

**Original**

# Examination of Chemical Reaction through Continuous Measurement of Specific Dielectric Constant

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Knowing that a determination of reaction velocity can be gotten from a measurement of the change of a physical constant, we developed a computerized apparatus for continuous measurement of the specific dielectric constant of a liquid reaction mixture. Principle of the measurement is based on a change of L-C oscillation frequency with change in stray capacitance of the coil due to a liquid sample inserted into a U-tube. The change in stray capacitance depends on the value of the dielectric constant of the sample, which varies with the amount of component in the mixture. The apparatus consists of a flow path that circulates the liquid mixture through a U-tube by a pump from a reaction vessel, an 18MHz L-C oscillator, a drive mechanism of coil hold the U-tube in a center and a micro-computer system to control the mechanism and to handle the measured data. For numerical calculation and for drawing, a commercial micro-computer was used, both sections connected with GP-IB. The specific dielectric constant ( $\epsilon_s$ ) was calculated by the following equation. At present, the reaction velocity of esterification and of hydrolysis have been measured. In addition the reaction mechanism of acylation of aniline has been determined from the  $\epsilon_s$  curve.

$$\epsilon_s = \frac{1/\{f_s^2 + [R/(4\pi L)]^2\} - 1/f^2}{(2\pi)^2 L K C o}$$

## KEYWORDS

reaction velocity, dielectric constant, reaction mechanism, micro-computer control

## Introduction

In this study, the primary concern was development of the most suitable device for continuous measurement of reaction velocity. There exist various principles applicable to such a measurement. But, most of them were not usable for development of a device suitable for the desired measurement.

We have adopted a method such that the reaction speeds can be obtained through continuous measurements of the dielectric constants of the liquid mixtures. For measurement of dielectric constants there are many reports on methods as well as devices, but these are concerned with static measurements for solids and liquids. Therefore, we had to design and construct a new device suitable for the desired continuous measurement.

In the design of a device, one of the practical difficulties was the design of a probe for continuous detection of dielectric constants and the other one was to find methods of correcting the frequency

of an LC circuit to be constant despite its being sensitively affected by ambient temperature, because the temperature of the liquid to be measured will change during the reaction.

To satisfy the above difficult requirements, the devices become necessarily complicated and indeed, various tests were, therefore, necessary to develop stable and reproducible devices. Thus, the present prototypes of the devices have been constructed after many improvements and modifications for the electrical and mechanical parts of the devices.

## I Principle of the method

We used the two methods, [1] and [2] as follows.

[1] Fig. 1 shows the principle of the measurement. The L-C resonant circuit consists of a coil of inductance L and a capacitor of capacitance C. Now the coil has stray capacitance. We cite a value of the stray capacitance in air as  $C_0$ , then, the resultant capacitance of the circuit is equal to sum of C and  $C_0$ . If a glass U-tube containing a liquid sample is inserted into the coil, then the stray capacitance will increase to  $K\epsilon_s C_0$  due to the inserted sample, where K is a constant depending on the geometries of the coil and the U-tube and  $\epsilon_s$  is the dielectric constant of the sample. Therefore, the resonant frequency of the L-C circuit will change in accordance with the value of  $\epsilon_s$ . We can thus obtain a value of  $\epsilon_s$  from the change in frequency of the LC circuit.

[2] On the other hand, if the U-tube is inserted into the parallel plate capacitor of capacitance C, then the capacitance changes from C to  $K\epsilon_s C$ , where K is a constant depending on the geometries of the U-tube and the capacitor. Consequently, the frequency of the L-C circuit changes. The dielectric constant can be obtained from the change in frequency similarly as explained in [1].

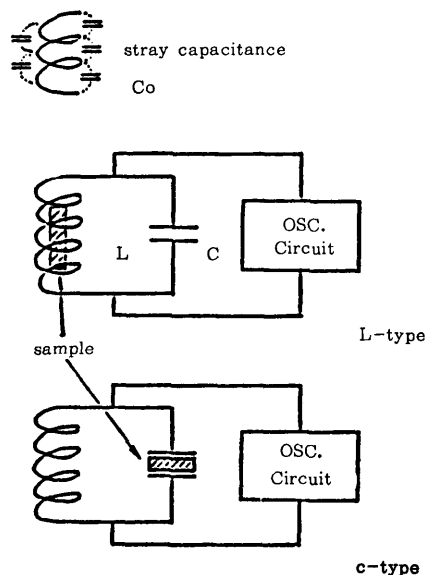


Fig. 1 Principle of the measurement.

## II Derivation of dielectric constant from frequency change

First, we explain the equations relevant to the method [1]. Eqs. (1) through (4) are necessary to obtain the dielectric constant of the sample from the frequency measurements.

Eq.(1) shows the relation between the dielectric constant  $\epsilon_s$  and the resonant frequency  $f_s$  when the sample is inserted.  $\epsilon_s$  in the equation is however a function of  $f$ ,  $LKC_0$  and  $R/4\pi L$ , so we can not obtain  $\epsilon_s$  from measured frequencies  $f_s$  without knowing these parameters.

$$\epsilon_s = \frac{1}{\frac{\{f_s^2 + [R/(4\pi L)]^2\}}{(2\pi)^2 LKC_0} - f^2} \dots\dots\dots(1)$$

These parameters can be obtained from measurements using at least three known dielectric

constants as reference samples. The equations necessary to obtain values of these parameters from the measurements are Eqs. (2), (3) and (4).

$$\frac{1}{f^2} = \frac{1}{f_{s1}^2 + [R/(4\pi L)]^2} - (2\pi)^2 L K Co \epsilon_{s1} \dots\dots\dots(2)$$

$$(2\pi)^2 L K Co = \frac{1}{\epsilon_{s1} - 1} \left\{ \frac{1}{f_{s1}^2 + [R/(4\pi L)]^2} - \frac{1}{f_a^2 + [R/(4\pi L)]^2} \right\} \dots\dots\dots(3)$$

$$\left( \frac{R}{4\pi L} \right)^2 = \frac{f_{s2}^2 \frac{\epsilon_{s2} - 1}{f_a - f_{s2}} - f_{s1}^2 \frac{\epsilon_{s1} - 1}{f_a - f_{s1}}}{\frac{\epsilon_{s1} - 1}{f_a - f_{s1}} - \frac{\epsilon_{s2} - 1}{f_a - f_{s2}}} \dots\dots\dots(4)$$

Notations used are as follows ;

$f_s$  is the frequency when the U-tube containing the sample is inserted into the coil.

$f_a$  is the frequency when the U-tube containing air (of dielectric constant unity) is inserted.

$f_{s1}$  is the frequency when a reference sample of dielectric constant  $\epsilon_1$  is used.

$f_{s2}$  is the frequency when a reference sample of dielectric constant  $\epsilon_2$  is used.

$R$  is the ohmic resistance of the resonant circuit.

$K$  is the geometrical correction factor mentioned above.

Now, if these parameters were actually obtained from measurements of reference samples at a fixed frequency of the resonant circuit, then the values are valid only for the fixed frequency. Thus we can not use these values at any other frequency. Consequently, in our measurements the resonant frequency must be held at the fixed frequency,  $f_a$  just before samples are inserted into the coil. From the frequency  $f_s$  measured under the condition, values of the dielectric constant can be obtained using equation (1). In addition, holding the frequency fixed is of great advantage to avoid a temperature effect on the resonant frequency as mentioned previously.

Next, we explain the equation's relevant to method [2]. The dielectric constant of the sample can be obtained by using Eqs. (5) through (9). The explanation for these equation's is quite similar to method [1]. The notation used in the equations are the same.

$$f_s = \frac{1}{2\pi} \sqrt{\frac{1}{L(C + K Co \epsilon_s)} \cdot \frac{L - (C + K Co \epsilon_s) R_1^2}{L - (C + K Co \epsilon_s) R_2^2}} \dots\dots\dots(5)$$

$$\epsilon_s = \frac{1/f_s^2 + X f_s^2 + Y}{Z} \dots\dots\dots(6)$$

$$X = \frac{\frac{1/f_{s2}^2 - 1/f_a^2}{\epsilon_{s2} - 1} - \frac{1/f_{s1}^2 - 1/f_a^2}{\epsilon_{s1} - 1}}{\frac{f_{s1}^2 - f_a^2}{\epsilon_{s1} - 1} - \frac{f_{s2}^2 - f_a^2}{\epsilon_{s2} - 1}} \dots\dots\dots(7)$$

$$Y = Z \epsilon_{s1} - 1/f_{s1}^2 - X f_{s1}^2 \dots\dots\dots(8)$$

$$Z = 1/(\epsilon_{s1} - 1) [X(f_{s1}^2 - f_a^2) + 1/f_{s1}^2 - 1/f_a^2] \dots\dots\dots(9)$$

### III Apparatus for the measuring system

Fig. 2 shows the measuring system, which consists of the following apparatus.

- (1) Reaction vessel.
- (2) Bypass for circulating liquid sample. The U-tube is connected with the bypass in series for the detection terminal of dielectric constant.
- (3) Reciprocal drive mechanism of the U-tube to insert or withdraw it into or out of the coil.
- (4) L-C oscillator.
- (5) PLL controller to hold the resonant frequency at the fixed frequency.

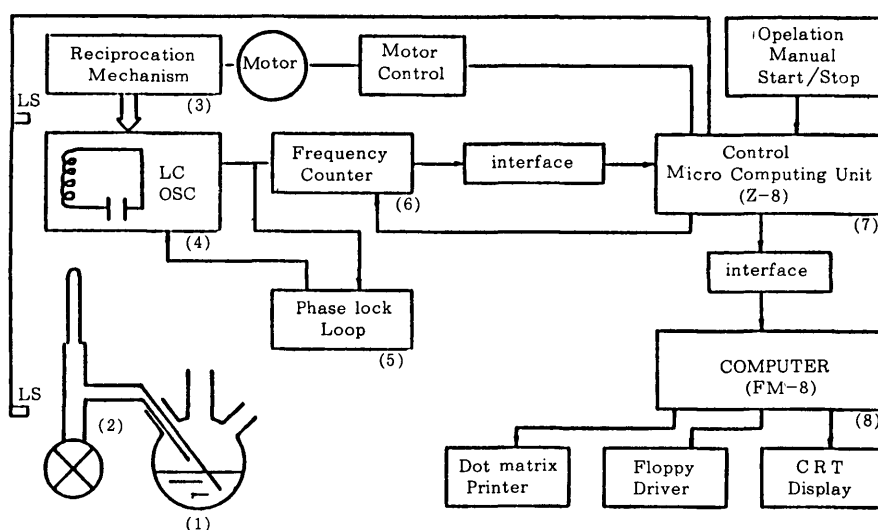


Fig. 2 Block diagram of the apparatus.

- (6) Frequency counter.
- (7) One-chip micro-computer to control timing sequences in various devices, and to transfer measured data to the personal computer (host computer).
- (8) Personal computer and peripherals.

1. Method for constant frequency control. We chose 18 MHz arbitrarily as the fixed resonant frequency  $f_a$ . In addition, 9 and 4.5 MHz were also chosen. We applied the Clapp circuit, which enables stable oscillation.

Fig. 3 is a block diagram to show the function of the most important phase locked loop which enables the resonance frequency to hold at 18 MHz while the U-tube is withdrawn. 9MHz divided out put from the 18 MHz resonant frequency of the L-C circuit which is preliminarily tuned is compared with About 9MHz output from a X'tal oscillator in the phase detector as shown in Fig. 3. The consequent output of D. C. voltage generated from the comparison is stored in the DC voltage memory of a sample and hold circuit and is also fed to a vari-cap diode whose capacitance varies with the applied D. C. voltage.

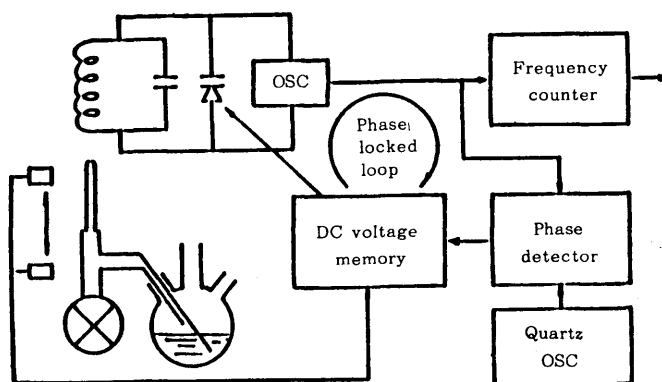


Fig. 3 Block diagram of the phase lock loop.

The vari-cap diode is connected in parallel with the capacitor C as is shown in Fig. 3. If the resonance frequency  $f_a$  changes, then the changed frequency is compared with that of the X'tal in the phase detector. The D. C. output voltage from the phase detector corrects the frequency so as to hold 18MHz.

The frequency correction by the PLL must be made with the U-tube withdrawn. For this purpose, a position limit switch is set to activate the PLL at this position. Thus, every time the U-tube is withdrawn, the resonant frequency  $f_a$  is corrected to 18 MHz by the PLL. Immediately after the correction, the U-tube is inserted, and the resonant frequency  $f_s$  is measured by the frequency counter. For this sequence, another position limit switch is set so as to initiate the measurement of  $f_s$ .

2. The data processing one-chip micro-computer reads the frequency via the interface and then transfers the data to the host computer, which is an 8 bit personal computer, FM-8. We can directly obtain numerical values of the dielectric constants from the computer which calculates equation (1), as soon as it accepts input values of  $f_s$ . Data acquired for the measurements in one run are stored temporarily in the computer memory and then, transferred to a floppy disk, if necessary.

#### IV Performance test with reference samples

Experimental results obtained from the performance test of the apparatus are as follows.

First of all, we must determine values of the parameters in equation (1). We used chlorobenzene and Methanol as reference samples, and the other samples shown in Fig. 4 are also used.

Fig. 4 shows relations between measured values and literature values for each dielectric constant of the samples in method [1]. The reference samples are labeled by a star (\*). In Fig. 4 (a) most of the measured points can be fitted by a straight line with an inclination of  $45^\circ$ . But, a point for water deviates above the line. Thus, the performance for samples with large dielectric constants seem to be inadequate. This is because, although it is very difficult to get pure water, the water used was distilled twice. Nevertheless, the deviation was too large.

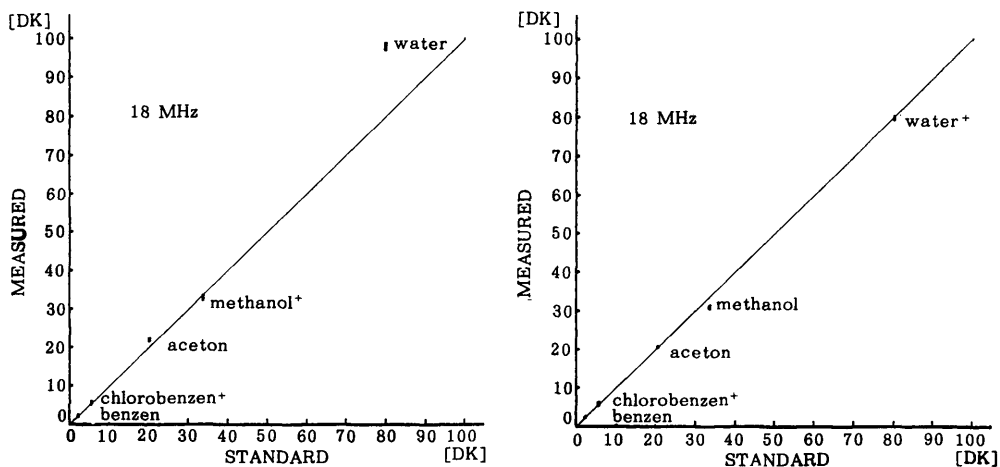


Fig. 4 (a) Characteristics on L detection calibrated with chlorobenzene and methanol. (b) Characteristics on L detection calibrated with chlorobenzene and water.

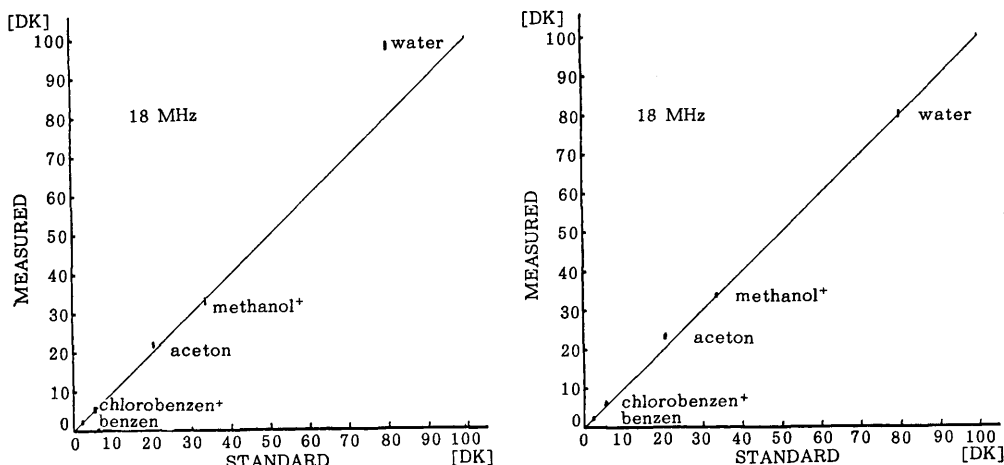


Fig. 5 (a) Characteristics on L detection calibrated with chlorobenzene and methanol. (b) Characteristics on C detection calibrated with chlorobenzene and methanol.

We then used the water as reference and points plotted similarly are shown in Fig. 4 (b). The points fit better than before. Thus, better fit can be obtained by using water as reference, though the difference between the former and the latter is not yet clear at present.

Results obtained from method [2] are shown in Fig. 5.

Distribution of the measured points is good compared to the former as is seen in Fig. 5.

Especially, the deviation for water is improved.

## V Running performance test

We show results obtained from continuous measurements of dielectric constant as a function of time during a reaction in progress.

Fig. 6 is obtained from measurements when Acetic Acid is dropping into anilines. A curve labeled by L is obtained from method [1] and labeled by C from method [2].

The curve L begins to decrease at ~5 minutes, shows a minimum value at ~12 minutes, and then, increases rapidly. A maximum value is seen after ~30 minutes followed by a gradual decrease.

On the other hand, the curve C seems to be natural and does not show any minimum and maximum points such as in the curve L, in spite of measuring the same reaction.

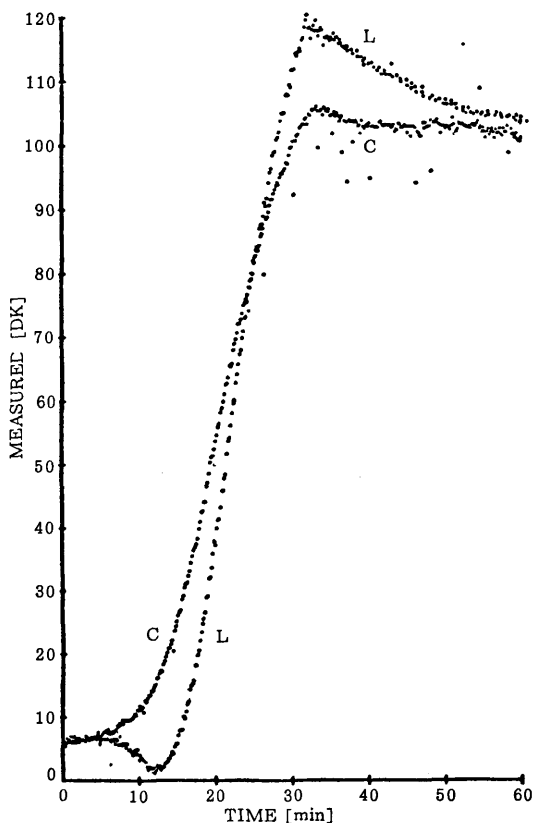


Fig. 6 Dielectric constant curves.  
(Acetic acid dropped into aniline)

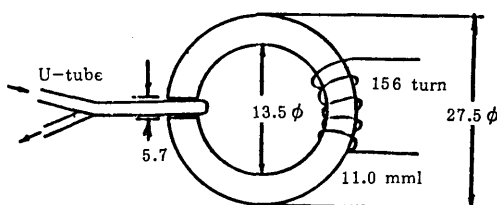
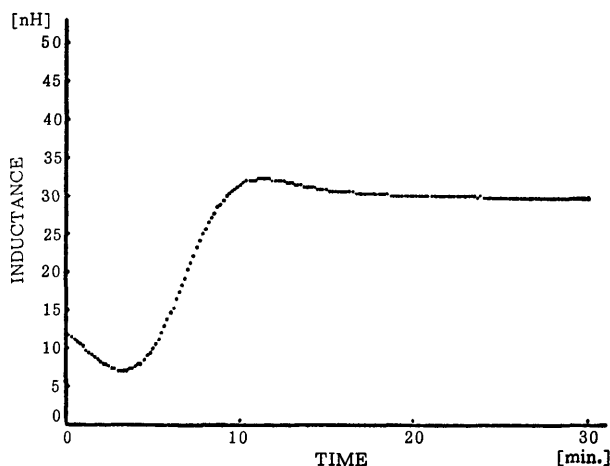


Fig. 7 (a) C Type coil with ferrite core.



(b) Inductance change of C type coil.

After our many examinations to explain the differences, we hypothesized that the differences may be caused by the magnetic properties of the reaction product and liquid mixture. To verify the hypothesis, we carried out the following experiment. An aim of the experiment is to measure the effect of the liquid mixture on the inductance of a coil while the reaction is in progress. For the purpose, we used a ferrite core coil as shown in Fig. 7. The shape of the ferrite core is like the letter C to provide a gap. The gap of the core is where the U-tube is inserted.

The inductance of the core was measured by an L-meter while the liquid mixture was circulated through the U-tube in the same manner as in the measurements of the dielectric constants. Changes in inductance measured during the reaction when Acetic Acid is dropping into Aniline is shown in Fig. 7 (b). As is seen, the measured value for the inductance changes with the elapsed time of the reaction. Therefore, the magnetic properties of the liquid mixture actually seem to change. From the shape of the curve vs. time, at the beginning of the reaction the mixtures must be diamagnetic. Because the inductance of the coil then measured is lower. Unfortunately we had not measured the inductance of the coil when the gap of the core was the air. Therefore, a quantitative argument is impossible.

Accordingly, when the inductance is increasing, the mixture must be paramagnetic and the inductance of the coil will increase with increases of the magnetic susceptibility of the mixture. From the above aspects for the magnetic property, the previously obtained strange curve labeled by L can be explained qualitatively as follows.

At the beginning of the reaction, the inductance of the coil of the L-C circuit will be decreased by the diamagnetism of the mixture. Consequently, the resonant frequency will increase. Therefore,

measured values of the dielectric constants are too small. On the contrary, after both curves labeled L and C cross, the inductance of the coil is increased by the paramagnetism of the mixture. Consequently, measured values of the dielectric constants become larger.

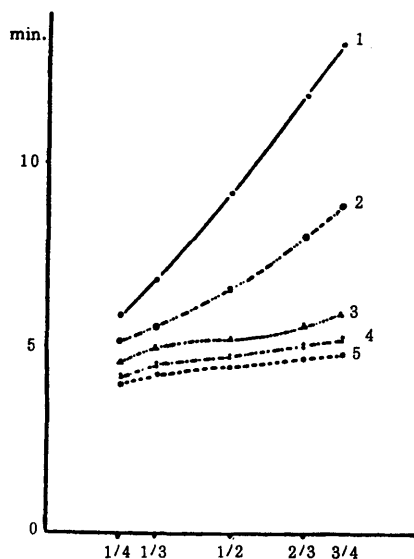
## VI Applications for some reaction speed measurements

We show curves of dielectric constant gotten for the following reactions with this apparatus.

Fig. 8 shows an example of the curves obtained by the esterification of alcohol with acid anhydride. From this figure, it was known that a small molecular alcohol had a large reaction velocity.

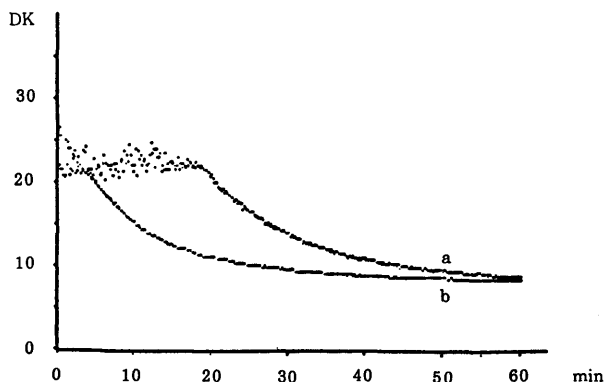
Fig. 9 shows the curve produced by the hydrolysis of propionic anhydride at 100°C, it was recognized that the existence of acetic acid as a solvent made the reaction go smoothly and rapidly.

Fig. 10 shows the acylation of furfural with acetic anhydride, in this figure, a peak definitely existed on the curve. It was located at a fixed time if the amount of furfural was fixed.



**Fig. 8** Esterification velocity of several alcohol with butyric anhydride.

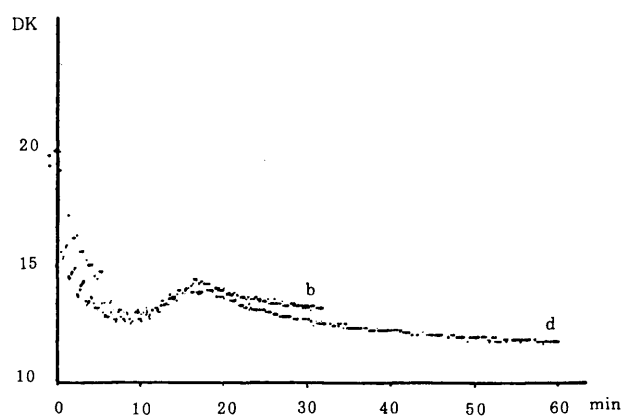
- 1: methanol    2: ethanol  
3: *n*-propanol    4: *n*-butanol  
5: 1-pentanol



**Fig. 9** Progressive state of hydrolysis of propionic anhydride by existence of solvent (Acetic acid).

	$(\text{CH}_3\text{CH}_2\text{CO})_2\text{O}$	$\text{CH}_3\text{COOH}$	$\text{H}_2\text{O}$	temp.
a	43.4g	—	9.0g	100°C
b	"	10g	"	"





**Fig. 10** Progress of reaction by alteration of amount of acetic anhydride.

	$(\text{CH}_3\text{CO})_2\text{O}$	fulfral	$\text{H}_2\text{SO}_4$	temp.	dropping amount
a	14.3g	19.2g	1 drop	15°C	1.0 ml/min
b	16.4	"	"	"	"
c	18.1	"	"	"	"
d	20.4	"	"	"	"
e	22.5	"	"	"	"