

Pure and partially converted PET particles were characterised by differential scanning calorimetry (Mettler Toledo DSC 822e) at a heating rate of 10 °C min^{-1}. The results are presented in Fig. 3. In the DSC curve of PET before the reaction it was observed that the heating scan showed a glass transition temperature at 75 °C, a crystallization exotherm at around 115 °C, and a melting endotherm at about 250 °C [14]. As for residual PET particles large endothermic bands were also evident. The results of Figs. 2 and 3 suggested that the process of hydrolysis in sodium hydroxide solution occurred on the external surface of the particles, and these were lamellarly depolymerised with increasing reaction time. Apparently no endothermic bands below 200 °C were noticeable which could be related to the oligomers produced on the surface of PET particles during reaction [15]. Further, a decrease in the crystallization peak area was noted, and was related to the polymer exposition for increasing times at temperatures above the glass transition temperature during the reaction. These results were also consistent with the observed decrease in PET particle size with increasing conversion as revealed by laser scattering (Malvern Mastersizer X).

On the other hand, after the removal of the unreacted particles by filtration and subsequent neutralisation of the liquid phase and filtration again, the liquid obtained was analysed by gas chromatography (Agilent Technologies 6890N Network GC System) for organic products. Only ethylene glycol was found. This was further confirmed by ^{13}C NMR (Bruker AC-250). On the other hand, results from titration and ^{1}H NMR (Bruker AC-250) revealed that high purity TPA was the major solid product obtained after neutralisation.

Fig. 4 illustrates the basic premises of the mechanism of the phase transfer-catalysed reaction. It is hypothesised that an ion pair between the reaction anion (OH$^-$) and the onium cation (Q$^+$) is necessary to be formed (step 1). Next the cationic part of the catalyst (alkyl groups) carries the hydroxide anion into the surface of the organic phase by means an interfacial mechanism (step 2). In this way the PET macromolecules on the surface of the particles can be easily attacked by the OH$^-$ group and subsequently depolymerised (step 3). The terephthalate anion produced returns into the aqueous phase and forms the disodium terephthalate salt with the Na$^+$ cation. The reaction proceeds until complete depolymerisation of PET to Na$_2$-TPA and ethylene glycol, while the catalyst remains in the aqueous phase (step 4). The PTC is regenerated in its added form and the PTC cycle continues [13]. The overall reaction scheme is summarised by Eqs. (2) and (3).

$$\mathrm{NaOH} + \mathrm{QBr} \rightleftarrows \mathrm{QOH} + \mathrm{NaBr} \tag{2}$$

$$2\mathrm{QOH} + \mathrm{PET} + 2\mathrm{NaBr} \rightarrow \mathrm{EG} + \mathrm{Na_2\text{-}TPA} + 2\mathrm{QBr} \tag{3}$$

In order to describe the moving boundary process of PET depolymerisation kinetics with a depleting soluble product layer in the presence of a quaternary salt, the following assumptions and simplifications were used:

a) The depolymerisation of PET under alkaline conditions is a slow, isothermal process and overall hydrolysis is kinetically controlled.
b) The PET particles consist of isotropic spherical particles of equal shrinking diameter. Further these are considered as a homogeneous phase for mathematical treatment. This assumption deserves an explanation. It is true that after cryogenic milling the size of the resulting particles may be certainly irregular and resembling more to a rectangular and not a sphere. However, since the particle size used in this study is quite small (2.5×10^{-4} m) it can be reasonably assumed that PET particles are spherical in shape.
c) The PET particles undergo negligible swelling during depolymerisation. The number of particles stays constant during hydrolysis.
d) Net reaction volume is constant throughout the depolymerisation process.
e) Reversible reaction of PET decomposition is neglected due to the formation of the soluble salt of terephthalic acid and monoethy-

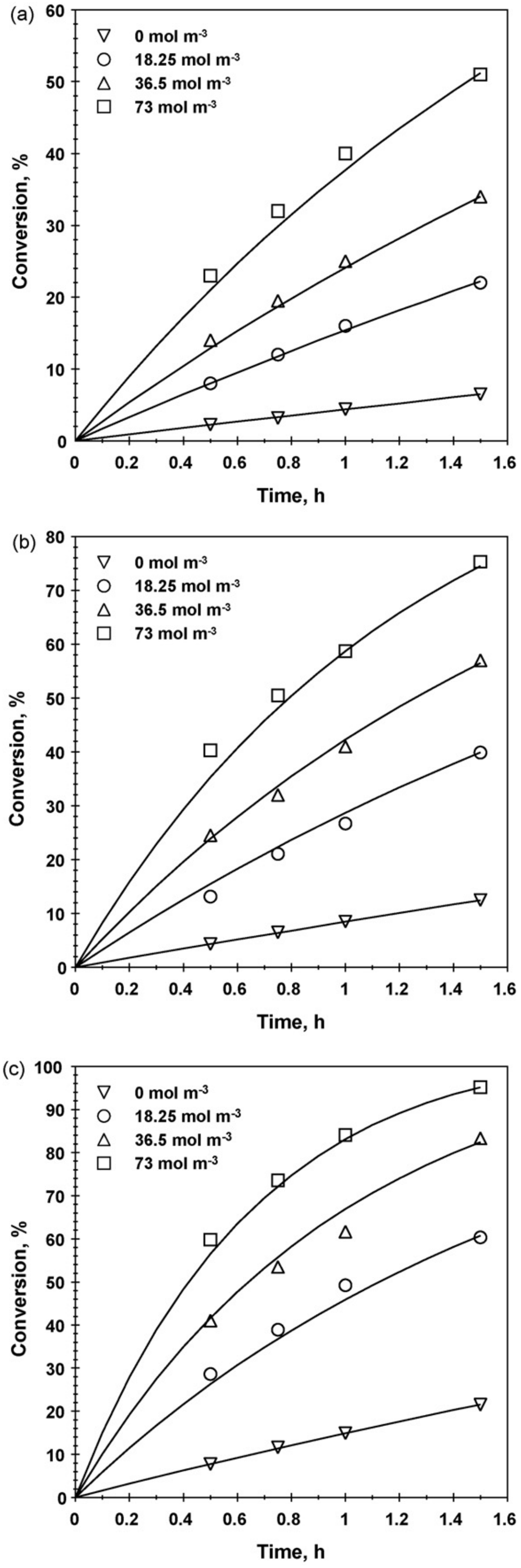

Fig. 2. Comparison of experimental conversion–time curves at several reaction temperatures ((a) 60 °C, (b) 70 °C, (c) 80 °C) with varying QX concentration and unreacted shrinking core model simulations (solid lines, equations (8–10)).

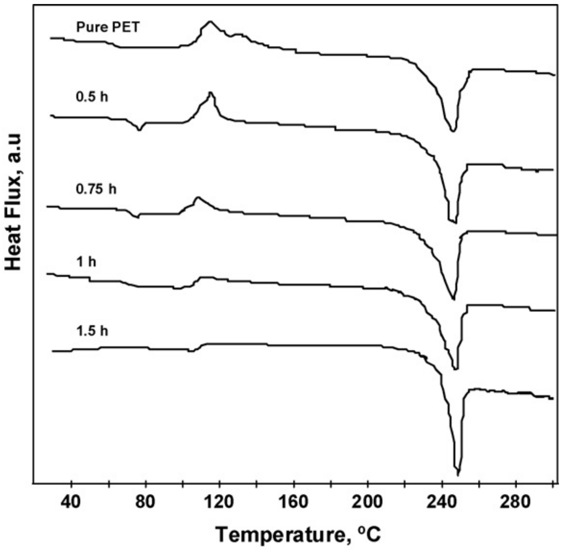

Fig. 3. DSC thermograms for partially converted PET particles submitted to alkaline hydrolysis ($T = 80\,^{\circ}C$, $C_{QX} = 18.25\ mol\ m^{-3}$).

lene glycol. Since the TPA produced as the reaction proceeds is dissolved in the solution as Na_2-TPA, the terephthalic salt will be inactive in an eventual nucleophilic substitution for the esterification (the reverse reaction for the alkaline hydrolysis) [16]. In addition, the concentration of the hydrolysis reagent is about six times greater than that of PET. Therefore, the reaction of PET hydrolysis under alkaline conditions can be considered as an irreversible reaction.

f) The phase transfer-catalysed reaction sequence involves ion exchange, interphase mass transfer steps and heterogeneous reaction between the anion ferried across and the PET repeating units. For modelling purposes the kinetics of ion exchange and external diffusion of the QOH catalytic entity from the liquid phase to the external surface of the solid reactant are considered to be very fast, thereby the global reactivity being controlled by the reaction at the solid (organic)–liquid (aqueous) interfacial moving boundary (rate controlling step) [17]. The concentration of the phase transfer catalyst in this layer is very high and so is the concentration of activated hydroxide ions.
g) The reaction rate is proportional to the particle surface area, the OH^- ion concentration and the QX concentration.
h) As noticeable PET conversion in the absence of QX is observed in the 60–80 °C range, as evidenced by Fig. 2, the reaction rate equation accounts for both reaction steps, namely the non-catalytic and QX-catalytic.

According to these suppositions the overall reaction rate of alkaline hydrolysis of PET ($-r_{PET}$), expressed as moles of PET repeating unit consumed per unit time, per unit area by the surface chemical reaction going to completion, in the presence of tributylhexadecylphosphonium bromide is

$$\begin{aligned}-r_{PET} &= -\frac{1}{4\pi R^2}\frac{dN_{PET}}{dt} = \nu C_{NaOH}\left(k_{NO\text{-}QX} + k_{QX}C_{QX}\right)\\ &= \nu k_{APP.}C_{NaOH} \qquad (4)\end{aligned}$$

where N_{PET} is the number of moles of PET repeating unit, C_{NaOH} is the molar concentration of aqueous sodium hydroxide solution, R is the radius of the unreacted PET particles, $k_{NO\text{-}QX}$ is the intrinsic non-catalytic depolymerisation rate constant, k_{QX} is the intrinsic catalysed depolymerisation rate constant, $k_{APP.}$ is the apparent rate constant, C_{QX} is the molar concentration of the quaternary salt, t

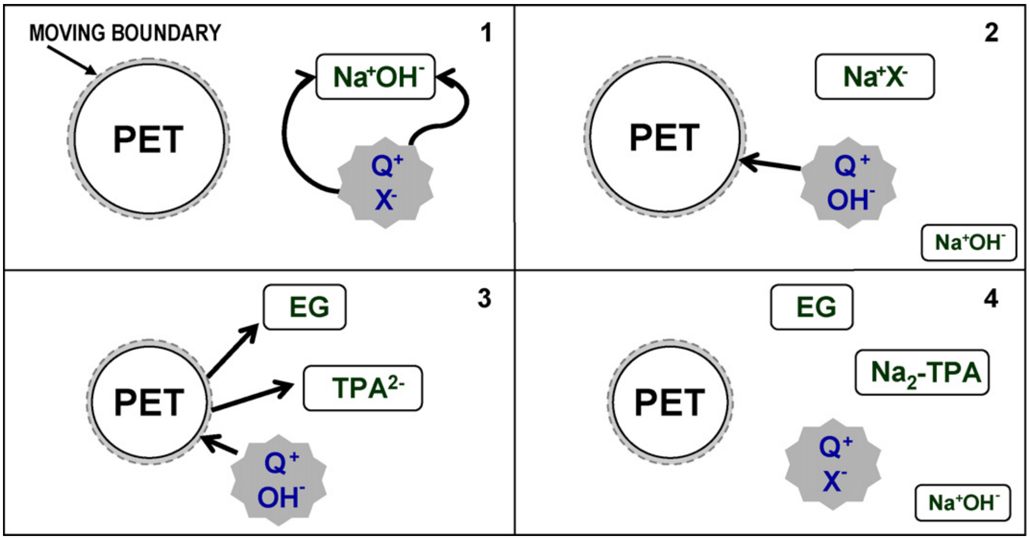

Fig. 4. Schematic representation of the probable mechanism.

is the time and υ is the stoichiometric coefficient of NaOH in the reaction (equal to 2). Writing Eq. (4) in terms of the shrinking core radius (R) and the molar density of PET (ρ_{PET}) gives

$$-\frac{1}{4\pi R^2}\frac{d\left(\rho_{\mathrm{PET}}(4/3)\pi R^3\right)}{dt} = -\rho_{\mathrm{PET}}\frac{dR}{dt} = \nu k_{\mathrm{APP.}} C_{\mathrm{NaOH}} \qquad (5)$$

where C_{NaOH} and R can be accordingly substituted by these expressions as function of conversion,

$$C_{\mathrm{NaOH}} = \left[C_{\mathrm{PET},0}(M-2X)\right] \qquad (6)$$

$$R = R_0(1-X)^{1/3} \qquad (7)$$

By combining Eqs. (5)–(7) the following expression (Eq. (8)) for determining the evolution of conversion of PET particles can be obtained, where k is a modified first order depolymerisation rate constant, $C_{\mathrm{PET},0}$ is the molar concentration of PET repeating units at the start of the batch, R_0 is the initial radius of the particles, X is the fractional conversion of PET, and M is the initial molar ratio of sodium hydroxide to PET repeating units.

$$\frac{dX}{dt} = k(M-2X)(1-X)^{2/3} \qquad (8)$$

$$k = \frac{3\nu k_{\mathrm{APP.}} C_{\mathrm{PET},0}}{\rho_{\mathrm{PET}} R_0} = \frac{3\nu C_{\mathrm{PET},0}}{\rho_{\mathrm{PET}} R_0}\left(k_{\mathrm{NO\text{-}QX}} + k_{\mathrm{PTC}} C_{\mathrm{QX}}\right) \qquad (9)$$

Eq. (8) can be integrated for $M > 2$ with the appropriate initial conditions (i.e., $t = 0$ when $X = 0$) to yield the following analytical solution [18]:

$$\begin{aligned} f(X) &= \frac{1}{4c^2}\ln\left[\frac{(c+z)^3}{c^3+z^3}\right] + \frac{\sqrt{3}}{2c^2}\arctan\left(\frac{2z-c}{c\sqrt{3}}\right) \\ &= -Kt + \frac{1}{4c^2}\ln\left[\frac{(c+1)^3}{c^3+1}\right] + \frac{\sqrt{3}}{2c^2}\arctan\left(\frac{2-c}{c\sqrt{3}}\right) \end{aligned} \qquad (10)$$

where

$$c^3 = \left[\frac{M-2}{2}\right] \qquad (11)$$

$$z = (1-X)^{1/3} \qquad (12)$$

Eq. (10) represents the conversion of PET particles as a function of time at any given value of the molar ratio. It is worth mentioning that other reported kinetic models based on the shrinking core model concept may be limited by its inability to account for a non-negligible change in alkali or acid concentration (when the concentration of these reactants is comparable to that of PET, and thus is not in excess) and the contribution of the non-catalysed reaction rate to the overall process [19–21]. Besides, from an economical point of view the use a limited amount of solvolytic reactant is preferable and, consequently proposed kinetics must account for this technical requirement.

The usefulness of the proposed shrinking core model was validated by evaluating the left hand side of Eq. (10), which is a function of PET conversion $f(X)$, and subsequent plotting against the reaction time for three different temperatures and varying concentration of

Table 1
Kinetic parameters of the alkaline hydrolysis of PET in the absence and presence of tributylhexadecylphosphonium at different temperatures.

		60 °C	70 °C	80 °C
$C_{QX} = 0\ \mathrm{mol\ m^{-3}}$	k ($\times 10^2\ \mathrm{h^{-1}}$)	$0.78 \pm 3.2 \times 10^{-3}$	$1.54 \pm 2.0 \times 10^{-2}$	$2.81 \pm 4.5 \times 10^{-2}$
	$k_{\mathrm{NO\text{-}QX}}$ ($\times 10^7\ \mathrm{m\ h^{-1}}$)	$0.86 \pm 3.5 \times 10^{-3}$	$1.69 \pm 2.2 \times 10^{-2}$	$3.08 \pm 5.0 \times 10^{-2}$
$C_{QX} = 18.25\ \mathrm{mol\ m^{-3}}$	k ($\times 10^2\ \mathrm{h^{-1}}$)	$2.90 \pm 6.6 \times 10^{-2}$	$5.86 \pm 2.5 \times 10^{-1}$	$10.57 \pm 5.1 \times 10^{-1}$
	$k_{\mathrm{APP.}}$ ($\times 10^7\ \mathrm{m\ h^{-1}}$)	$3.18 \pm 7.2 \times 10^{-2}$	$6.43 \pm 2.7 \times 10^{-1}$	$11.60 \pm 5.6 \times 10^{-1}$
$C_{QX} = 36.5\ \mathrm{mol\ m^{-3}}$	k ($\times 10^2\ \mathrm{h^{-1}}$)	$4.79 \pm 1.1 \times 10^{-1}$	$9.47 \pm 2.9 \times 10^{-1}$	18.56 ± 1.2
	$k_{\mathrm{APP.}}$ ($\times 10^7\ \mathrm{m\ h^{-1}}$)	$5.26 \pm 1.2 \times 10^{-1}$	$10.32 \pm 3.2 \times 10^{-1}$	20.37 ± 1.3
$C_{QX} = 73\ \mathrm{mol\ m^{-3}}$	k ($\times 10^2\ \mathrm{h^{-1}}$)	$8.19 \pm 3.3 \times 10^{-1}$	$15.04 \pm 6.0 \times 10^{-1}$	$28.36 \pm 5.4 \times 10^{-1}$
	$k_{\mathrm{APP.}}$ ($\times 10^7\ \mathrm{m\ h^{-1}}$)	$8.99 \pm 3.6 \times 10^{-1}$	$16.51 \pm 6.6 \times 10^{-1}$	$31.13 \pm 6.0 \times 10^{-1}$
	k_{QX} ($\times 10^8\ \mathrm{m^4\ mol^{-1}\ h^{-1}}$)	$1.11 \pm 4.1 \times 10^{-2}$	$2.00 \pm 1.5 \times 10^{-1}$	$3.82 \pm 3.5 \times 10^{-1}$

Table 2
Arrhenius parameters of the intrinsic catalysed and non-catalytic depolymerisation rate constants.

$Ea_{(QX)}$ (kJ mol^{-1})	60.6 ± 2.6
$\ln(k_{QX,0})$	3.5 ± 0.90
$Ea_{(NO\text{-}QX)}$ (kJ mol^{-1})	62.6 ± 1.2
$\ln(k_{NO\text{-}QX,0})$	6.4 ± 0.41

the quaternary phosphonium salt. The slope of the corresponding linear plot gave the value of the kinetic parameter k. The results are shown in Fig. 5 and indicated that this kinetic model provided good linear relationships with correlation factors (r^2) higher than 0.99 in all cases. The values of this kinetic parameter are included in Table 1. Substituting appropriate values for R_0 (2.5×10^{-4} m), $C_{PET,0}$ (292.1 mol m^{-3}), υ (2), and ρ_{PET} (76.4 mol m^{-3}) in Eq. (9), individual values for the apparent reaction rate constant $k_{APP.}$ could be determined for all three temperatures and four QX concentration values. Note that $k_{APP.}$ is equivalent to $k_{NO\text{-}QX}$ when the QX is not present in the reaction mixture. Values of $k_{NO\text{-}QX}$ were thus obtained independently from reaction runs without the phase transfer catalyst.

On the other hand, Fig. 6 shows statistically reasonable ($r^2 > 0.98$) linear relationships between the values of the apparent constant rate ($k_{APP.}$) and the concentration of the quaternary salt at 60, 70 and 80 °C. Hence, this observation clearly evidenced that the reaction behaves as first order with respect to QX. Further, the reaction rate related to the catalysed reaction (k_{QX}) could be determined from the slope of this plot. These are shown in Table 1 for all three temperatures. The comparable values of k_{QX} and $k_{NO\text{-}QX}$ indicated that the non-catalytic reaction is of relevant significance. In other words, under these operating conditions the measured conversion (or reaction rate) is dependent partly on the phase transfer-catalysed hydrolysis and partly on the non-catalytic depolymerisation.

Temperature effects on the hydrolysis rate constants ($k_{NO\text{-}QX}$ and k_{QX}) were also investigated. According to the relationship of the rate constants with the reaction temperature, the Arrhenius plots are shown in Fig. 7. Data fell on straight lines with linear correlation factors (r^2) higher than 0.99, and this lines were practically parallel. The activation energy for the phase transfer-catalysed reaction calculated from the slope was 61 ± 2 kJ mol^{-1}. This value is relatively close to that found by Dayte and Palan with alkyl(C_{12}–C_{14})-dimethylbenzylammonium chloride (63 kJ mol^{-1}) [22] and significantly lower than 83 kJ mol^{-1} reported by Kosmidis et al. using trioctylmethylammonium bromide [13]. On the other hand, the activation energy for the QX-free reaction is 63 ± 1 kJ mol^{-1}, comparatively similar to that reported by Wan et al. [15] and Ramsden and Phillips [23] (69 kJ mol^{-1}) and Grancaric and Kallay [24] (66 kJ mol^{-1}). Note that the activation energy of the process under acid (100–110 kJ mol^{-1}) [20,25], neutral (90–123 kJ mol^{-1}) [26,27] and nonaqueous alkaline (172 kJ mol^{-1}) [28] conditions is much higher.

Comparing the values of the activation energies of the catalytic and non-catalytic reaction steps (Table 2), it was seen that the activation energy was slightly lower in the presence of the quaternary salt. This result was in conformity with earlier findings by Glatzer and Doraiswamy [29]. These authors reported nearly identical values of the activation energy for the alkaline hydrolysis of hexyl acetate and octyl acetate in the presence (44.3 and 48.8 kJ mol^{-1}, respectively) or absence (48.8 and 47.0 kJ mol^{-1}, respectively) of benzyltributylammonium chloride. Taking into account the relatively close proximity and the intrinsic deviations due to experimental error of the activation energy values calculated for both non-catalysed and catalysed processes, it could be reasonably considered that the alkaline hydrolysis of PET followed

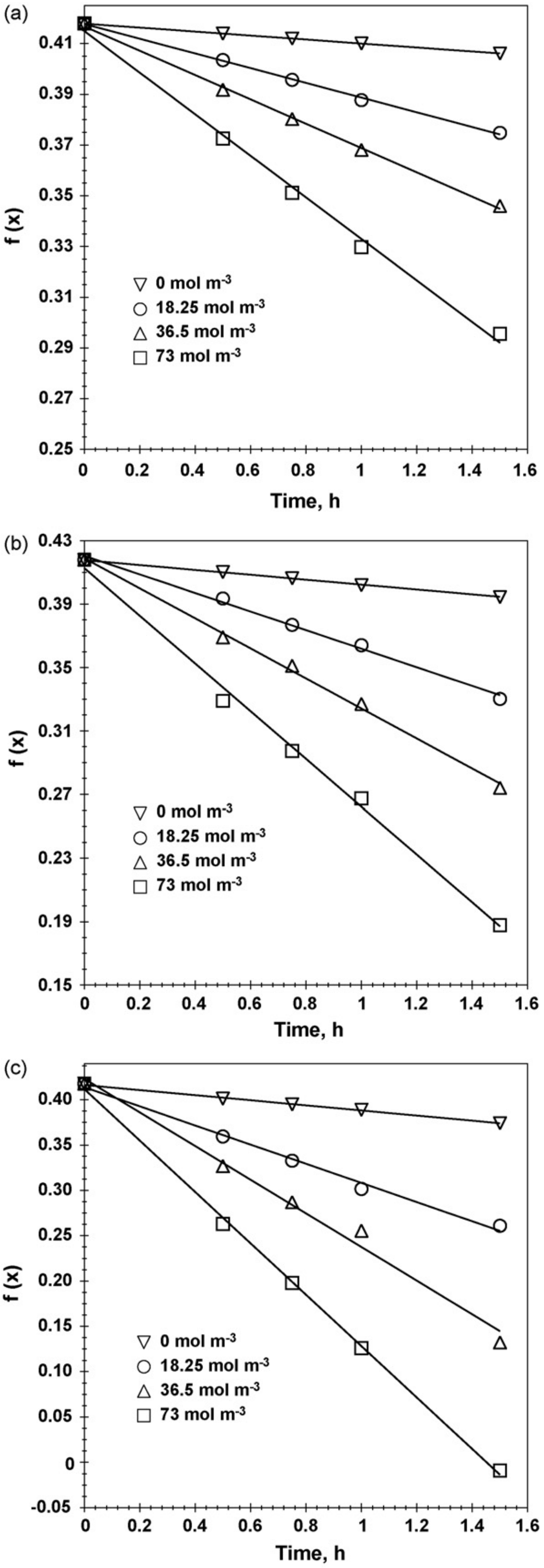

Fig. 5. Fitting of kinetic data according to Eq. (8) at different temperatures ((a) 60 °C, (b) 70 °C, (c) 80 °C) and QX concentration.

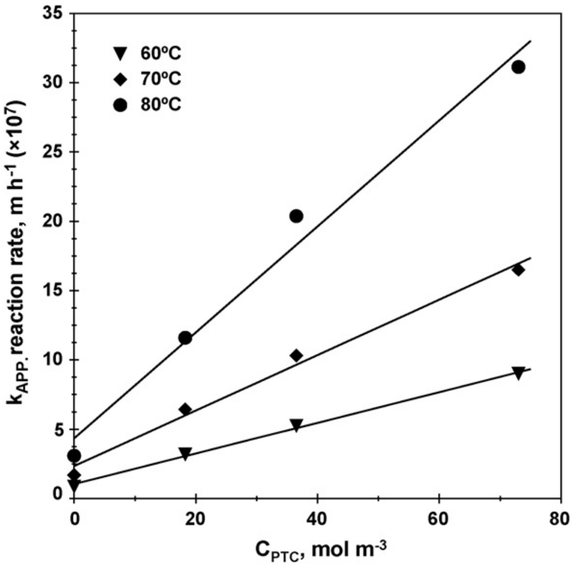

Fig. 6. Plot of the apparent rate constant ($k_{\mathrm{APP.}}$) vs. the QX concentration.

the same intrinsic mechanism in the presence or absence of the phase transfer catalyst in the reaction mixture. Therefore, the positive effect of the presence of the quaternary salt could not be related to a change of the activation energy of the reaction.

The reaction rate with QX evaluated as the term $k_{\mathrm{QX}} \times C_{\mathrm{QX}}$ is between 2.3 and 9 times greater than that observed in the absence of the quaternary salt ($k_{\mathrm{NO\text{-}QX}}$). Further, it was noted that this increase, expressed as the $k_{\mathrm{QX}} \times C_{\mathrm{QX}}/k_{\mathrm{NO\text{-}QX}}$ ratio, was proportional to the concentration of the phase transfer catalyst irrespective of the reaction temperature (Fig. 8). Thus, it is thought that the observed difference in the reaction rate was a result of a difference in the number of effective collisions resulting in PET hydrolysis, which were remarkably promoted by the presence of the QX. Numerically this can be demonstrated if the contribution of temperature to both reaction rates is assumed to be of the same magnitude (due to the almost identical value of the activation energy) and the value of the pre-exponential factor of $k_{\mathrm{NO\text{-}QX}}$ having units m h^{-1} (indicative of the number of collisions leading to reaction) is compared with the term $k_{\mathrm{QX,0}} \times C_{\mathrm{QX}}$ also having units m h^{-1} (related to the number of collisions leading to reaction in the presence of QX). It was noticed that the latter was about 2–9 times greater depending on the concentration of QX and reaction temperature.

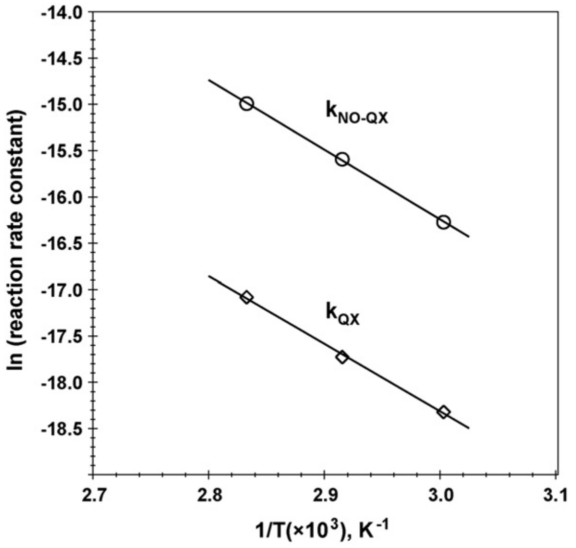

Fig. 7. Comparison of Arrhenius plots for the alkaline hydrolysis of PET in the presence and absence of tributylhexadecylphosphonium bromide.

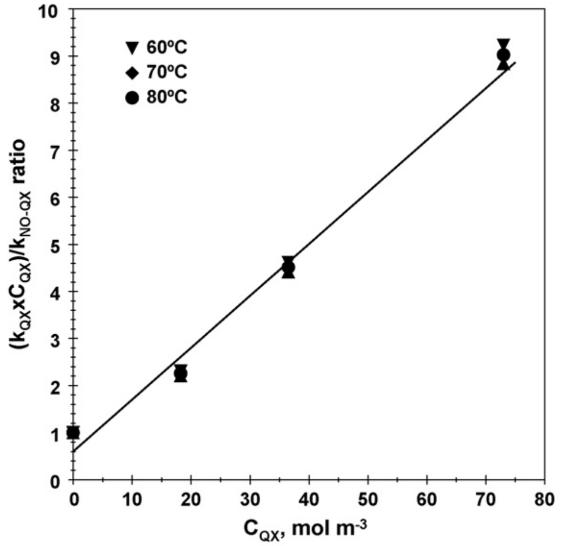

Fig. 8. Influence of QX concentration on the reaction rate of the alkaline hydrolysis of PET.

Hence, the catalytic role of the quaternary salts is to favour the transport of the reactive OH$^-$ anion from the NaOH/H$_2$O mixture to the external surface of the organic particle where hydrolytic reaction takes place. In other words, the concentration of this reactant in the liquid–solid interphase is greatly increased by the presence of the phase transfer catalyst. Finally, the profiles corresponding to the evolution of PET conversion with reaction time deduced by applying the kinetic parameters estimated from the proposed shrinking core model are shown in Fig. 2. It was noticed that the theoretical prediction values were in reasonable agreement with the experimental data.

4. Conclusions

The kinetics of the chemical recycling of PET by means of alkaline hydrolysis in the presence of tributylhexadecylphosphonium bromide was analysed. To model the reaction several simplifications were made and the utility of the unreacted shrinking core model was considered. The analysis based on this kinetic model showed a reaction-controlled regime at temperatures varying from 60 to 80 °C and concentrations of the quaternary salt in the range 0–73 mol m^{-3}. A good correlation was obtained when the proposed kinetic approach was applied to virtually all experimental data for predictive and quantitative evaluations.

The reaction rate was a linear function of the concentration of the quaternary salt. As revealed by the parallel nature of the Arrhenius plots both non-catalysed and phase transfer-catalysed processes presented roughly the same activation energy (63 kJ mol^{-1} in the absence of the quaternary salt and 61 kJ mol^{-1} with tributylhexadecylphosphonium bromide). Note that the difference lies within the limits of experimental error, suggesting that the quaternary salt has no effect on the intrinsic hydrolysis mechanism. The rate of alkaline hydrolysis was between 2.3 and 9 times faster using this quaternary salt. It is believed that this quaternary phosphonium salt acts as a shuttling agent by extracting the OH$^-$ anion from the aqueous phase into the organic interfacial region (the surface of solid PET particles) where the anion can freely react with the organic reactant. As a result, the concentration of this reactant in the liquid–solid boundary layer is greatly increased with a consequent enhancement of the reaction rate.

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