

# Effects of detergent concentration and ethylene oxide chain length of the detergent molecule on stress-cracking of low-density polyethylene

KÖKSAL TONYALI,\* HUGH R. BROWN†

*Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106, USA*

Stress-cracking behaviour of low-density polyethylene is investigated using a fracture mechanics approach. It is experimentally observed that  $K_I$  independent crack speed is directly proportional to the concentration of Igepal CO-630 up to 25% concentration.  $K_{ISCC}$  is found to increase with detergent concentration; and the increase in  $K_{ISCC}$  is attributed to the larger amounts of detergent absorption in the higher concentrations, which decreases the strain localization at the crack tip. Micelle formation of detergents in water is thought to enhance the rate of cracking because of their ability to increase plasticization efficiency at the local area because the micelles contain larger amounts of aggressive molecules. In contrast to Williams' model, the cracking behaviour in the constant crack speed region is found to be not controlled by the flow properties of the environment.

## 1. Introduction

Very little work has been published on the effect of the concentration of surfactant solutions on stress cracking of polyethylene. There exist a few studies which mention the subject, but do not touch on it directly. The conclusions from these studies do not agree well with each other. For instance, Howard [1, 2] reported that the addition of water to Igepal CO-630 markedly enhances the rate of failure of polyethylene. McFedries *et al.* [3] stated that there was no change in the effectiveness in the range 3 to 100% CO-630 under biaxial loading. However, McFedries *et al.* observed a decrease of the effectiveness of the solutions in causing cracking when they contained less than 3% detergent. Linkins *et al.* [4] reported that the cracking agent becomes more aggressive as the concentration decreases and this was probably due to the increase in the mobility of the detergent molecules in the solution, i.e. decrease in viscosity. Ohde and Okamoto [5] conducted experiments to determine the effect of the surfactant concentration on the crack growth rate. They observed an increase in the growth rate as the concentration increased.

In this paper, the effect of detergent concentration on the variation of crack speed ( $\dot{c}$ ) with stress intensity factor ( $K_I$ ) will be discussed. The structure of the detergent molecule and the solution structure of the environment will be related to the crack speed to explain the mechanism of stress-cracking of polyethylene.

## 2. Experimental details

The material was a low-density polyethylene of nominal density 0.918 (Dow polyethylene 681). It had a

melt flow index of 0.22. The beads were compression moulded into a sheet at 185°C and cooled slowly to room temperature.

The crack growth rates were measured on specimens having dimensions 120 mm × 35 mm × 2.5 mm. The detergent Igepal was diluted by distilled water to concentrations of 1.0, 2.5, 5.0, 7.5, 10.0, 15.0, 20.0, 25.0, and 30.0% (vol/vol) Igepal. Pure detergent was also used. The specimens were all single edge-notched and stressed in a stress-cracking test rig (Fig. 1). The crack growth rates were determined at 23°C and plotted against the stress intensity factors.

To study the effect of the length of the ethylene oxide unit in a detergent molecule on the cracking behaviour, Igepals CO-530, CO-630, and CO-710 were used as the environments. They contain 6, 9, and 10 to 11 ethylene oxide units, respectively. The detailed description of the experimental methods is given in [6].

## 3. Results and discussion

### 3.1. Effect of Detergent Concentration on the $K_I$ - $\dot{c}$ plots

A plot of  $K_I$  against  $\dot{c}$  is shown in Fig. 2. The graph contains the results obtained using 1.0, 5.0, 10.0, and 20.0% detergent solutions. The results show the normal three regions of crack growth that have been described before [6]. These are region I, where the crack growth rate increases with  $K_I$ , region II where the crack growth rate is constant and independent of  $K_I$ , and region III where the crack growth rate decreases with increasing  $K_I$ . We have shown previously that linear elastic fracture mechanics is no longer applicable by region III [6]. An interesting

\* Present address: Department of Physics, Washington State University, Pullman, Washington 99164-2814, USA.

† Present address: IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099, USA.

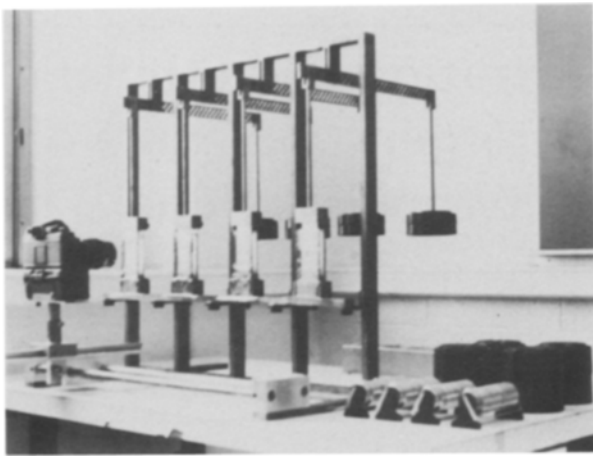


Figure 1 Environmental stress-cracking test rig.

observation is the dependence of the crack growth rate on the detergent concentration in region II. As the concentration of the detergent solution is increased the  $K_I$  independent crack speed also increases. Table I shows the effect of concentration on the constant crack growth rate ( $\dot{c}_c$ ) for all the experiments carried out. The test between 30 and 100% solutions could not be done satisfactorily because the solutions became cloudy and gelled in this concentration range. A plot of the constant crack speed ( $\dot{c}_c$ ) against per cent concentration is shown in Fig. 3. The plot is a straight line up to 25% concentration. The results from the 30% solution can perhaps be omitted, because the solution was a gel as stated earlier. The equation of the straight line is

$$\dot{c}_c = 0.046\phi + 0.130 \quad (1)$$

where  $\dot{c}_c$  is the constant crack speed in  $\text{mm h}^{-1}$  and  $\phi$  is the percentage concentration of the surfactant in vol/vol. The constant crack speed in the 100% solution was found experimentally to be  $10.02 \text{ mm h}^{-1}$ . The calculated value from Equation 1 is  $4.73 \text{ mm h}^{-1}$ , approximately half the experimental value. It seems likely that this effect is caused by the nature of the solution. It has been known for many years that detergent solutions in water have a micellar structure. However, pure detergent is not micellar and so has a structure quite different from that of the solutions.

TABLE I Constant crack speed dependence on concentration of Igepal CO-630

% Concentration (vol/vol)	Constant crack speed ( $\text{mm h}^{-1}$ )
1.0	0.17
2.5	0.25
5.0	0.38
7.5	0.46
10.0	0.64
15.0	0.81
20.0	1.05
25.0	1.32
30.0	1.23
100.0	10.02

Therefore, it may be possible to classify these two fluid structures as different environments.

The intersection of the line with the  $\dot{c}_c$  axis occurs at  $\dot{c}_c = 0.13 \text{ mm h}^{-1}$ . This means that the constant crack growth rate of  $0.13 \text{ mm h}^{-1}$  is predicted if no detergent is present in the environment (pure water). In fact the material did not show brittle cracking in a water environment. A possible explanation for the finite intersection on the  $\dot{c}_c$  axis is also connected with the structure of surfactant solutions. Above the critical micelle concentration (CMC), which is  $\sim 0.01\%$ , the amount of surfactant dissolved in water as free molecules does not increase; rather, the volume fraction of micelles increases. Perhaps this apparent pure water growth rate is really that caused by free molecules of surfactant in the solution.

The comparison of the data presented here with the available literature results is quite interesting. Neither Howard's results [1, 2] nor McFedries *et al.*'s results [3] agree with the data obtained in this laboratory. Earlier it was stated that McFedries *et al.* did not observe any noticeable change of failure behaviour with changing concentration and Howard reported that the addition of water makes the solution more active. However, it should be noted that they only carried out experiments to measure the failure time. As can be observed from the results presented here, the effect on the three regions of the crack growth has to be considered with care, because time to failure will depend on factors such as crack initiation time and initial crack length. The behaviour is quite complex

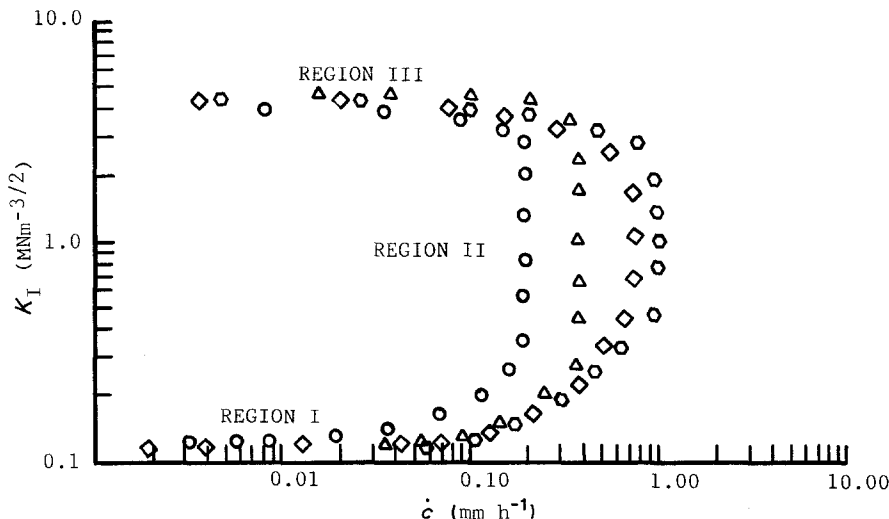


Figure 2 Effect of concentration of Igepal CO-630 on the  $K_I$ - $\dot{c}$  plots. (○) 1%, (△) 5%, (◇) 10%, (□) 20%.

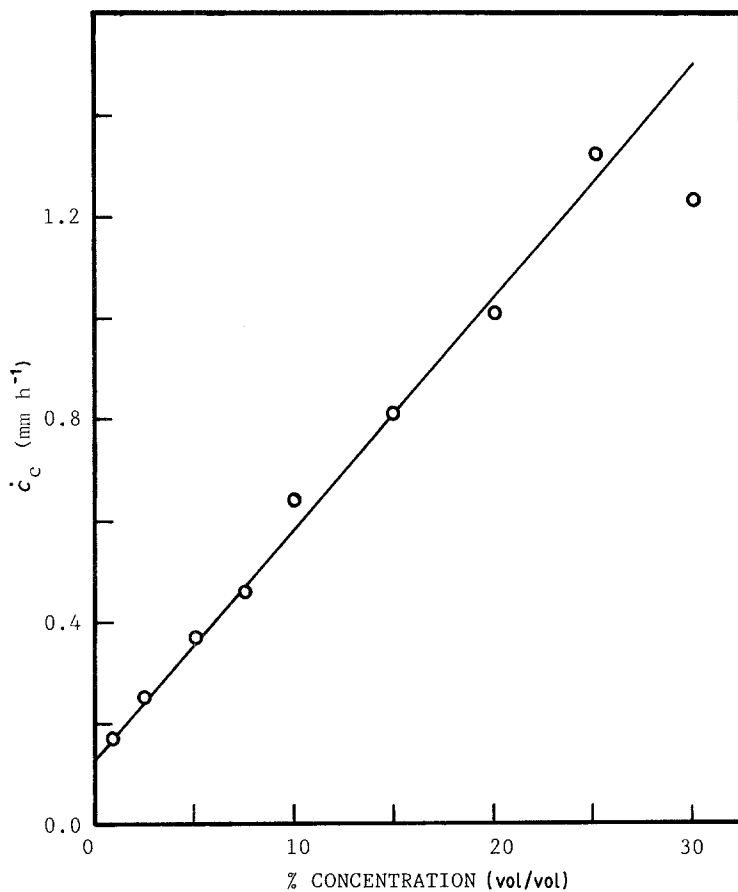


Figure 3 Constant crack speed dependence on concentration of Igepal CO-630.

and the results depend on the region in which the experiment is carried out. Assuming that their experiments were conducted in region II, Howard's and McFedries *et al.*'s results do not agree with our results. The environment becomes more aggressive in this region with increasing detergent concentration. However, the observations of Ohde and Okamoto [5] seem to be in agreement with the results presented here.

Williams and Marshall [7, 8], and Bandyopadhyay and Brown [9] have argued that the crack growth in region II must be flow controlled. If this is the case then the crack growth rate should be controlled by the fluid viscosity. Williams and Marshall [7] showed experimentally the existence of an inverse relationship between the viscosity and the crack velocity by using a number of different cracking agents. It is well known that the viscosity of the surfactant solutions increases

in an exponential manner with respect to the concentration [10–13]. It was experimentally observed in the current work that the constant crack speed increases with detergent concentration hence with the solution viscosity. Therefore, it follows that region II is not controlled by the hydrodynamic flow properties of the environment.

The behaviour in region I is also of interest, as is emphasized by the results shown in Fig. 4. It is clear that the  $K_I$  values for the initiation of crack growth ( $K_{ISCC}$ ) are different for different concentrations. An increase in detergent concentration initially lowers the susceptibility of polyethylene to stress-cracking, a reversal of the phenomenon observed in region II that was discussed earlier. However, the effect is not large at lower concentrations;  $K_{ISCC}$  changes from  $0.11 \times 10^6 \text{ N m}^{-3/2}$  for 1 to 5% to  $0.24 \times 10^6 \text{ N m}^{-3/2}$  at 100%

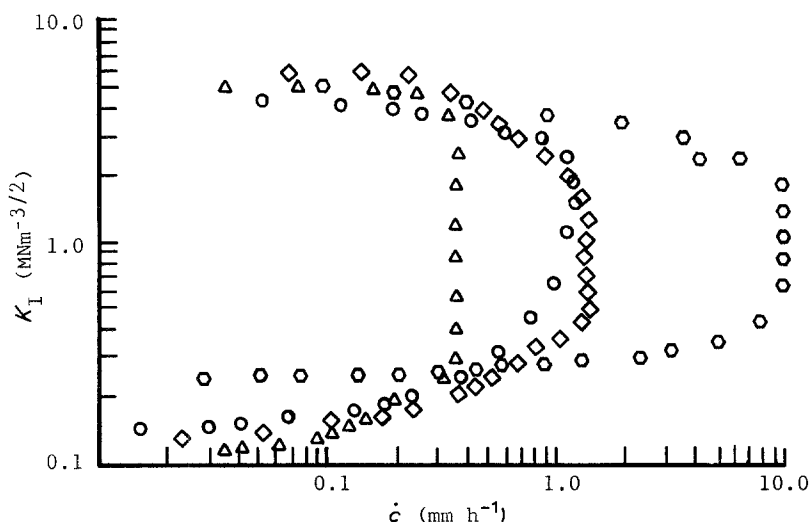
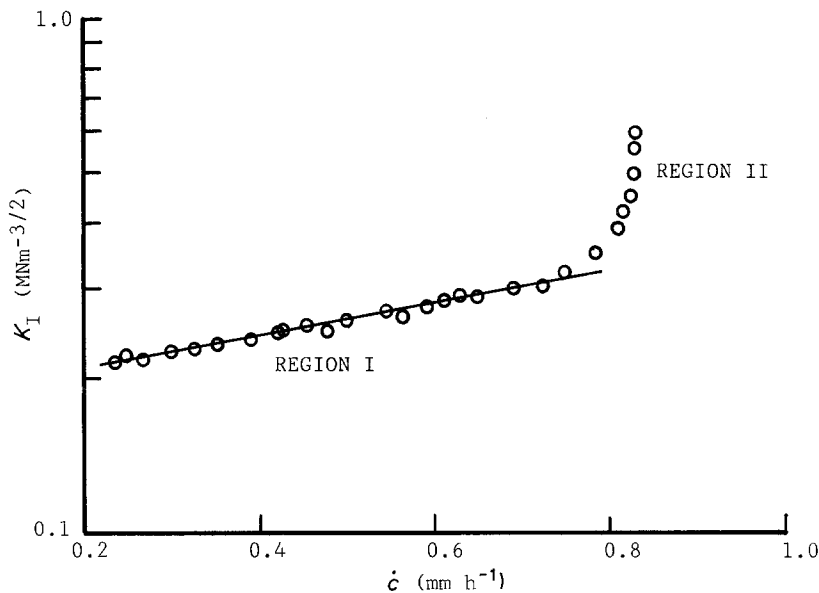


Figure 4 Effect of concentration of Igepal CO-630 on crack initiation. ( $\Delta$ ) 5%, ( $\diamond$ ) 25%, ( $\circ$ ) 30%, ( $\square$ ) 100%.

Figure 5 The relationship between the stress intensity factor and crack speed.



Igepal CO-630. Fig. 5 shows that the  $K_I$ - $\dot{c}$  data in region I are best represented, not by a power law, but by an equation of the form

$$\dot{c} \propto \log (K_I/K_{ISCC}), (K_I \geq K_{ISCC}) \quad (2)$$

The curve in Fig. 5 is obtained in the 15% solution and the same relationship is also observed for all concentrations.

The increase of  $K_{ISCC}$  with detergent concentration is a surprising result;  $K_{ISCC}$  is not obviously a rate-dependent property so one might expect it to decrease with increasing "aggression" of the fluid, and hence to either decrease or stay constant with increasing fluid concentration. A possible explanation of the observed behaviour is connected with the basic nature of the environmental crack process. Environmental cracking and crazing in polymers probably occur by a mechanism of stress-induced environmental absorption around the crack tip. The absorbed environment reduces the flow stress in that region thereby causing strain localization with the constraint from the less plasticized lower stress surroundings causing cavitation and a porous structure along which the fluid can flow. A crucial part of this process is the existence of localized stress-enhanced sorption, bulk sorption and plasticization decreases the tendency to crack. In the cracking test the samples were first immersed in the fluid and then loaded. Perhaps more fluid was absorbed from the higher concentration solutions before loading, decreasing the tendency for strain localization and cracking.

The results presented in both a previous paper [6] on ESC and here are not consistent with the current models of crack propagation in this system. It is, therefore, worth considering alternative explanations for the observed behaviour.

It is necessary first to consider the properties of surfactant solutions because the solution structure is believed to play an important role in the ESC behaviour. The detergent solutions in water are known to have micellar structures [14, 15]. The detergent used in this work is the nonionic Igepal CO-630 (obtained from GAF Corporation). The Igepals have critical micelle concentration (CMC) which is in the

order of  $10^{-3}$  to  $10^{-4}$  mol dm $^{-3}$ . They are not pure as obtained and contain a range of adducts of poly-(oxyethylene) nonyl phenol which will lead to different sizes of micelles. It has been predicted that micelles at concentrations close to their CMC are roughly spherical [14, 15] and some water molecules may be trapped inside. As the concentration of the detergent solution increases from the CMC, only the micelle concentration is believed to increase for nonionic surfactants; the micelle shape and size stay approximately constant [16]. This is in distinction to ionic detergents which form rod-like and lamellar structures.

An explanation has already been proposed for the behaviour in region I, namely that the higher concentrations are less "aggressive" because they cause more bulk absorption and hence less strain localization. In region II the crack growth rate increases linearly with the detergent concentration and is independent of  $K_I$  so is probably controlled by the amount of aggressive environment present at the crack tip. As the structure of the solution stays approximately constant, only the micelle concentration increases. If it is assumed that the detergent is absorbed from the aqueous solution at a craze tip, the amount of absorption will increase with the micelle concentration and hence the crack speed will increase. At present we are not able to explain convincingly why the constant crack speed increases linearly with concentration. In the 30% solution, we observed a decrease in the crack growth rate (Table I) which is probably caused by the viscosity of the solution. The 30% solution flowed with a difficulty and hence the viscosity may be the controlling parameter which determined the crack speed. Therefore, it seems likely that below 25% concentration; plasticization will be enhanced by increasing the detergent concentration. One explanation for the linear dependence of the constant crack speed on concentration may be that it is a balance between the plasticization efficiency and the viscosity-controlled behaviour with increasing the concentration.

The fracture surfaces of samples that failed in the solutions having different detergent concentrations were examined but they did not reveal any effect of

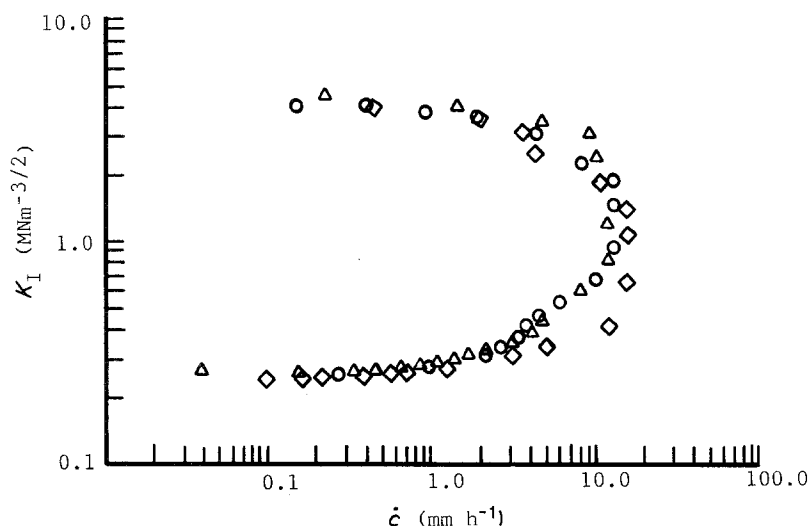
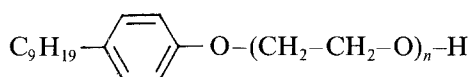


Figure 6 Effect of different Igepals on the stress-crack behaviour. (○) CO-530, (◇) CO-630, (△) CO-710.

concentration (only the specimens from the 1, 5, and 10% solutions were examined).

### 3.2. Effect of the mole ratio of ethylene oxide of surfactant on stress-cracking

The chemical structure of polyoxyethylated nonyl-phenol used is given below.



To determine the effect of the  $\text{CH}_2\text{CH}_2\text{O}$  group on ESC of polyethylene, the three Igepal surfactants, CO-530, CO-630, and CO-710, were used. The mole ratio,  $n$ , is different in each type such that  $n$  is 6, 9, and 10 to 11, respectively. The specimen dimensions were  $120 \text{ mm} \times 35 \text{ mm} \times 2.55 \text{ mm}$ . The initial stress level was  $8.0 \times 10^5 \text{ N m}^{-2}$  and the temperature was  $28^\circ \text{C}$ . The plot of  $K_I$  against  $\dot{c}$  is shown for different systems in Fig. 6. Examination of the curves shows that the chain length of ethylene oxide group does not affect the cracking phenomena in a specific way. The viscosities of these surfactants [13] at  $25^\circ \text{C}$  are given as 180 to 280 cps for CO-530, 190 to 290 cps for CO-630, and 210 to 310 cps for CO-710 ( $1 \text{ cps} \approx 10^{-3} \text{ N s m}^{-2}$ ). The values seem to be approximately equal.

One can make the following observations from the results in Fig. 6: for different Igepals, the behaviour is similar in region I. The cracks start to grow at about

$K_I = 2.35 \times 10^5 \text{ N m}^{-3/2}$ . The curves also superimpose in region III. However, the behaviour is different in region II where the maximum crack speeds obtained are  $12.8 \text{ mm h}^{-1}$  for CO-530,  $16.0 \text{ mm h}^{-1}$  for CO-630, and  $12.0 \text{ mm h}^{-1}$  for CO-710. If region II is controlled by the flow properties of the environment, the crack speeds will be inversely proportional to the viscosity [8]. Because the viscosities of the surfactants used here were about the same, the constant speeds would then be similar for all three surfactants. The experimental results do not confirm this statement, but show that the flow-controlled model [7, 8] is inadequate to describe the behaviour. The effectiveness of the surfactant is a complex phenomenon and not only dependent on the viscosity or chain length of the ethylene oxide group of the environment molecule.

Temperature changes also affect the growth rates. A comparison of the curves for CO-630 in Fig. 7 shows that the increase of the temperature leads to an increase in the crack speeds. The constant crack growth rate is  $16.0 \text{ mm h}^{-1}$  at  $28^\circ \text{C}$  and  $10.02 \text{ mm h}^{-1}$  at  $23^\circ \text{C}$  in Fig. 7. Although a  $5^\circ \text{C}$  difference causes a great effect on the constant crack speed, the effect in region I is not large. The effect may be due to the increased mobility of the environment molecules [4, 5] and partly due to the softening of the specimen with the increase of temperature. The effect of the temperature deserves detailed studies which will not be discussed here.

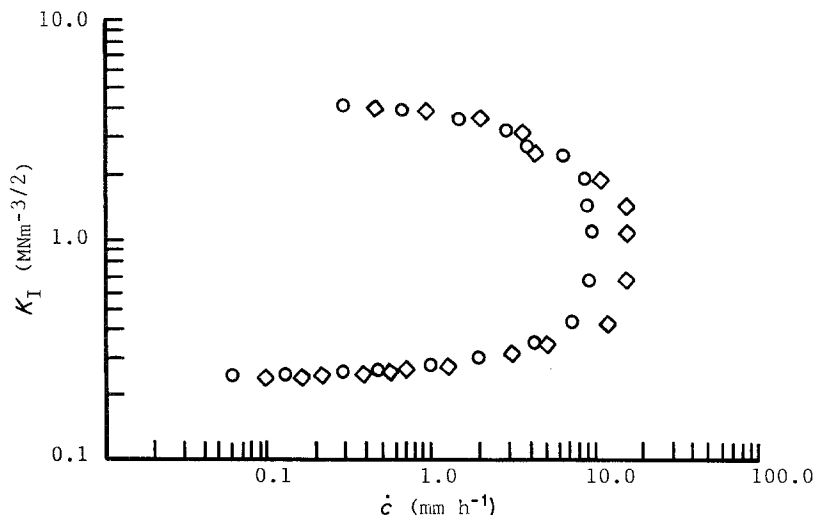


Figure 7 Effect of temperature on the ESC behaviour. (○)  $23^\circ \text{C}$ . (◇)  $28^\circ \text{C}$ .

#### 4. Conclusions

The following conclusions can be drawn from our studies.

1. It has been observed experimentally that the constant crack growth rate is directly proportional to the concentration of Igepal CO-630 up to 25% concentration and is not flow controlled.

2. Region I seems to be controlled by  $K_I$  and the detergent concentration. An increase in  $K_{ISCC}$  is obtained by increasing the concentration. The higher the concentration, the more absorption and hence the lower strain localization at the crack tip, which increases  $K_{ISCC}$ .

3. The solution structure of the environment affects the cracking behaviour. The increase in the micelle concentration is thought to increase the crack speed.

4. Region III is not affected by the detergent concentration.

5. It was shown that the number of the ethylene oxide units in the detergent molecule did not give rise to a simple relationship on the crack growth rates.

#### Acknowledgement

The financial support of the Army Research Office is gratefully acknowledged (ARO no. DAAG29-82K-0174).

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Received 21 October 1986

and accepted 22 January 1987