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Kinetics of Polymerisation of Furfuryl Alcohol in Aqueous Solution

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SUMMARY:

Kinetic information on the polymerisation of furfuryl alcohol catalysed by Clark-Lubs' aqueous buffer in the pH range of 1.0–2.2 has been derived from the rate of increase of colour intensity measured with a photoelectric colorimeter. The polymerisation reaction is found to be of zero order, with the activation energy increasing exponentially with pH. The time required to reach the extent of reaction at which a resin layer separates out from the aqueous solution decreases with increasing temperature but increases with increasing pH. An exponential expression relating the time for phase separation with temperature and pH has been derived.

ZUSAMMENFASSUNG:

Einblicke in die Kinetik der Polymerisation von Furfurylalkohol, die durch eine wäßrige Pufferlösung nach Clark-Lubs im pH-Bereich von 1,0 bis 2,2 ausgelöst wurde, konnten aus der Geschwindigkeit der Zunahme der Farbintensität, die mit einem photoelektrischen Kolorimeter gemessen wurde, gewonnen werden. Die Reaktionsordnung der Polymerisation wurde zu null bestimmt; die Aktivierungsenergie nimmt mit dem pH-Wert exponentiell zu. Die Zeitspanne bis zu einem Umsatz, bei dem sich eine Polymerphase von der wäßrigen Phase abtrennt, nimmt mit steigender Temperatur ab, steigt jedoch mit zunehmendem pH-Wert. Ein exponentieller Zusammenhang zwischen der Zeitspanne bis zur Phasentrennung und der Temperatur sowie dem pH-Wert wurde abgeleitet.

Introduction

Polymerisation of furfuryl alcohol in presence of acid catalysts yields thermosetting furan resins having exceptional resistance to acids and alkalies. There are numerous patents covering the methods of preparation and applications

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of furan resins. Rathi and Chanda[1] have recently reviewed the literature in this field. Relatively little is known however about the chemistry of the polymerisation process. Dunlop and Peters[2] presented an exhaustive review of the literature up to 1951. Recently, Barr and Wallon[3] reported the chemical composition of furfuryl alcohol resins. Very little has been reported in the literature on the kinetic aspect of furfuryl alcohol polymerisation. Some kinetic results are presented in this paper.

Since furfuryl alcohol resins are only partly soluble in water, polymerisation of furfuryl alcohol either in pure state or in aqueous solution results in separation into two layers. Thus in aqueous medium, the kinetics of the polymerisation process cannot be studied beyond a certain degree of conversion at which phase separation takes place. The time required to reach the stage of phase separation (t_s) may be regarded as a rough measure of the rate of the polymerisation reaction. Shono and Hachihama[4] measured t_s as a function of pH, using a 50% aqueous solution of furfuryl alcohol and observed that log t_s increases proportionately to pH.

The main problem encountered in studying the kinetics is, firstly, the highly exothermic nature of the acid-catalysed polymerisation of furfuryl alcohol which makes isothermal polymerisation difficult to achieve and, secondly, the difficulty of estimation of furfuryl alcohol in presence of its polymers, due to which the extent of conversion of furfuryl alcohol cannot be directly determined. Thus, though furfuryl alcohol can be estimated chemically by bromine oxidation method[5], the method cannot be used to estimate furfuryl alcohol in mixture with its polymerisation products, since the latter also react with bromine. Clearly, in this case a physical method of analysis is necessary. Since the polymers of furfuryl alcohol are yellowish brown in colour and the intensity of the colour increases with the extent of reaction, a measure of the polymerisation rate could be obtained from the rate of increase of colour intensity measured colorimetrically. This method was employed in the present work. Isothermal conditions were ensured by conducting the reaction in a batch reactor heated by a constant boiling liquid under total reflux.

Experimental Details

Materials

BDH (England) Technical Grade furfuryl alcohol was purified by vacuum distillation for use in the present work. The common impurities present in furfuryl alcohol are
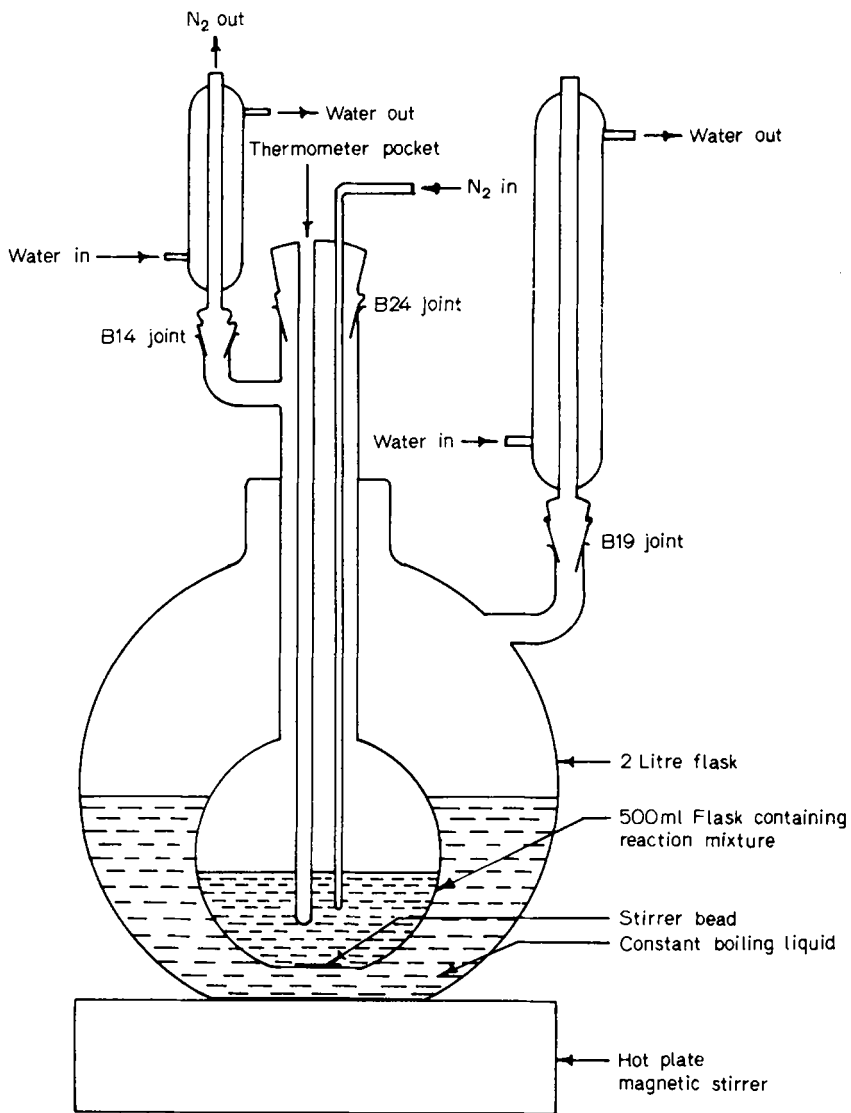
Fig. 1.   Reactor for isothermal resinification of furfuryl alcohol.

furfural and low polymers of furfuryl alcohol. The furfural content of the above technical grade material, as determined by the sodium bisulphite method[6], was 0.14% and its cloud point[6], which is a measure of the amount of polymer present, was found to be 8.5°C. (For commercial furfuryl alcohol the cloud point should not exceed 10°C). After purification by vacuum distillation the cloud point was 4.5°C.

Apparatus

A diagrammatic sketch of the apparatus is shown in Fig. 1. The apparatus consisted of two round flasks, one placed inside the other. The inner flask containing the reaction mixture was provided with a vertical water-cooled condenser, a thermometer pocket and an inlet for nitrogen. The reaction mixture was kept under a slow stream of nitrogen and stirred with a magnetic stirrer. The outer flask served as a jacket for the constant boiling liquid used as the heating medium. A gap of about 1 cm was provided between the bottoms of inner and outer flasks in order to prevent direct transfer of heat from the hot plate to the inner flask. The reaction mixture was maintained at a constant temperature by boiling a suitable liquid in the outer jacket under total reflux.

Procedure

The rate of polymerisation of furfuryl alcohol is greatly influenced by the acidity of the solution. For kinetic studies a constant pH should therefore be maintained during the period of reaction. Since acid-catalysed polymerisation of furfuryl alcohol in aqueous solution is also accompanied by a side reaction in which furfuryl alcohol reacts with water to form levulinic acid[2] causing a lowering of pH, an acidic buffer solution instead of a pure acid was used to catalyse the polymerisation of furfuryl alcohol.

Kinetic experiments were made on 50 vol.-% solutions of furfuryl alcohol in Clark-Lubs' aqueous buffer[7] mixtures of different pH values, prepared by mixing calculated volumes of KCl and HCl solutions of known strengths. The actual pH of the mixture was measured with a pH meter. The acidic component (HCl soln.) of the buffer was added to the reaction mixture, when the latter reached a constant temperature, almost equal to the boiling temperature of the liquid in the outer flask. The reaction period was counted from the moment the acidic component was added. Samples of the reaction mixture were drawn at different intervals of time and their percentage transmissions (relative to the percentage transmission of the initial reaction mixture as 100) were quickly measured with a Systronics Photoelectric Colorimeter Type 101 fitted with Ilford blue filter. A stream of purified nitrogen was constantly passed through the reaction flask in order to prevent entry of air. The process was continued till the clear solution became cloudy due to separation of resin layer. The time required to reach this stage of phase separation was noted. Experiments were conducted at different pH and temperature levels.

Results and Discussion

Percentage transmission (T_r) has been plotted against reaction time (t) on a semilogarithm plot for different pH and temperature levels in Figs. 2 to 5. Interestingly, in each case the plot consists of two linear regions
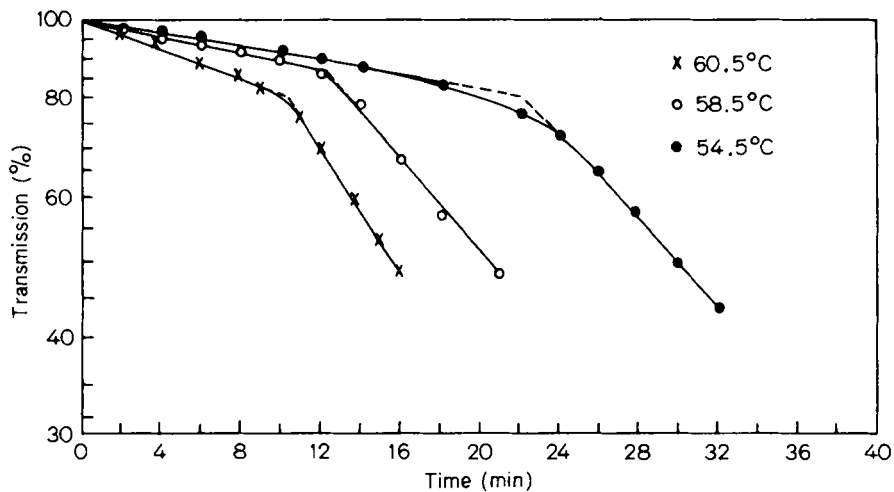
Fig. 2.   Semilog plot of percentage transmission versus time of polymerisation of furfuryl
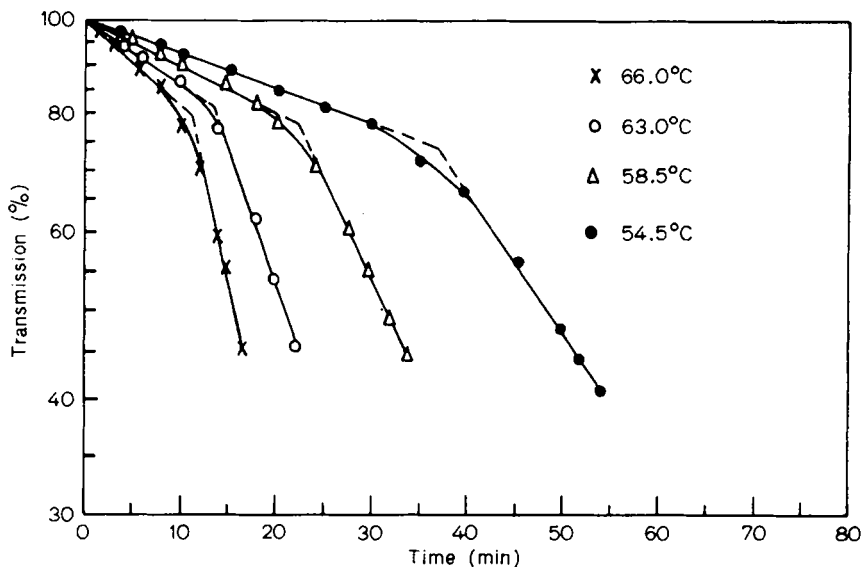alcohol in Clark-Lubs' buffer (50 vol.-%) at pH = 1.695.

Fig. 3.   Semilog plot of percent transmission versus time of polymerisation of furfuryl
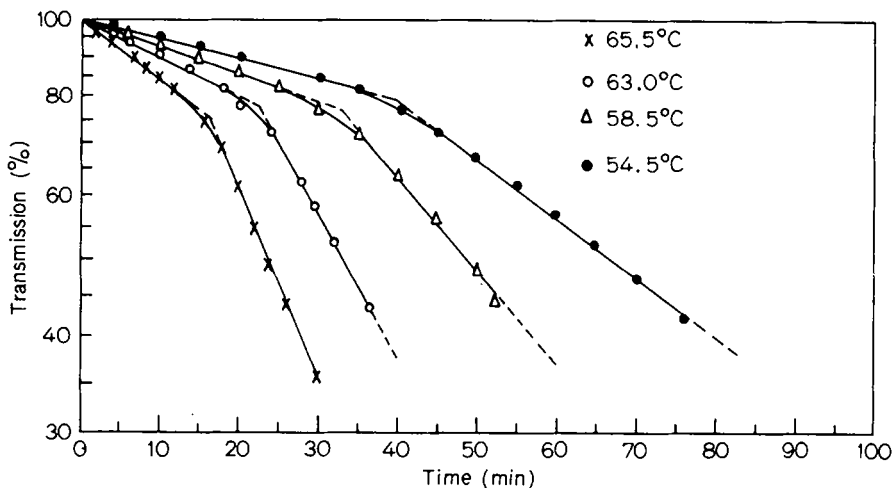alcohol in Clark-Lubs' buffer (50 vol.-%) at pH = 1.830.

Fig. 4. Semilog plot of percentage transmission versus time of polymerisation of furfuryl alcohol in Clark-Lubs' buffer (50 vol.-%) at pH = 1.962.
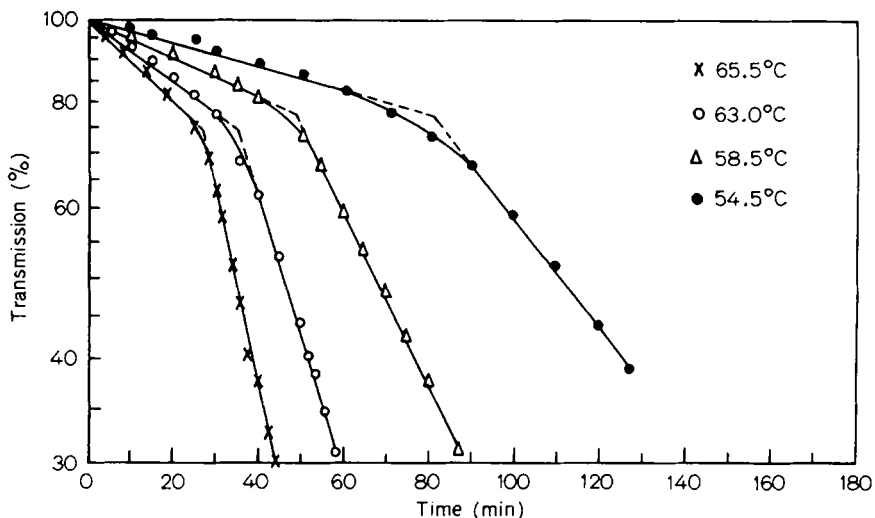

Fig. 5. Semilog plot of percentage transmission versus time of polymerisation of furfuryl alcohol in Clark-Lubs' buffer (50 vol.-%) at pH = 2.084.

(labelled I and II) having different slopes. Evidently, for the linear region I we can express T_r as a function of t by an equation of the form

$$T_r = 100 \exp(-kt) \tag{1}$$

where k is a constant, given by the slope of the plot.

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The linear semilogarithmic plot of T_r versus t observed in the case of polymerisation of furfuryl alcohol can be explained by assuming that the polymerisation reaction is of zero order and that the products of reaction consist of a similar type of chromophoric component as the repeating unit. Thus defining I_0 as the original intensity of light and I as the intensity after absorption, in a path length l, by a solution of polymerisation reaction products, the dependence of the transmission on the concentration, c, of the chromophoric component in solution can be expressed by Beer-Lambert law as

$$I/I_0 = \exp(-\varepsilon cl) \qquad (2)$$

where ε is the extinction coefficient of the chromophoric component.

Since $T_r = (I/I_0) \times 100$, comparison of Eq. (1) and (2) gives

$$\varepsilon cl = kt$$
$$\text{or} \quad dc/dt = k/\varepsilon l = k'. \qquad (3)$$

Since dc/dt can be taken as a measure of the rate of polymerisation of furfuryl alcohol, Eq. (3) signifies that this polymerisation reaction is of zero

Tab. 1. Apparent rate constants and times for phase separation at different temperature and pH levels.

pH	Temp. (°C)	Apparent rate constant		Time for phase separation t_s (min)
		$k_I \times 10^2$	$K_{II} \times 10^2$	
1.695	60.5	1.320	9.196	23.0
	58.5	1.150	8.325	29.0
	54.5	0.941	5.400	42.5
1.830	66.0	1.620	10.018	23.5
	63.0	1.236	7.410	31.5
	58.5	0.913	4.630	47.5
	54.5	0.798	3.505	70.0
1.962	65.5	1.239	5.773	39.0
	63.0	0.989	4.211	49.5
	58.5	0.668	2.917	78.0
	54.5	0.518	1.965	114.0
2.084	65.5	0.950	5.020	68.0
	63.0	0.756	3.824	83.0
	58.5	0.423	2.509	130.0
	54.5	0.296	1.648	200.0

order. It may be noted that zero order is often an indication of a complex reaction involving a number of steps in succession.

The polymerisation rate constant k′ is related to the constant k, defined earlier. The constant k will be called the apparent rate constant.

The apparent rate constants have been determined for the regions I and II, shown in Fig. 2 to 5, and are denoted by k_I and k_{II}. The values of k_I and k_{II} at several pH and temperature levels are recorded in Tab. 1. The time periods required to reach the stage of separation of resin layer under different pH and temperature conditions are also included in Tab. 1. The reaction rate is evidently faster in region II than in region I, the difference being more marked at lower temperatures.

Activation Energy

Assuming that ε is unaffected by temperature, the apparent rate constant can be plotted in the Arrhenius fashion to derive the activation energy for polymerisation. The Arrhenius plots of k_I and k_{II} corresponding to different pH levels are shown in Fig. 6 and the respective activation energies are listed in Tab. 2. The logarithm of activation energy is found to have a

Tab. 2. Activation energy (E) for resinification at different pH levels.

pH	Activation energy (kcal/mole)	
	E_I	E_{II}
1.695	11.586	19.026
1.830	13.424	20.143
1.962	18.112	21.963
2.084	23.877	23.901

linear relationship with pH both in regions I and II, as shown by the plots of Fig. 7. The relationships are derived as

Region I

$$E = 0.4532 \exp(1.895\,pH) \quad kcal/mol \tag{4}$$

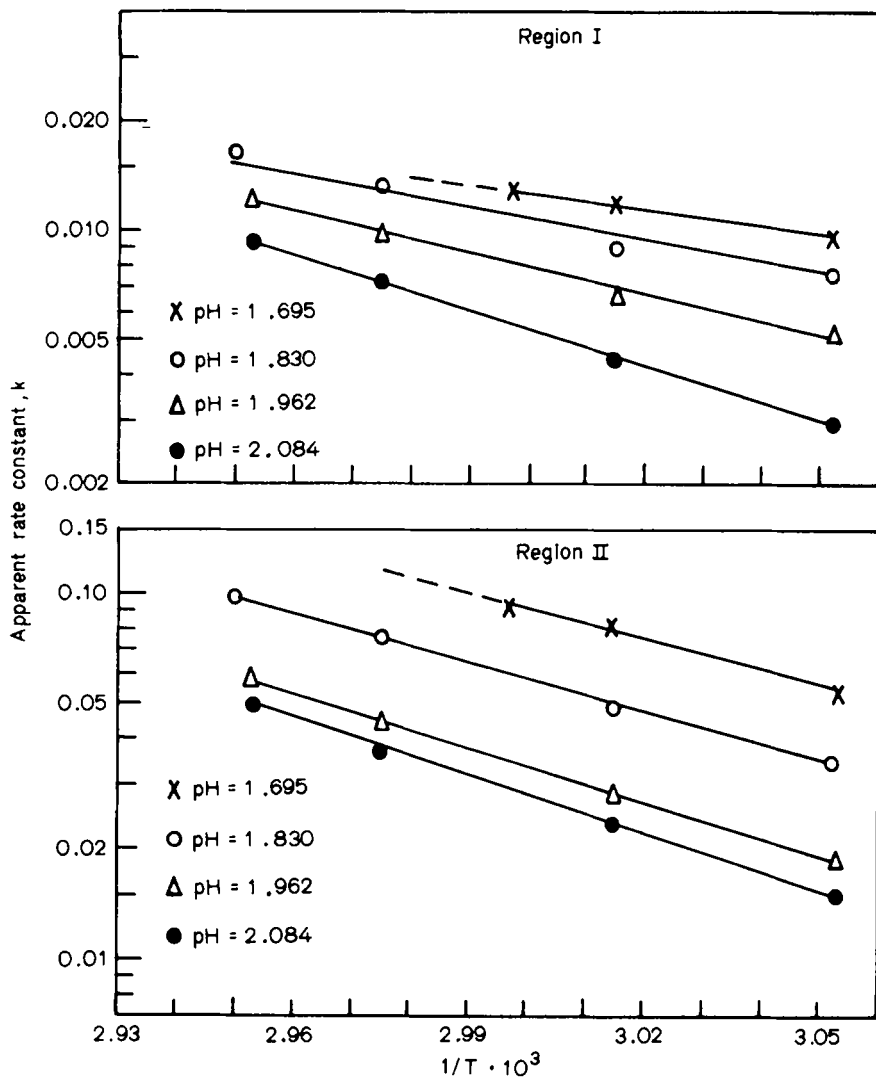*Region II*

$$E = 6.915 \exp(0.592\,pH) \quad kcal/mol \tag{5}$$

Fig. 6. Arrhenius plot of apparent rate constant (k) versus 1/T.

Time for phase separation

The logarithm of the time for phase separation (t_s) bears a direct proportionality to pH (Fig. 9), in agreement with observations of Shono and Hachihama[4]. It is further observed that for a given pH, log t_s decreases linearly with
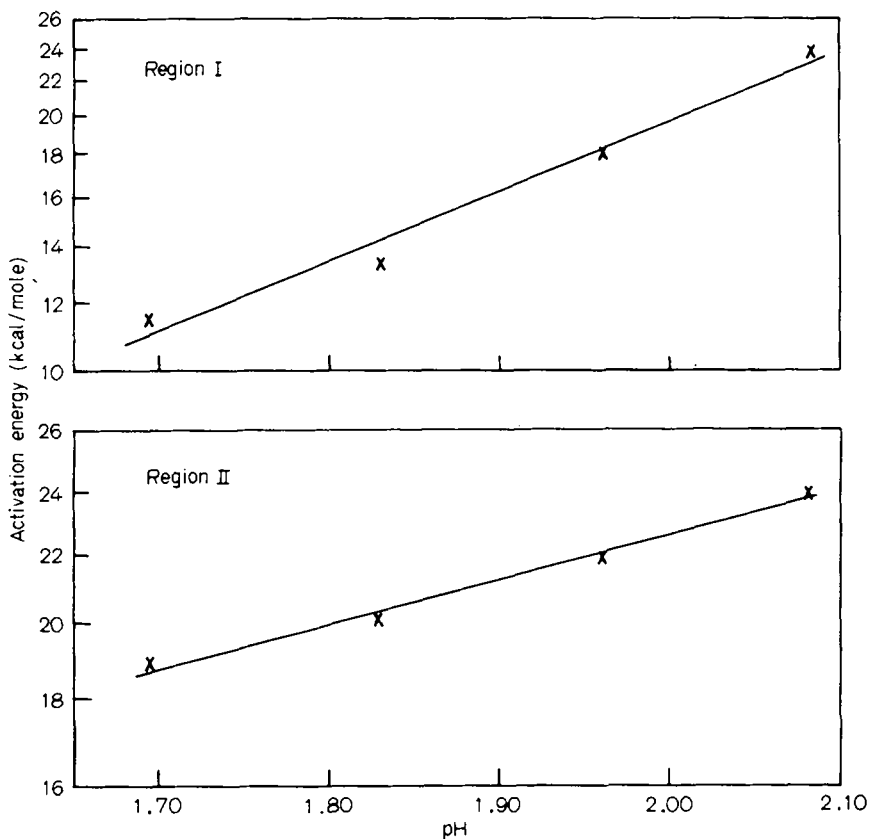
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Fig. 7. Semilog plot of activation energy versus pH.

increasing temperature (Fig. 8). On the basis of the plots shown in Figs. 8 and 9, t_s has been correlated with temperature T (°C) and pH by the expression

$$t_s = 3.051 \exp[4.541\, pH - (0.0767 + 0.01\, pH)T] \qquad (6)$$

The values of t_s calculated from Eq. (6) agree with the experimental values with less than $\pm 5\%$ deviation.

Conclusions

The polymerisation of furfuryl alcohol in Clark-Lubs' aqueous buffer solution in the pH range of 1.0–2.2 and at different temperatures has been followed
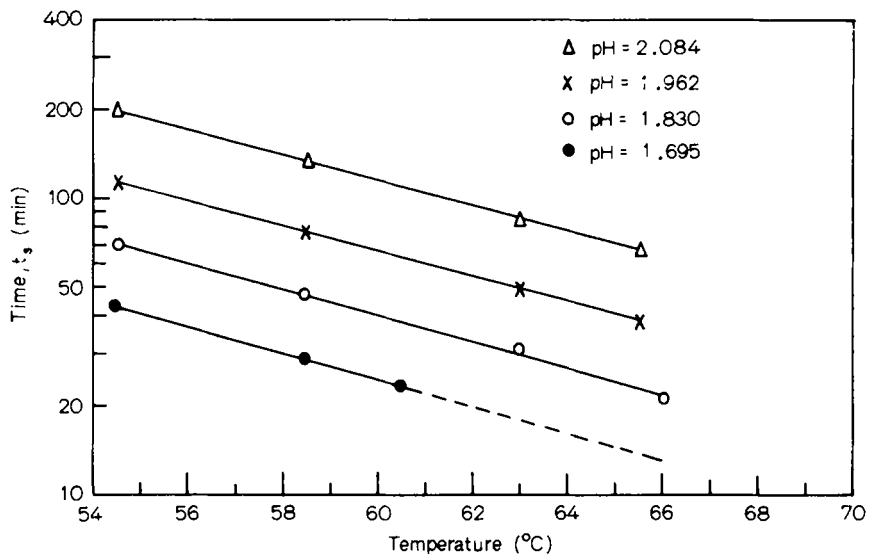
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Fig. 8. Semilog plot of time for phase separation versus temperature at different pH levels.
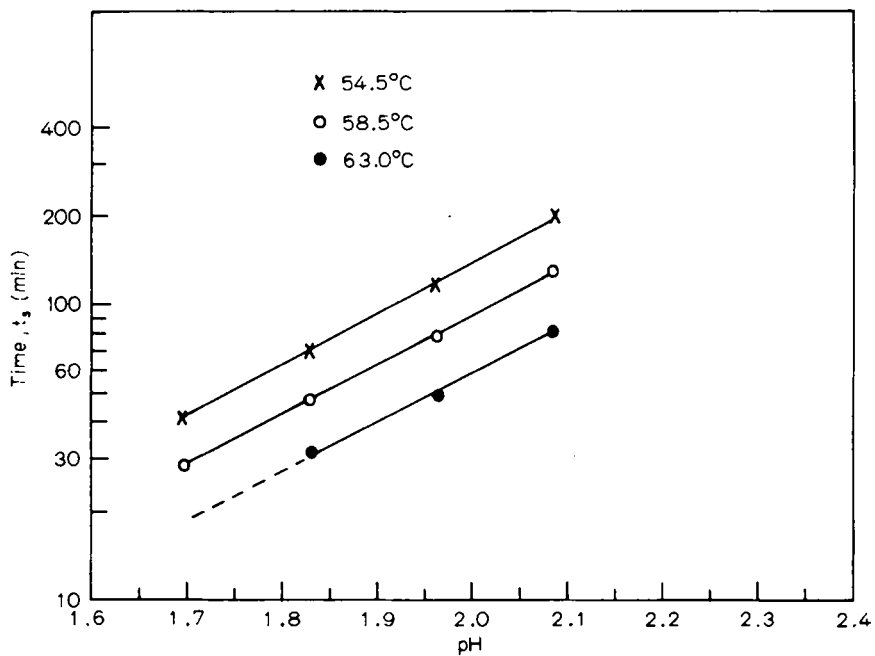

Fig. 9. Semilog plot of time for phase separation versus pH at different temperature levels.

colorimetrically. The analysis of the colorimetric data reveals zero-order kinetics for the polymerisation reaction. The reaction is marked by two constant rate periods. The initial period of slow rate of reaction is followed by a period of higher rate of reaction. This feature of two rate periods is however observed only when pure furfuryl alcohol is used. The polymerisation of technical grade furfuryl alcohol, which contains furfuryl alcohol polymers as impurities, exhibits[8] only one reaction rate under similar conditions.

The activation energy for polymerisation of furfuryl alcohol is always lower in the initial period than in the later period. This may be indicative of a shift in the reaction mechanism to a less favourable one after an initial period of reaction.

At a given temperature, the logarithm of the time for separation of resin layer increases linearly with increasing pH, and at a given pH it decreases linearly with increasing temperature. The logarithm of activation energy in both the initial and later periods of reaction bears a direct proportionality to pH.

Acknowledgement

[1] A. K. A. Rathi, M. Chanda, Popular Plastics **18**/12 (1973) 28
[2] A. P. Dunlop, F. N. Peters, The Furans, ACS Monograph, Reinhold, New York 1953, p. 213
[3] J. B. Barr, S. B. Wallon, J. Appl. Polym. Sci. **15** (1971) 1079
[4] T. Shono, Y. Hachihama, J. Chem. Soc. Japan, Ind. Chem. Sect. **56** (1953) 520
[5] M. Szakacs-Pinter, L. Maros, Acta Chim. (Budapest) **56** (1968) 37
[6] G. M. Kline, Analytical Chemistry of Polymers, Interscience Publishers, New York 1959, p. 203
[7] H. T. S. Britton, Hydrogen Ions, Chapman and Hall, London 1955, vol. 1, p. 325
[8] A. K. A. Rathi, M. Chanda, J. Appl. Polym. Sci., in press