

Kinetics of Resinification of Furfuryl Alcohol in Aqueous Solution

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Synopsis

Kinetic information on the resinification of furfuryl alcohol has been derived from the rate of increase of color intensity measured with a photoelectric colorimeter, the resinification being carried out isothermally in Clark-Lubs aqueous buffer solutions in the pH range of 1.0-2.2. The activation energy for polymerization is found to increase exponentially with pH. The time required for emulsification (which is quickly followed by separation of resin layer) to occur in an aqueous solution of furfuryl alcohol also increases exponentially with pH, but it decreases exponentially with temperature. This is described quantitatively by a single expression.

INTRODUCTION

Polymerization of furfuryl alcohol in the presence of acid catalysts yields furan resins having exceptional resistance to acids, alkalis, chemicals, and solvents. There are numerous patents covering the methods of preparation and a wide variety of applications of furfuryl alcohol resins. Several reviews of the properties and uses of these resins have appeared.¹⁻⁵ Relatively little is known however of the chemistry of resinification of furfuryl alcohol. Dunlop and Peters⁶ reviewed the published literature up to 1951. Barr and Wallon⁷ reported the chemical composition of furfuryl alcohol resins. Very little has been reported in the literature on the kinetic aspects of this reaction.

The main problems encountered in studying the polymerization of furfuryl alcohol are, firstly, the difficulty in maintaining isothermal conditions because of the highly exothermic nature of the reaction and, secondly, the difficulty of analysis of furfuryl alcohol in the presence of its polymers, owing to which the extent of reaction of the monomer cannot be directly determined. For kinetic investigation, Shono and Hachihama⁸ employed a 50% aqueous solution of furfuryl alcohol and measured the time t required to reach emulsification in the presence of a definite hydrogen ion concentration. This was taken as a measure of the rate of reaction. They observed that $\log t$ increases proportionately to pH.

The products of resinification of furfuryl alcohol are yellowish brown in color, and the intensity of the color increases with the extent of reaction. So a measure of the resinification rate could be obtained from the rate of

increase of color intensity measured colorimetrically. This method was employed in the present study. The reaction was carried out in a batch reactor heated by a constant-boiling liquid under total reflux, which ensured isothermal conditions.

EXPERIMENTAL

Materials. BDH (England) technical-grade furfuryl alcohol was used. Its furfural content, as determined by the bisulfite method,⁹ was 0.14%;

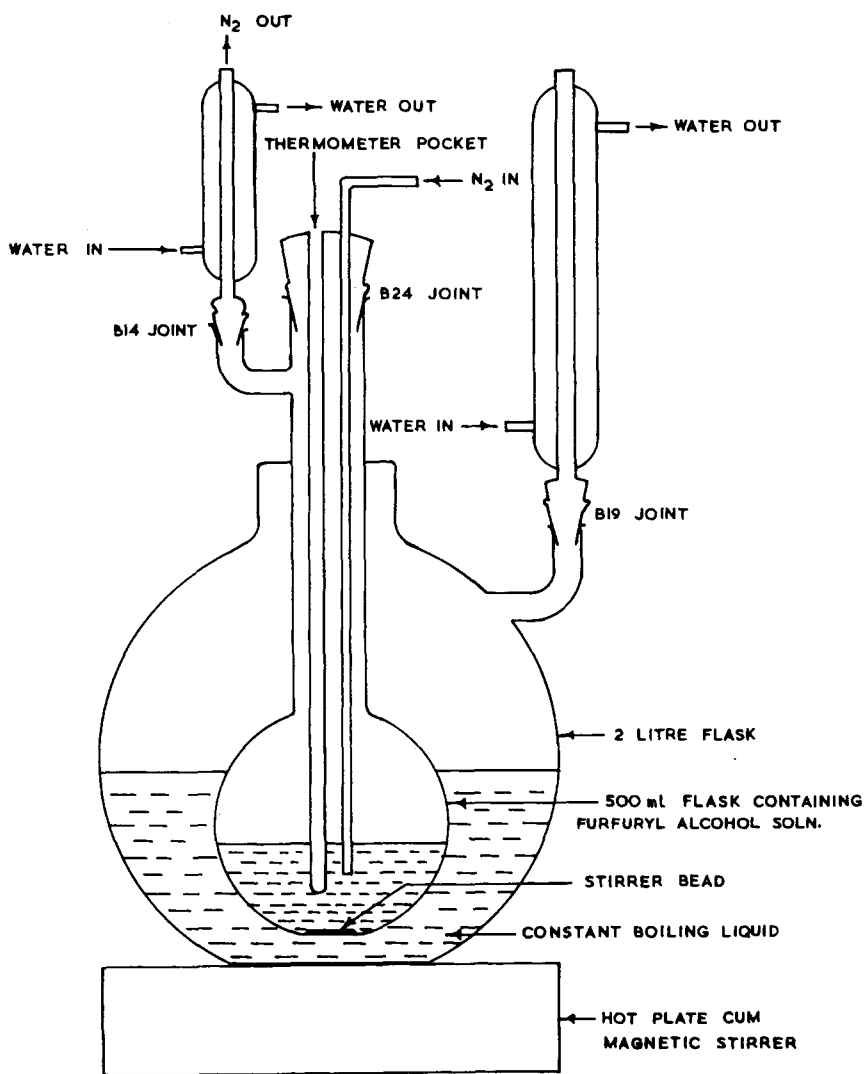


Fig. 1.

and its cloud point,⁹ 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.)

Apparatus. A diagrammatic sketch of the reactor setup is shown in Figure 1. The reactor consisted of two round flasks, one inside the other. The inner flask, which contained the reaction mixture, was provided with a vertical water-cooled condenser, a thermometer pocket, and an inlet for nitrogen. The reaction mixture was blanketed with nitrogen and stirred with a magnetic stirrer. The outer flask, also fitted with a water-cooled condenser, served as a jacket for the constant-boiling liquid used as the heating medium. In order to prevent direct transfer of heat from the hot plate to the inner flask, a gap of about 5 mm was kept between the bottoms of inner and outer flasks. The reaction mixture was maintained at a constant temperature by boiling a suitable liquid in the outer flask under total reflux.

Procedure. The resinification reaction was carried out in the presence of a buffer mixture in order to overcome the catalytic effect of levulinic acid which could be formed⁶ by the reaction of furfuryl alcohol with water. A 50% (by vol) solution of furfuryl alcohol in aqueous Clark-Lubs buffer,¹⁰ prepared by mixing calculated volumes of KCl and HCl solutions of known strengths, was used. The actual pH was determined with a pH meter. The acidic component (HCl) of the buffer was added when the solution in the reaction flask reached a constant temperature, almost equal to boiling temperature of the liquid in the outer flask. The reaction period was reckoned from the moment the acidic component was added. Samples were drawn from the reaction flask at different intervals of time and their percentage transmission (relative to percentage of transmission of distilled water as 100) was quickly measured with a Systronics photoelectric colorimeter Type 101 fitted with Ilford blue filter. A stream of purified nitrogen was constantly passed over the reaction mixtures in order to prevent entry of air during sampling. The process was continued till the clear solution became cloudy due to emulsification. The emulsification was quickly followed by separation of resin layer. The time required to reach the emulsification stage was noted.

RESULTS AND DISCUSSION

It is interesting to observe that the logarithm of percentage transmission (Tr) falls linearly with reaction time (t), as shown by the semilogarithmic plots of Tr versus t in Figures 2 to 4 for different pH and temperature levels. On the basis of this observation, an expression for the variation of Tr with t can be written as follows:

$$Tr = Tr_0 e^{-kt} \quad (1)$$

where Tr_0 is the initial transmission and k is a constant.

It may be postulated that the color of the polymeric species formed by resinification of furfuryl alcohol is due to the presence of one or more of the same chromophoric constituent in the molecule. Defining I_0 as the original

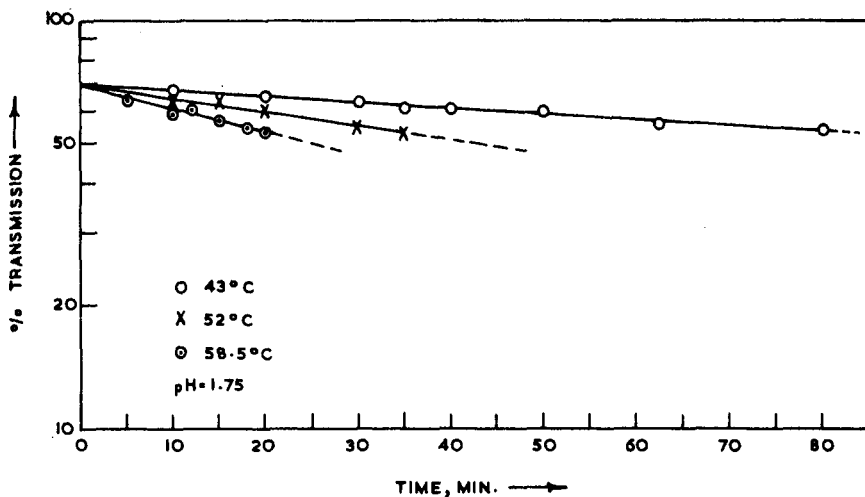


Fig. 2.

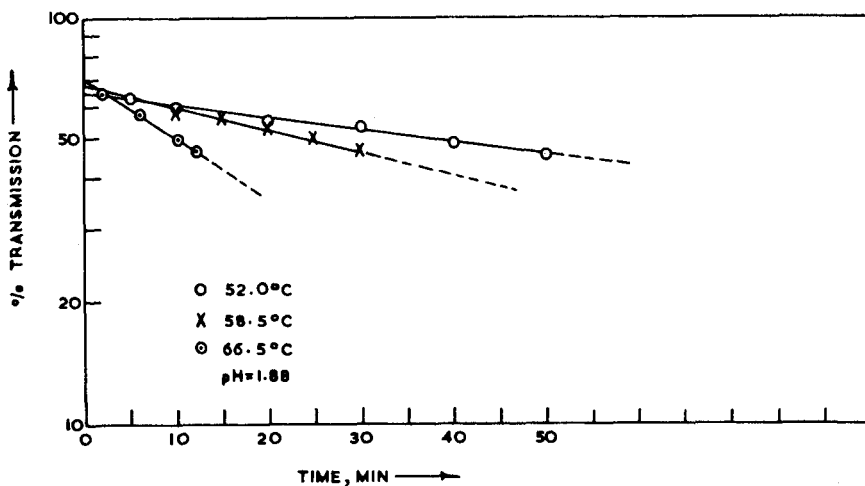


Fig. 3.

intensity of light and I as the intensity after absorption in a path length l by a solution of furfuryl alcohol resins, the dependence of the transmission on the concentration c of the chromophoric component in solution can be expressed by the Beer-Lambert law as

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

where ϵ represents the extinction coefficient of the chromophoric component.

Since $Tr = (I/I_0) \times 100$, a comparison of eqs. (1) and (2) gives

$$e^{-\epsilon cl} = (Tr_0/100) e^{-kt}$$

TABLE I
Values of Apparent Rate Constant (k) and Time of Emulsification (t_e) at Different pH and Temperature Levels

pH	Temp., °C	$k \times 10^3, \text{min}^{-1}$	t_e, min
1.75	43.0	3.543	118
	52.0	7.803	50
	58.5	12.84	27
1.88	52.0	6.558	81
	58.5	12.86	43
	66.5	32.42	20
2.00	52.0	3.353	130
	58.5	9.266	68
	66.5	29.75	33

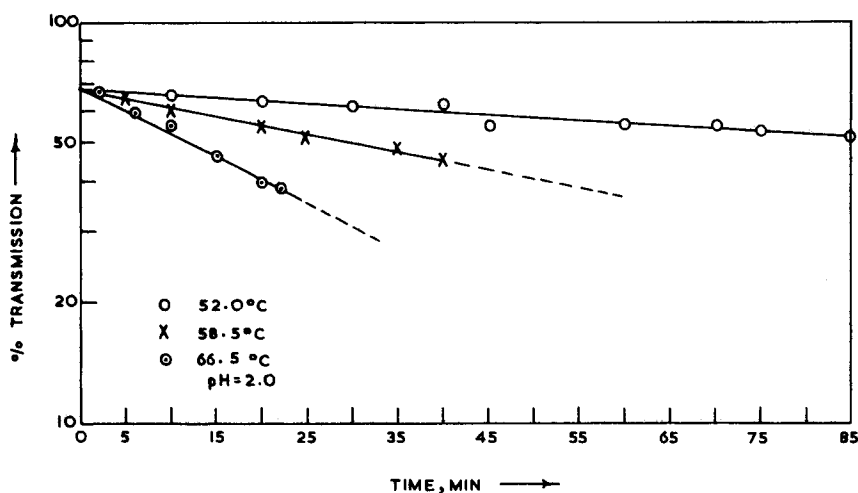


Fig. 4.

or

$$\epsilon cl = -\ln (Tr_0/100) + kt.$$

Therefore,

$$\frac{dc}{dt} = \frac{k}{\epsilon l} = k'. \quad (3)$$

Considering dc/dt as a measure of the rate of resinification of furfuryl alcohol, eq. (3) is taken to signify that this resinification reaction is of zero order. It may be noted that zero order is often an indication of a complex reaction involving a number of steps in succession. The resinification rate constant k' is related to the constant k , obtained from the slope of the linear semilog plot of percentage transmission versus reaction time. The constant k will be called the apparent rate constant.

TABLE II
Activation Energy (E) for Resinification at Different pH Levels

pH	E , kcal/g-mole
1.75	17.41
1.88	25.03
2.00	33.90

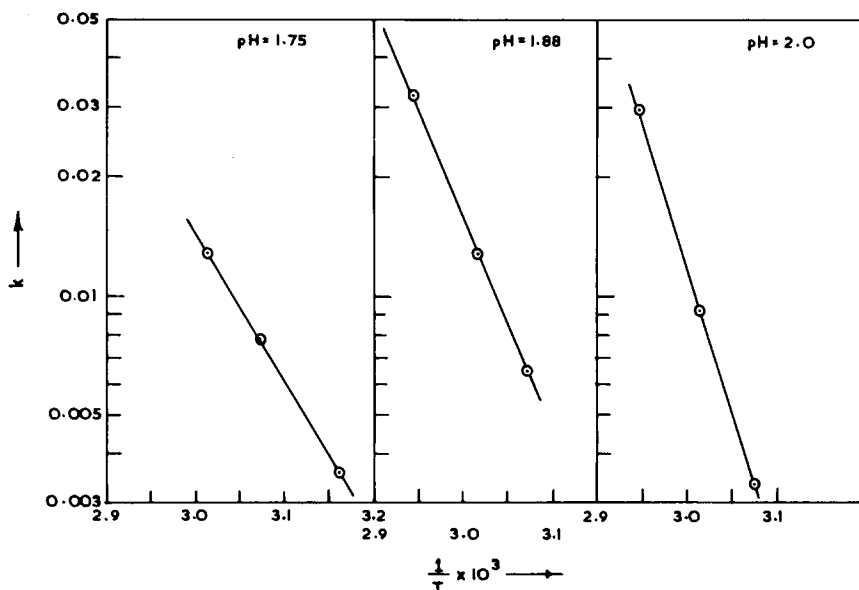


Fig. 5.

The values of k for several pH and temperature levels are recorded in Table I. The time periods required to reach emulsification under respective pH and temperature conditions are also included in Table I. On the premise that ϵ is unaffected by temperature, the activation energy for resinification of furfuryl alcohol can be derived from the Arrhenius plot of the apparent rate constant k . The Arrhenius plots corresponding to different pH levels are shown in Figure 5, and the respective activation energies are given in Table II. The logarithm of activation energies has a linear relationship with pH, as revealed by Figure 6. The relationship is derived as follows:

$$E = 0.215 \exp (2.53 \text{ pH}) \text{ kcal/g-mole.} \quad (4)$$

In agreement with the observations of Shono and Hachihama,⁸ the logarithm of the time of emulsification (t_e) reveals a direct proportionality to pH. In addition, for a given pH, $\log t_e$ decreases linearly with increasing temperature, as shown by the plots in Figure 7. On the basis of these plots, t_e has been correlated with temperature ($T^\circ\text{C}$) and pH by the expression

$$t_e = 8.865 \exp (3.822 \text{ pH} - 0.0954T) \text{ min.} \quad (5)$$

It should be noted that eqs. (4) and (5) are applicable for furfuryl alcohol resinification by Clark-Lubs buffer (pH 1.0–2.2). To test the validity of eq. (5), several experiments have been conducted to determine t_e for 50% aqueous solution of furfuryl alcohol at different pH levels in the range

TABLE III
Observed Vs. Calculated Time of Emulsification (t_e)

pH	Temp., °C	t_e , min	
		Observed	Calculated from eq. (5)
1.20	43.0	14.6	14.4
1.33	43.0	23.6	23.7
1.52	43.0	49.1	48.8
1.65	43.0	80.1	80.3
2.10	63.0	67.0	66.6
2.15	63.0	81.5	80.7

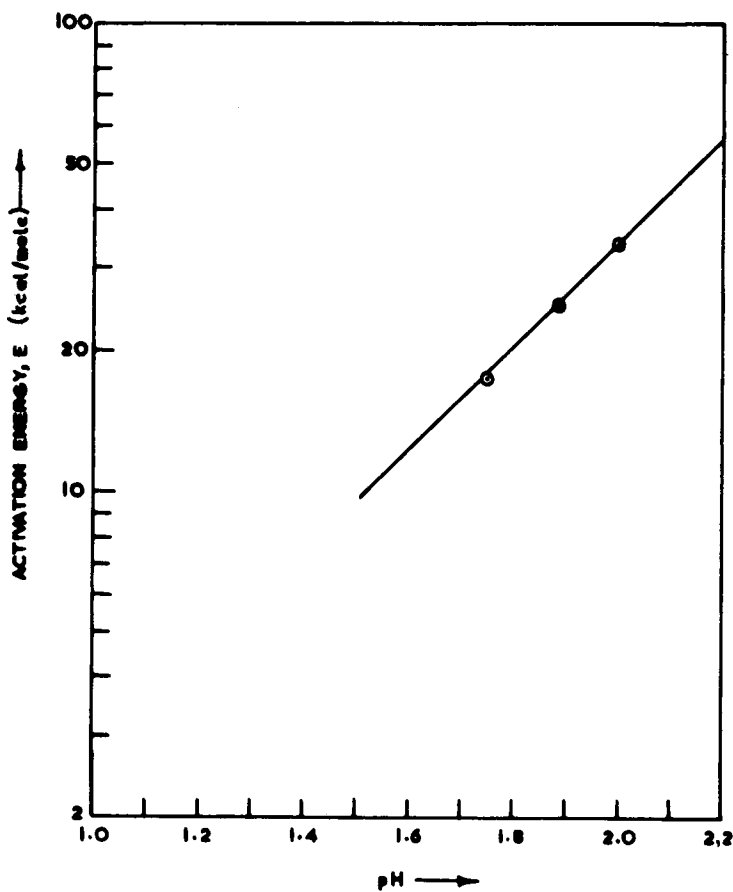


Fig. 6.

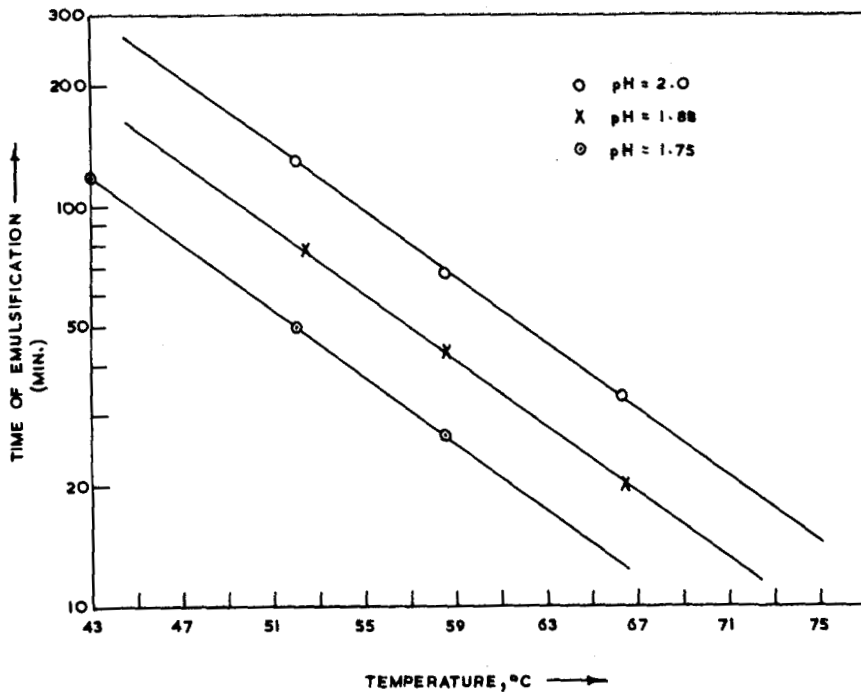


Fig. 7.

of 1.0–2.2. The observed t_e values, given in Table III, are seen to be in good agreement with the values calculated from eq. (5).

References

1. A. J. Norton, *Ind. Eng. Chem.*, **40**, 236 (1948).
2. T. F. Wisniewski, *Prezemysl. Chem.*, **27**, 633 (1948).
3. E. Becker, *Kunststoffe*, **42**, 314 (1952).
4. G. Fabre, *Ind. Plast. Mod. (Paris)*, **5**(8), 37 (1953).
5. M. Ignatius, *Adhesive Age*, **12**(9), 25 (1969).
6. A. P. Dunlop and F. N. Peters, *The Furans*, ACS Monograph Series, Reinhold, New York, 1953.
7. J. B. Barr and S. B. Wallon, *J. Appl. Polym. Sci.*, **15**, 1079 (1971).
8. Toshiyuki Shono and Yoshikazu Hachihama, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **56**, 520 (1953).
9. G. M. Kline (Ed.), Analytical Chemistry of Polymers, in *High Polymers*, Vol. XII, H. Mark, C. S. Marvel, H. W. Melville, and G. S. Whitby, Eds., Interscience, New York, 1959, p. 202.
10. H. T. S. Britton, *Hydrogen Ions*, Vol. 1. Chapman and Hall, London, 1955, p. 352.

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