

KINETICS OF SOLUTION POLYMERISATION OF FURFURYL ALCOHOL

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POLYMERISATION of furfuryl alcohol in presence of acid catalysts yields furan resins which can be used in a wide variety of applications¹⁻³. Very little has been reported so far on the kinetics of this polymerisation reaction. The present study was prompted by this consideration.

To obviate the problem of phase separation, in the present work, the polymerisation was carried out in solution in 1, 4-dioxane, which is miscible with both water and furan resins. Isothermal conditions were achieved by using a jacketed reactor heated by a constant boiling liquid under total reflux. The furfural content⁴ of the distilled furfuryl alcohol used in the work was 0.14% and the cloud point⁴ was 4.5°C.

Since the polymerisation products of furfuryl alcohol are yellowish brown in colour and the colour intensity increases with the extent of conversion, a measure of the polymerisation rate could be obtained from the rate of increase of the colour intensity measured colorimetrically. Samples of the reaction mixture were drawn at different intervals and their percentage transmission was quickly measured with a Systronics Photoelectric Colorimeter Type 101 fitted with Ilford blue filter.

It is interesting to observe that the logarithm percentage transmission (*Tr*) decreases linearly with reaction time (*t*), as revealed by the semi-logarithmic plots of *Tr* vs. *t* in Fig. 1. The variation of *Tr* with *t* can therefore be written as

$$Tr = 100e^{-kt} \quad (1)$$

where *k* is a constant, given by the slope of the semi-logarithmic plot.

It may be postulated that the colour of the molecular species formed by polymerisation of furfuryl alcohol is due to the presence of one or more of the same chromophoric component in the molecule. Denoting the extinction coefficient of this chromophoric component by ϵ , the dependence of transmission on the concentration *c* of the chromophoric component in solution can be expressed by Beer-Lambert law as

$$\frac{I}{I_0} = e^{-\epsilon cl} \quad (2)$$

where I/I_0 is the ratio of intensities of the transmitted and original light and *l* is the path length.

Comparison of Eqs. (1) and (2) gives $\epsilon cl = kt$ or $dc/dt = k/\epsilon l = k'$ (say), indicating that the polymerisation of furfuryl alcohol follows a zero-order kinetics.

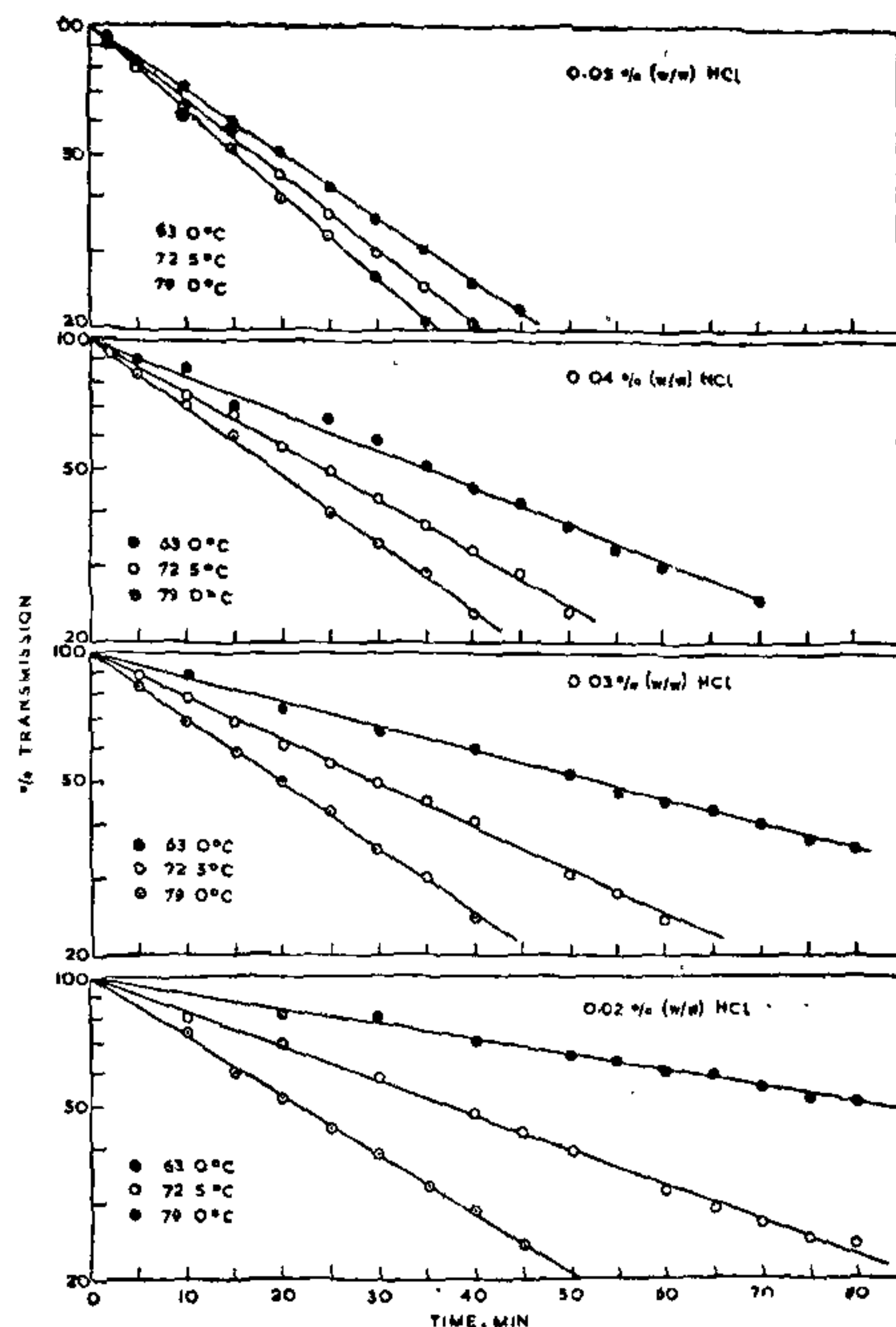


FIG. 1. Semilogarithmic plot of per cent transmission versus reaction time.

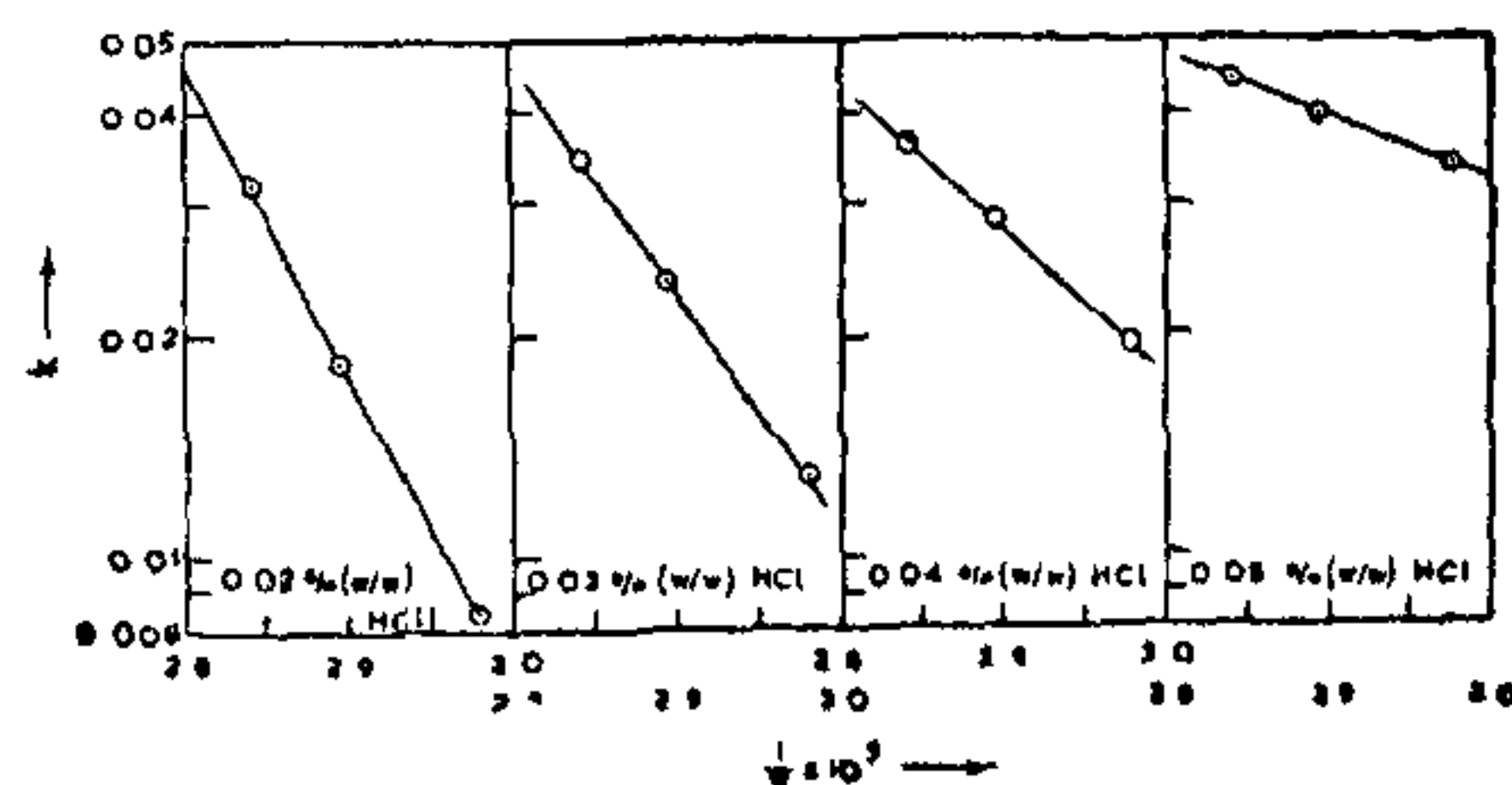


FIG. 2. Arrhenius plots of the constant *k* for different catalyst concentrations.

TABLE I
Values of the constant k and activation energy E

Catalyst (HCl) conc., C_{cat} (% w/w)	Temp. (°C)	$k \times 10^2$ (min^{-1})	E (k cal/mole)
0.02	63.0	0.843	19.50
	72.5	1.852	
	79.0	3.260	
0.03	63.0	1.300	14.32
	72.5	2.315	
	79.0	3.440	
0.04	63.0	1.952	9.08
	72.5	2.826	
	79.0	3.600	
0.05	63.0	3.367	3.74
	72.5	3.962	
	79.0	4.400	

Assuming ϵ to be unaffected by temperature, the activation energy for polymerisation could be obtained from the Arrhenius plot of k . Values of k have been derived from the slopes of the plots in Fig. 1 and these are given in Table I. Figure 2 shows the corresponding Arrhenius plots. Activation energies (E) derived from these plots, corresponding to the different concentrations (C_{cat}) of HCl catalyst, are included in Table I. The following linear expression relating E with C_{cat} has been derived:

$$E \text{ (k cal/mole)} = 30.25 - 530 C_{cat} (\% \text{ w/w})$$

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HIGH PHOSPHOROUS STROMATOLITIC LIMESTONES FROM NANDINI, DRUG DISTRICT MADHYA PRADESH, INDIA

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ABSTRACT

The Raipur series of the Chattisgarh basin (Precambrian) is extremely rich in stromatolites belonging to the *Collenia* group. After a detailed study of the mineralogy, morphology and chemistry of the stromatolitic limestones of this series, it is reported for the first time that these rocks from Nandini has in a bulk sample 18.49% and in separated stromatolite portion 24.20% P_2O_5 .

INTRODUCTION

NANDINI limestone quarries of the Bhilai steel project, Drug district, Madhya Pradesh, are situated 16 km north of Bhilai town (81° 30' E; 21° 06' N). This forms one of the type localities for the cycle-succession of the Raipur series of Schnitzer²⁴ (1971) in the Chattisgarh area. This carbonate series is extremely rich in stromatolites. These were earlier reported under different types of concretions by King¹⁶ (1885); Griesbach¹⁵ (1898) and Dutt⁷ (1963). Sen²⁶ (1966) and Murti²² (1970) have described to some extent the morphology of the stromatolites. Dutt⁶ (1962) studied the feasibility of the limestones of Madhya Pradesh to be used either as a raw material for cement or as a flux in steel industry and has published only the partial chemical analyses of the limestones of Chattisgarh basin. The Precambrian stromatolite bearing calcareous rocks of Udaipur

(Banerjee¹, 1971) and of Kumaun Himalayas (Valdiya²⁹, 1972) have been reported to be phosphorus bearing. Nandini limestones which are stromatolite bearing have attracted the attention of the authors to study in detail the mineralogy, morphology of stromatolitic remains and the chemistry of the rock types.

The limestones of Nandini which stands as a type locality for the cycle-succession of Schnitzer²⁴ (*op. cit.*) are well exposed in the quarries of the Bhilai steel project. These have an approximate maximum thickness of 100 meters. The dolomitic limestones of the Bhatapara subcycle underlie the Nandini limestones and is overlain by the chalcedony and limestones of Patharia-Umraya cycle of rocks.

These limestones have a varied range of colours: steel-grey, white and pink. The steel-grey limestones have an abnormal concentration of stromatolitic remains. Systematic representative samples of the