Thermal Decomposition of Polyvinyl Chloride for the Removal of Chlorine

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ABSTRACT

When heated at elevated temperatures, polyvinyl chloride (PVC) decomposes to HCl and polyene, a process which is known as dehydrochlorination and is expressed as $[CH_2CHCl]_n = n(HCl) + [C_2H_2]_n$. If the resulting polyene is free from chlorine, it can be used as a reducing agent or fuel for blast furnace ironmaking. The present study revealed that if dehydrochlorination of PVC is conducted at temperatures greater than 623 K, it is possible to eliminate chlorine from the reaction products $[C_2H_2]_n$.

INTRODUCTION

Our daily life depends to a great extent upon various types of "new" materials. When such "new" materials are discarded as wastes, however, we often encounter a number of serious social problems. Plastic products are a typical example of such wastes. In 1999, the volume of plastic disposed of as waste in Japan was about 8 million tons, 40 % (3.2 million tons) of which was disposed of by landfill, 35 % (2.8 million tons) by incineration, with the remaining 25 % (2.0 million tons) being recycled for reutilization /1/. Impetus for more recycling was proposed by national legislation that went into effect in April 2000. The law for recycling containers and packaging has increased the need for commercialized processes. It requires the recycling of all plastics, with the exception of polyethylene terephthalate (PET) bottles /2/.

Recently, the Japanese steelmaking industry has developed innovative technology for recycling general-purpose waste plastics at their iron and steelmaking complexes. For example, Wakimoto *et al.* /3/ have been injecting waste plastic into blast furnaces after separating polyvinyl chloride (PVC) from non-chlorine plastic. PVC is difficult to use in the ironmaking process because it generates corrosive chlorine gas, which is harmful to blast furnaces. The concentration of Cl in PVC, $(CH_2CHCl)_n$, is 56.8 % by wt, $Cl/(CH_2CHCl) = 35.45 / (12x2 + 1x3 + 35.45) = 0.568$.

From the foregoing comments it is evident that there is a strong incentive to develop a technology to remove chlorine from PVC. With respect to this, attention should be focused on thermal decomposition

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of PVC /4/, which is known as dehydrochlorination and is expressed as:

$$[CH_2CHCl]_n = n\,(HCl) + [C_2H_2]_n \qquad (1)$$

At ambient temperatures, the reaction product, i.e., polyene, $[C_2H_2]_n$, occurs at solid state, and hence would be suitable for injection into blast furnaces as a reducing agent or fuel. In practice, however, dehydrochlorination involves much more complicated processes than that expressed by the reaction in Eq.(1) /4/. For example, in addition to HCl, reaction products involve Cl-bearing gaseous species. More than 170 products, including aliphatic, aromatic and Cl-containing hydrocarbons, have been identified /4/. In addition, the residue, $[C_2H_2]_n$, may also contain chlorine. Namely, after dehydrochlorination, chlorine would present in (i) HCl, (ii) residue, $[C_2H_2]_n$ and (iii) other gaseous species rather than HCl. Based upon these considerations, dehydrochlorination would also be expressed by:

$$[CH_2CHCl]_n = \text{á}\,(HCl) + \text{â} <\text{Cl-containing } [C_2H_2]_n> + \text{ã}\,(\text{Cl-bearing gaseous species}) \qquad (2)$$

In order to be utilized as a reducing agent or fuel for blast furnace ironmaking, chlorine has to be eliminated from the residue, $[C_2H_2]_n$. The objective of this study is to establish the appropriate temperature to remove chlorine from the residue through dehydrochlorination.

EXPERIMENTAL ASPECTS

Polyvinyl chloride, obtained from Nakarai Tesque, Kyoto, was in the form of a powder with an average diameter of 0.1 to 0.2 mm. Figures 1 and 2, respectively, show the experimental set-up and the associated gas purification trains used in the present study. A Pyrex crucible of 18-mm height, 35-mm o.d., and 30-mm. i.d., was charged with 6 g of PVC, and heated in a stream of purified argon. The purification train for argon consisted of silica gel, magnesium perchlorate, phosphorous pentoxide and magnesium chips (823 K).

A resistance furnace equipped with a Pyrex reaction tube of 750-mm length, 55-mm o.d. and 50-mm i.d. was employed to heat the sample. Temperatures were measured with a Pt-PtRh13 thermocouple placed within 20 mm of the sample. The furnace was assembled with a crucible of PVC and the thermocouple, sealed at both ends with rubber stoppers, and then heated to the experimental temperature within a stream of argon. Initially the Pyrex crucible was positioned at the end of the furnace tube. After the temperature reached the desired value, experimental duration for dehydrochlorination was initiated, by moving the crucible to the homogeneous temperature zone with a molybdenum push rod, Figure 1.

The exhaust gas from the furnace was injected into two bottles of distilled water through porous plugs, in order to absorb gaseous HCl generated within the furnace. These bottles were connected in series and located within a water bath kept at a constant temperature. Absorption of HCl was, however, completed within the first bottle. The variations of the HCl concentrations were monitored *via* conductivity measurements, which were calibrated through titration with standard NaOH solution. The experimental duration was continued until conductivity became constant. Preliminary experiments revealed that the

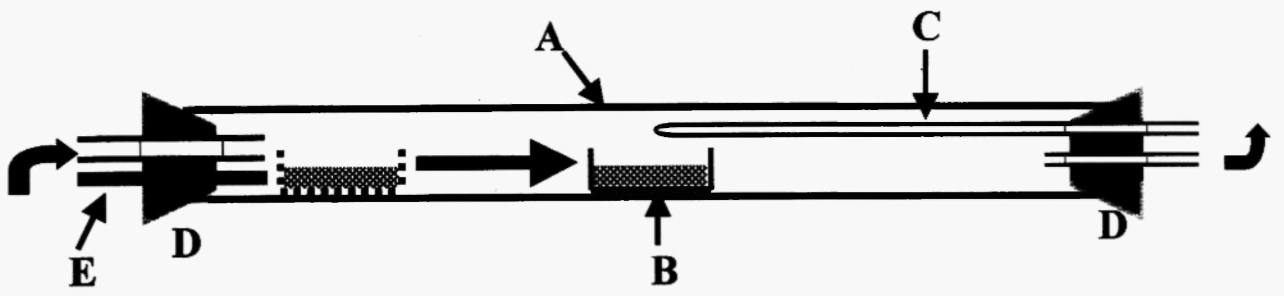

Fig. 1: Experimental set up. A: Electrical resistance furnace with Pyrex tube. B: Pyrex crucible. C: Thermocouple sheath. D: Rubber stopper. E: Molybdenum push rod.

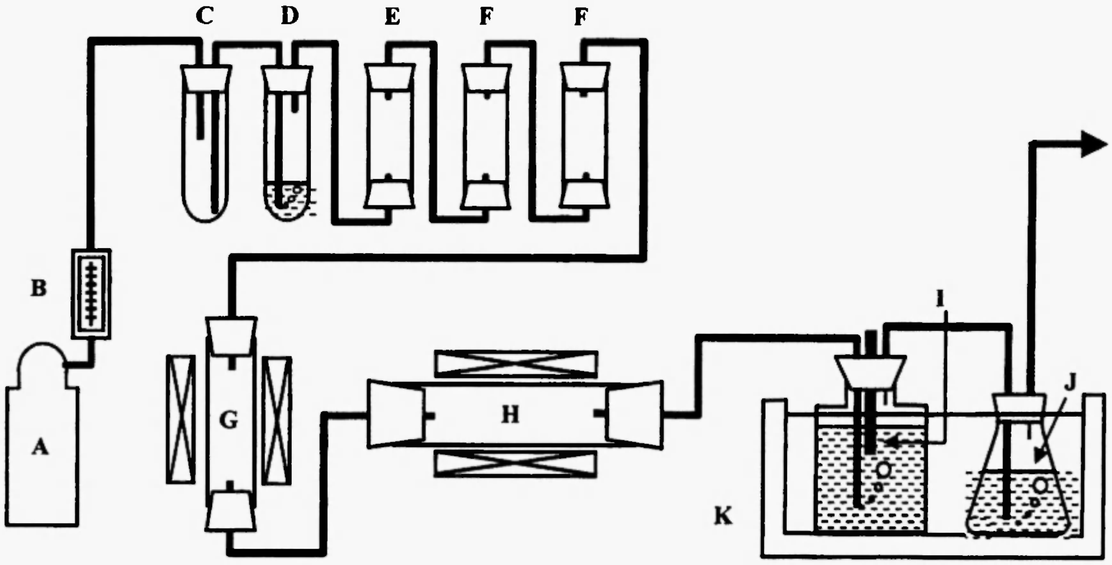

Fig. 2: Associate gas train. A: Argon gas cylinder. B: Gas flow meter. C: Empty bottle. D: Di-n-buthyl phthalate. E: Magnesium perchlorate. F: Phosphorous pentoxide. G: Magnesium chips. H: Furnace assembly. I: Conductivity measuring cell. J, K: water bath

flow rate of argon did not affect the rate of HCl generation, provided gas flow rate is greater than 600 cc/min. The subsequent experiments were, hence, conducted at a fixed flow rate of 1000 cc/min.

After dehydrochlorination, the residue was weighed and submitted to chemical analysis for chlorine by wet chemical analysis /5/. Figures 3(a) through (e) show, respectively, the appearance of the PVC samples before and after dehydrochlorination.

EXPERIMENTAL RESULTS AND DISCUSSION

The present results are summarized in Table 1, where $[PVC]^o$, *[HCl]*, *[residue]* and *[non-HCl]* are the quantities (gram) of PVC submitted to dehydrochlorination, HCl generated, residue and Cl-bearing gaseous species rather than HCl, t is time (second), and *(%Cl)* is the concentration (% by weight) of Cl in the residue.

In Figure 4, values for $[HCl] / [PVC]^o$ are plotted against time t. Durations of 100 to 600 seconds, depending upon temperature, were required before dehydrochlorination took place. This delay is probably due to the time required for heating up the PVC sample to the experimental temperatures within the furnace. Subsequently, linear behavior was observed between $[HCl] / [PVC]^o$ and t, as exemplified by dotted lines drawn through the data points. The rate of HCl generation, $r = d\{[HCl] / [PVC]^o\} / dt$, was then obtained from the slope. The Arrhenius-type plot, as shown in Figure 5, resulted in

$$\log r = (-9500/4.575\,T) + 4.41 \qquad (3)$$

where T is absolute temperature (K).

As shown in Figure 4, values for $[HCl] / [PVC]^o$ did not reach the theoretical value of 0.584. This value of 0.584 arises from reaction (1): HCl / $[CH_2CHCl]$ = (35.45 + 1) / (12x2 + 1x3 + 35.45) = 0.584. This behavior indicates either that chlorine still remains within the PVC sample, or that both HCl and the other Cl-bearing gaseous species are generated during dehydrochlorination. It is noted that quantities of Cl within the distilled water, as determined by conductivity measurements, correspond solely to HCl; other Cl-bearing gases cannot be detected through conductivity measurements.

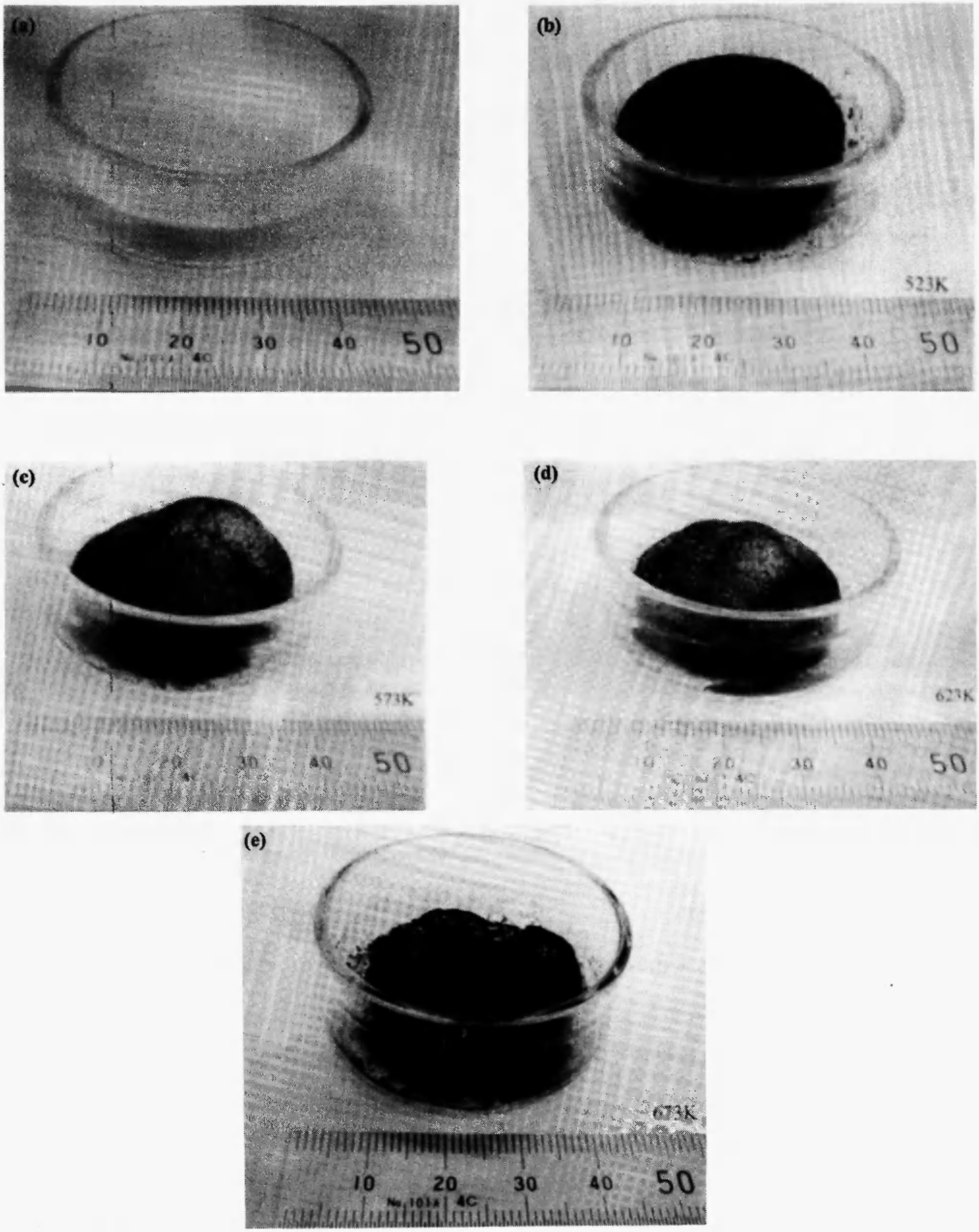

Fig. 3: Appearance of the PVC samples.
(a): before dehydrochlorination.
(b) through (e): after dehydrochlorination at 523 K, 573 K, 623 K and 673 K, respectively.

Table 1
Experimental results

T	Duration	*[PVC]*^{0}	*[HCl]*	*[residue]*	*[HCl]*	*[residue]*	*[non--HCl]*	*(%Cl)*
(K)	(min)	(g)	(g)	(g),	*[PVC]*	*[PVC]*	*[PVC]*	(%)
573	45	5.9999	2.996	2.632	0.499	0.439	0.062	9.81
573	20	6.0000	3.161	2.388	0.527	0.398	0.075	4.95
623	15	5.9998	3.337	2.171	0.556	0.362	0.082	0.00
673	10	5.9999	3.356	1.899	0.559	0.317	0.124	0.00

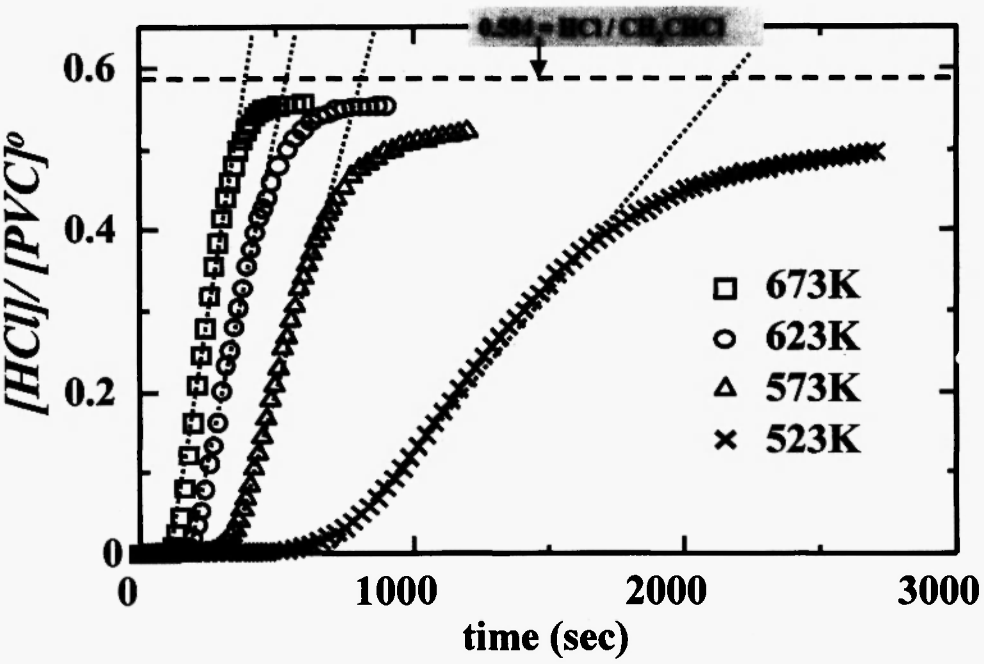

Fig. 4: Relation between *[HCl]/[PVC]*^{0} as the function of time.

Figure 6(a) shows the values for *[HCl] / [PVC]*^{0}, *[residue] / [PVC]*^{0} *and [non-HCl] / [PVC]*^{0}, attained after duration was completed, as the function of temperature, while the concentrations of chlorine in the residue after dehydrochlorination are shown in Figure 6(b). At 523 K, for example, values for *[HCl] / [PVC]*^{0} and *[residue] / [PVC]*^{0} were 0.499 and 0.439, respectively, while 0.499 + 0.439 < 1. The difference, 0.06 = 1- (0.499 + 0.439), corresponds to *[non-HCl] / [PVC]*^{0}. At 523 K, the concentration of Cl *(%Cl)*

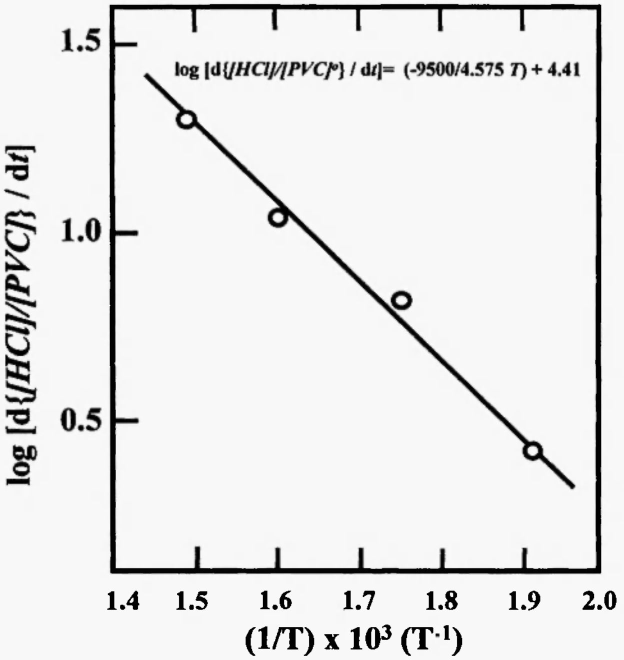

Fig. 5: Relation between log {d$[HCl]/[PVC]^{o}$ / d t} and $1/T$.

within the residue was 9.81 pct by weight, decreased with an increase in temperature, and, at temperatures greater than 623 K, reached substantially zero.

In summary, it can now be stated that in order to remove chlorine from the residue, dehydrochlorination has to be conducted at temperatures greater than 623 K. With such temperatures, Cl-free residue, i.e., polyene, would be obtainable for injecting into blast furnaces. However, it is noted that values for $[non\text{-}HCl] / [PVC]^{o}$ increased with an increase in temperature. At 673 K, $[non\text{-}HCl] / [PVC] = 0.124$. Hence, recovery of such gases would be essential from an environmental point of view. Based upon the present results, at any rate, a pilot plant for dehydrochlorination of waste plastic has now been constructed at NKK.

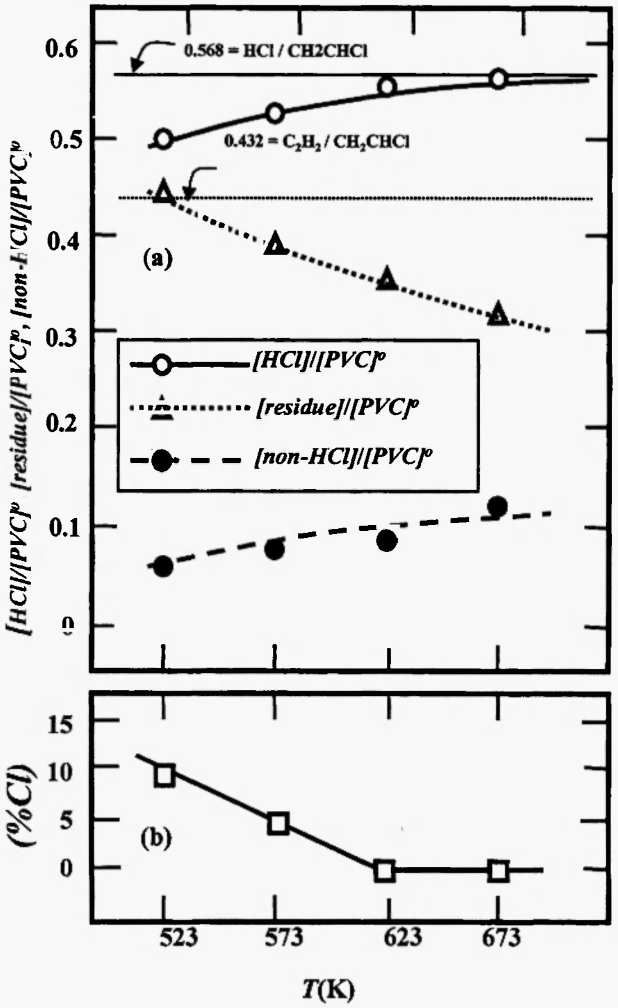

Fig. 6: (a): Values for $[HCl]/ [PVC]^{o}$, $[residue] / [PVC]^{o}$ and $[non\text{-}HCl]/[PVC]^{o}$ as the function of temperature. (b): Concentration of chlorine, $(\%Cl)$, in the residue as the function of temperature.

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