CHAPTER 4

RESULTS AND DISCUSSION

It is clear that the extent of the reactivity of sodium ions in this experimental system and the etherification of cellulose using immediately prepared sodium chloroacetate as etherifying agent do really depend on various reaction variables- temperature, reaction time and reaction medium. From this experiment, the results obtained are shown in Tables 1-9 and in graphical representations (see Figures 1-33. For easy understanding, th results are interpreted and discussed as follows:

4.1 At 26 ± 2°C

4.1.1 Non-polar organic solvents as reaction media

Non-polar solvents, such as benzene, toluene, cyclohexane and n-hexane, are used as reaction media. The D.S.'s of the products obtained from such reaction media are shown in Table 1 and their graphical representations are presented in Figures 1-4. The reactivity of sodium ions in the system in terms of D.S. shows slight difference (with about 0.021 between the maximum value to the minimum one) among non-polar media, the reactivity of sodium ions is in the following decreasing order: benzene (D.S. 0.515), toluene (D.S. 0.502), cyclohexane (D.S. 0.497), n-hexane (D.S. 0.494).

The results obtained (see Table 1 and Figures 1-5) show that the promotion of further etherification increases with longer reaction time. The D.S. above 0.500 is obtained on the first day for benzene and toluene and on the third day for all non-polar media used under the experimental conditions. After 7 days, the product with highest D.S. (0.707) is obtained for benzene whereas the D.S.'s of others are 0.686, 0.663 and 0.659.

In short, benzene (compared with toluene, cyclohexane and n-hexane) is one that can be used as reaction medium with preferred (not the best) reactivity of sodium ions and satisfied promotion for further etherification of cellulose.

Table 1 D.S.'s of the products obtained from experiment using non-polar organic solvents as reaction media and various reaction times at 26 ± 2°C

Reaction medium	D.S.*			
	Reaction time (day)			
	1	3	5	7
benzene	0.515	0.638	0.675	0.707
toluene	0.502	0.620	0.670	0.686
cyclohexane	0.497	0.630	0.662	0.663
n-hexane	0.494	0.617	0.645	0.659

* D.S. listed with 2.1% of overall experimental-error.

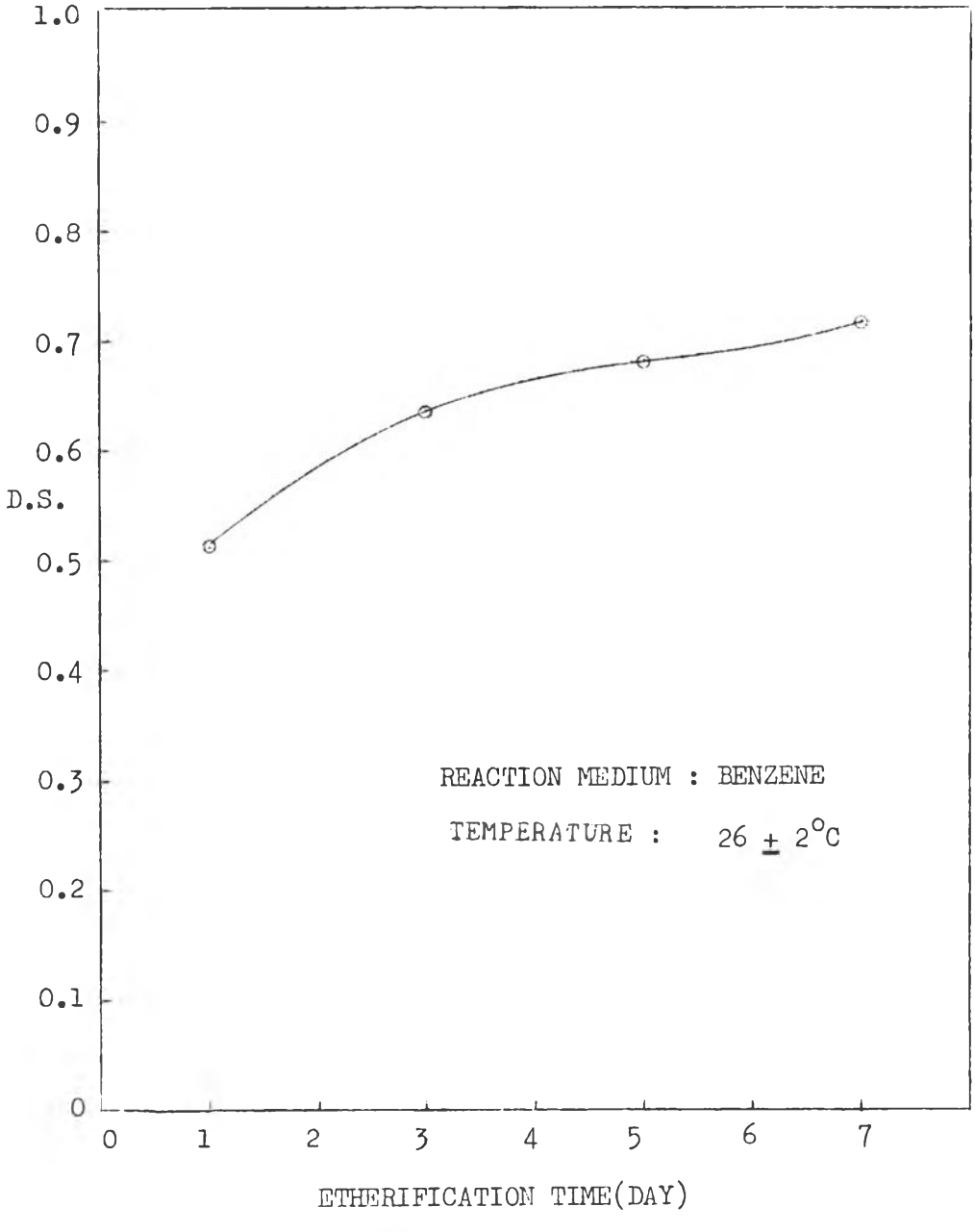

FIGURE 1 D.S. vs. ETHERIFICATION TIME

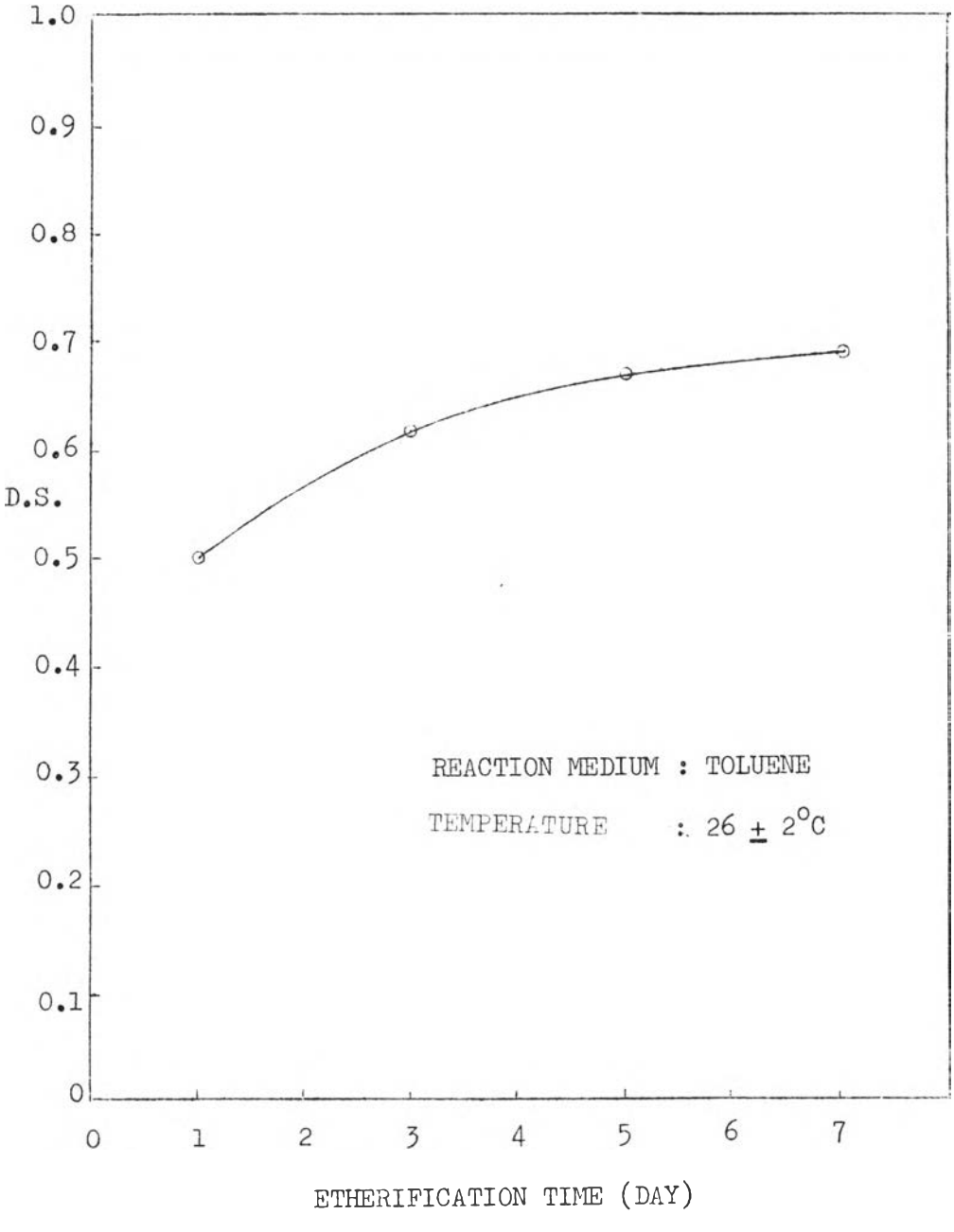

FIGURE 2 D.S. vs. ETHERIFICATION TIME

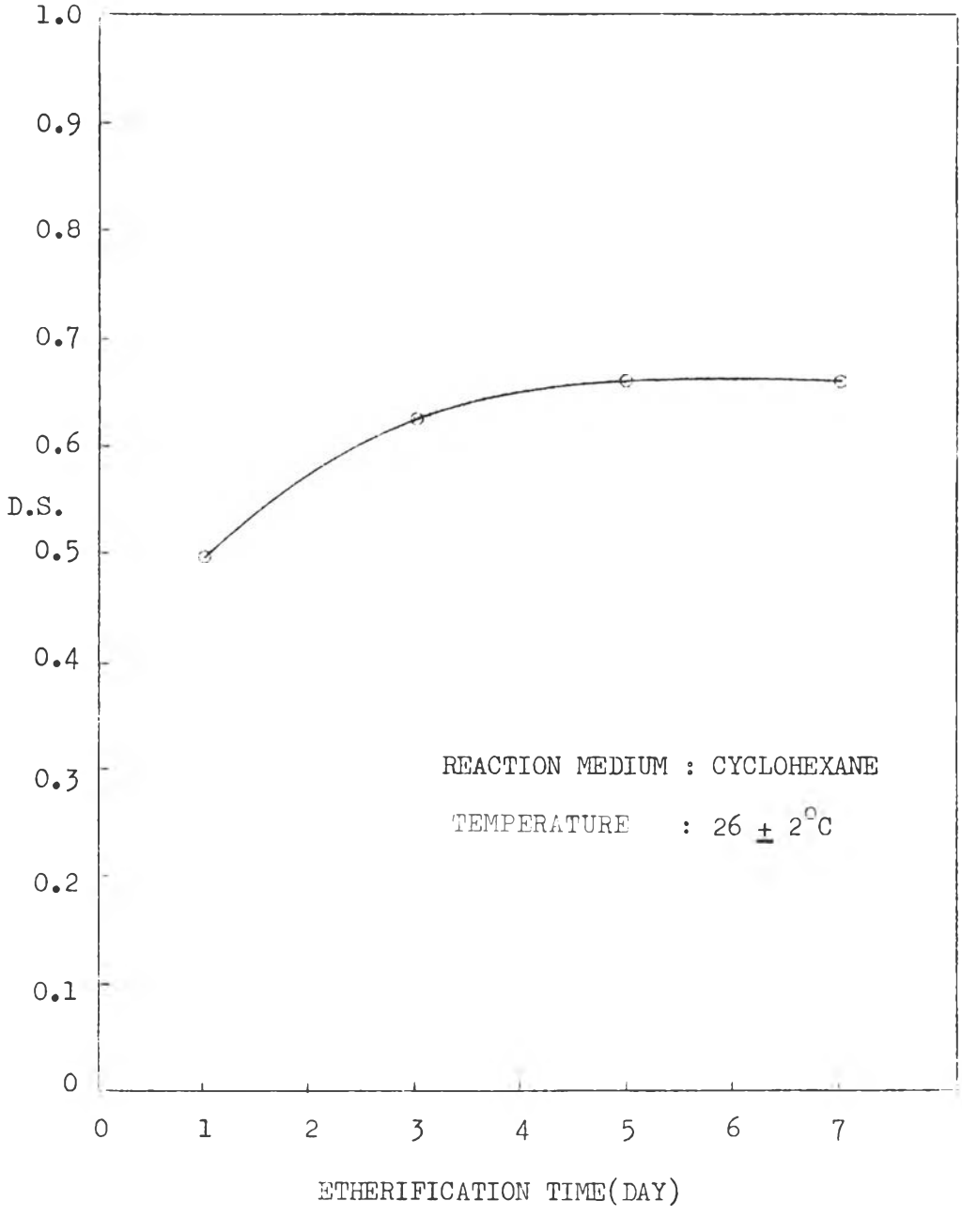

FIGURE 3 D.S. vs. ETHERIFICATION TIME

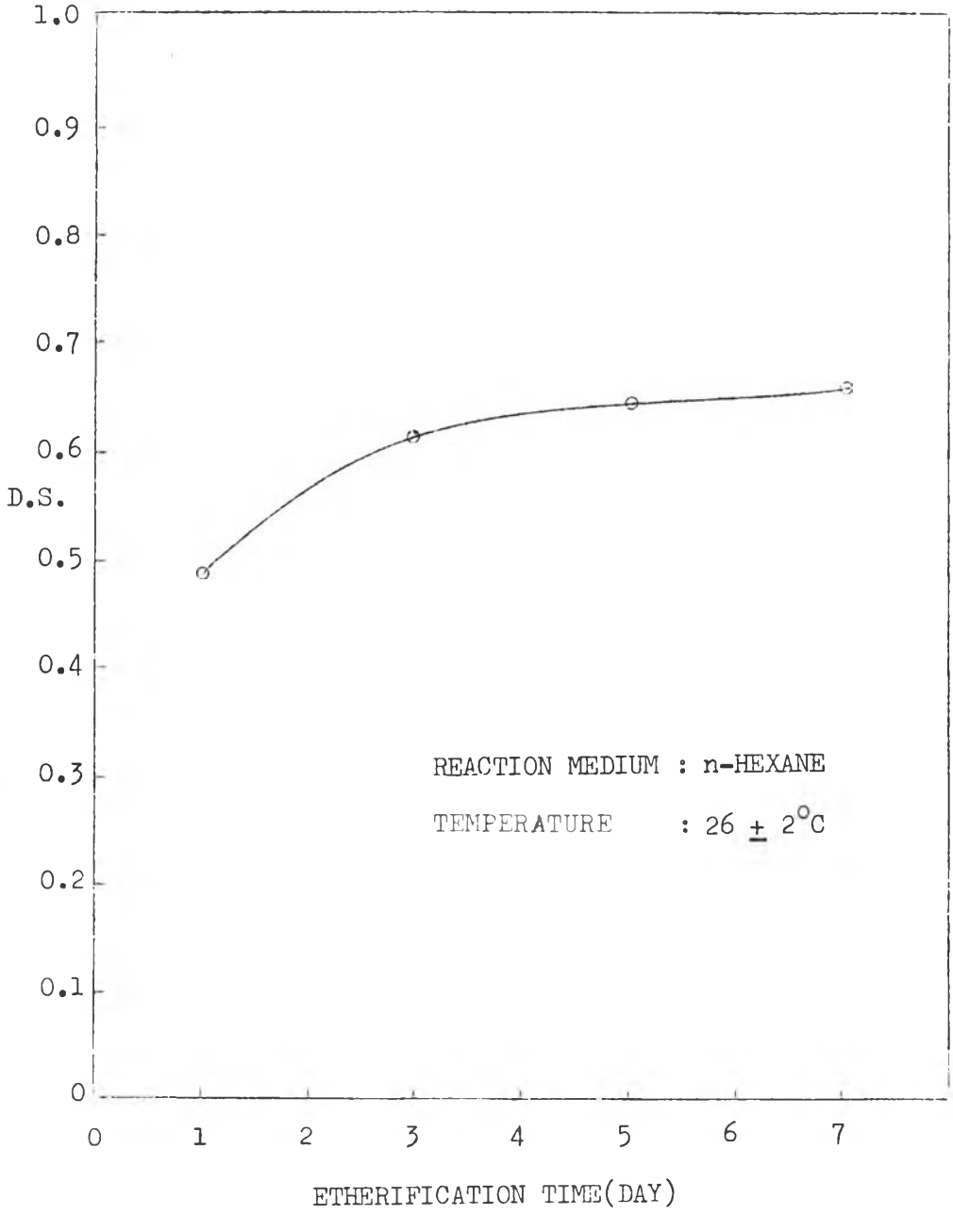

FIGURE 4 D.S. vs. ETHERIFICATION TIME

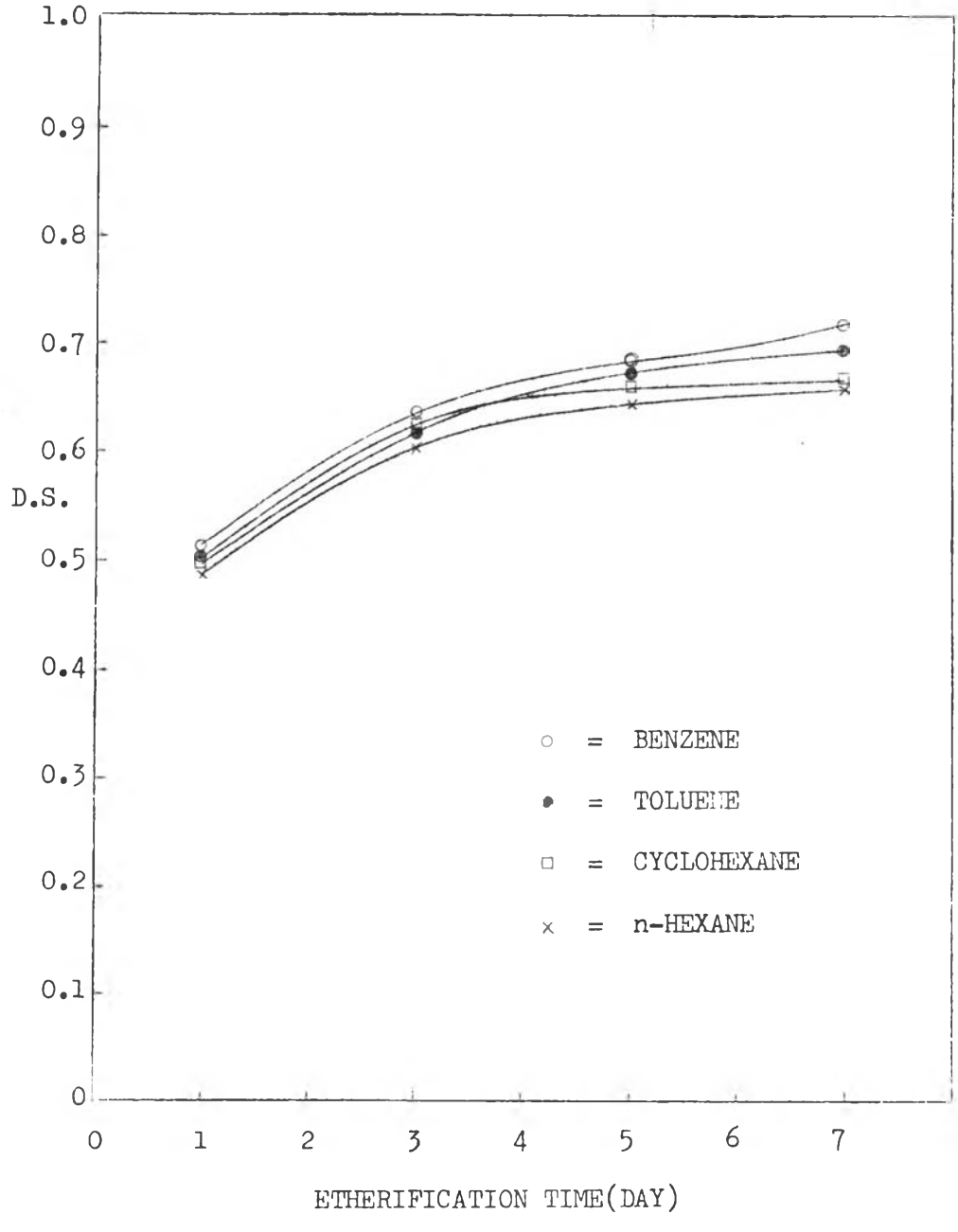

FIGURE 5 COMPARISON OF D.S.'s THE PRODUCTS OBTAINED BY USING NON POLAR SOLVENTS AS REACTION MEDIA, ETHERIFICATION AT 26 ± 2°C

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4.1.2 Polar organic solvents as reaction media

Among the common polar organic solvents, methyl ethyl-ketone, acetone, iso-propyl alcohol, n-propyl alcohol and ethyl-alcohol are chosen for reaction media in this work. The D.S.'s of the products obtained from the mentioned reaction media are shown in Table 2 and their graphical representations are presented in Figures 6-11. Such representations show that the reactivities of sodium ions in these various reaction media are quite different. From Figure 11, the reactivities of sodium ions in the ketones systems are higher than ones in alcohols. Considering alcohols as reaction media, the appearances of graphs are the same but with very slight difference in D.S. for iso-propyl alcohol. For ketones as reaction media, the reactivity of sodium ions is high when methyl ethyl ketone is used as reaction medium. It is also higher than one obtained from benzene. Acetone gives higher D.S. value than alcohols but less than one obtained from methyl ethyl ketone. In other words, the reactivity of sodium ions in acetone is better than ones in alcohols but worse than one in methyl ethyl ketone. The extent of reactivities of sodium ions are in the following order : methyl ethyl ketone (D.S. 0.643) > acetone (D.S. 0.174) > iso-propyl alcohol (D.S. 0.029) > ethyl alcohol (D.S. 0.021) ≈ n-propyl alcohol (D.S. 0.020).

From the result in Figure 11, the further etherification is sharply increased when methyl ethyl ketone is used. After 7 days of etherification, the D.S.'s of the products are 0.880, 0.205, 0.042,

0.041 and 0.041 for methyl ethyl ketone, acetone, iso-propyl alcohol, n-propyl alcohol and ethyl alcohol respectively.

From 4.1.1 and 4.1.2, it is clear that D.S., at 26 ± 2°C, of the products obtained from non-polar solvents as reaction media is better than ones from polar media (except methyl ethyl ketone). Benzene and methyl ethyl ketone are good reaction media in terms of both the reactivity of sodium ions and the promotion of further etherification of cellulose. However, methyl ethyl ketone is better reaction medium for etherification of cellulose at 26 ± 2°C than benzene.

Table 2 D.S.'s of the products obtained from experiment using polar organic solvents as reaction media and various reaction times at 26 ± 2°C

Reaction medium	D.S.*			
	Reaction time (day)			
	1	3	5	7
methyl ethyl ketone	0.643	0.788	0.868	0.880
acetone	0.174	0.187	0.195	0.205
iso-propyl alcohol	0.029	0.035	0.038	0.042
n-propyl alcohol	0.020	0.029	0.031	0.041
ethyl alcohol	0.021	0.028	0.032	0.041

* D.S. listed with 2.20% of overall experimental-error.

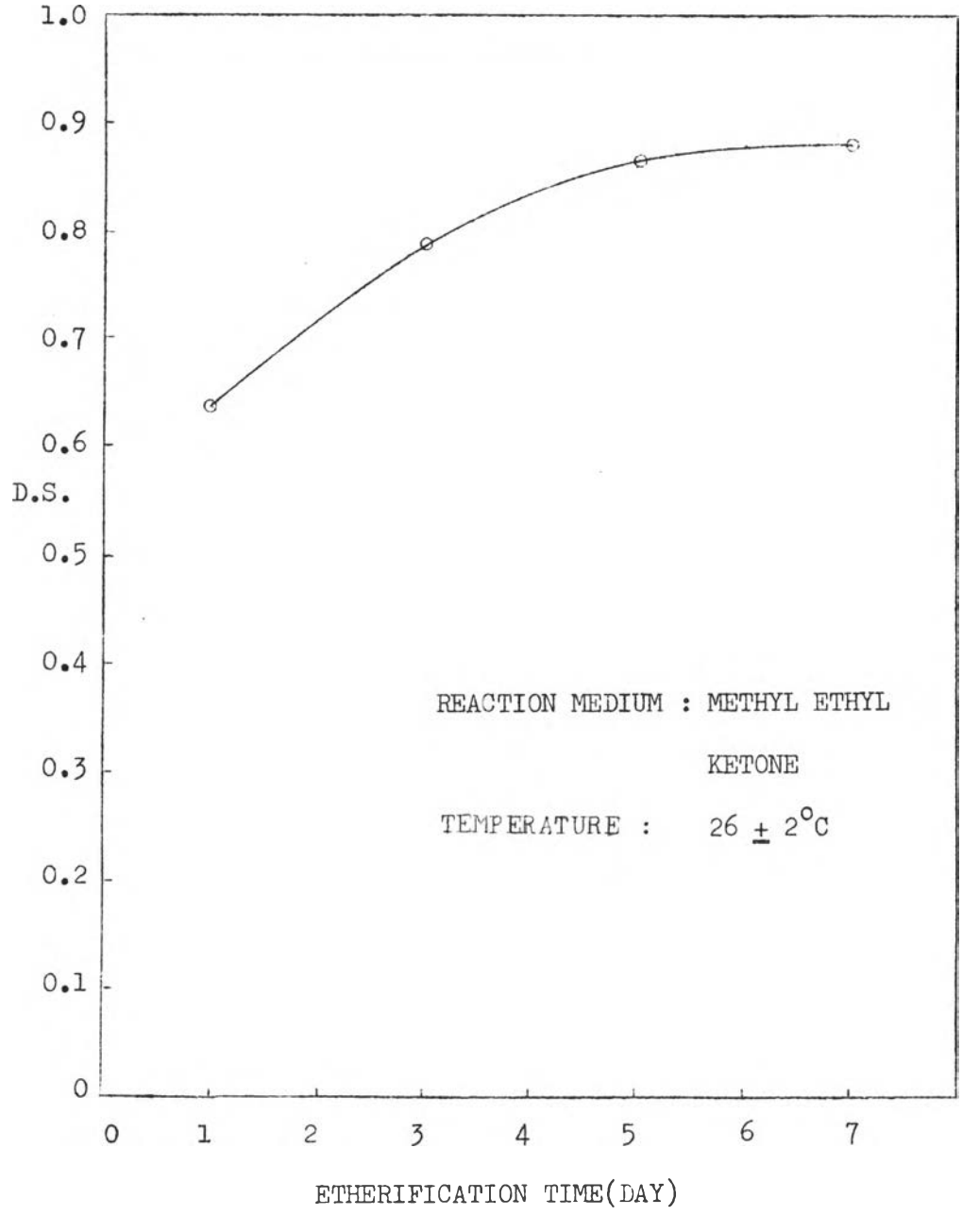

FIGURE 6 D.S. vs. ETHERIFICATION TIME

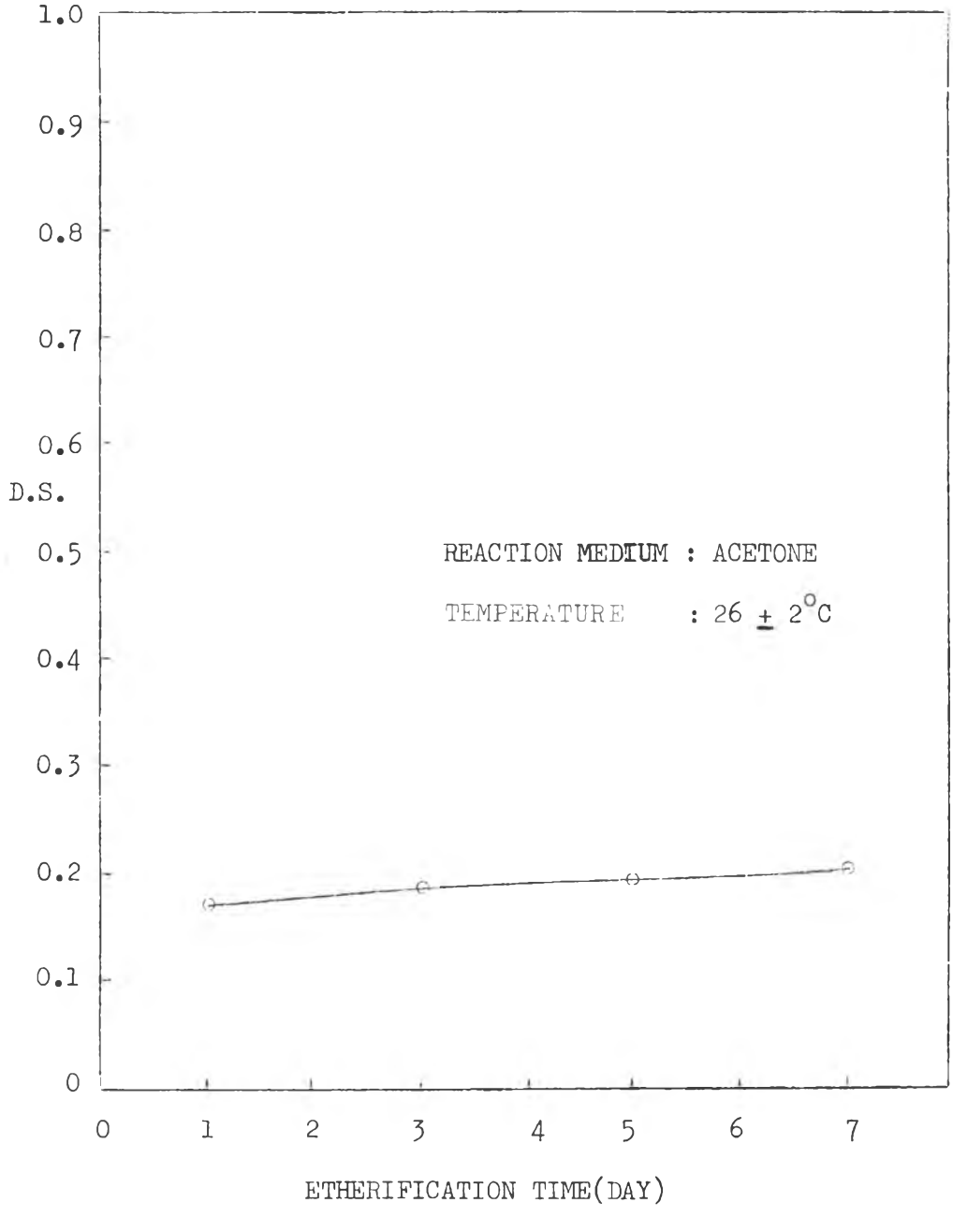

FIGURE 7 D.S. vs ETHERIFICATION TIME

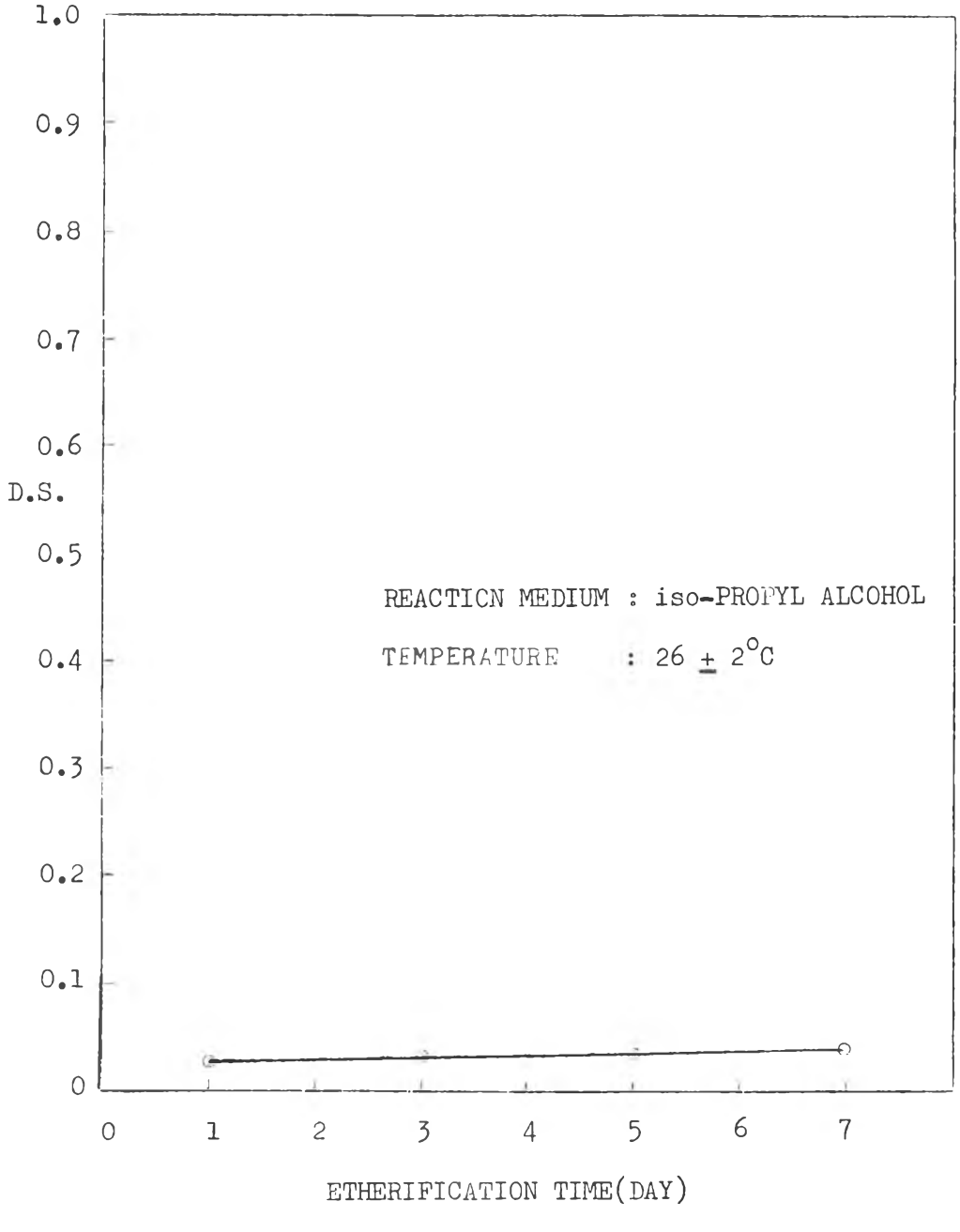

FIGURE 8 D.S. vs. ETHERIFICATION TIME

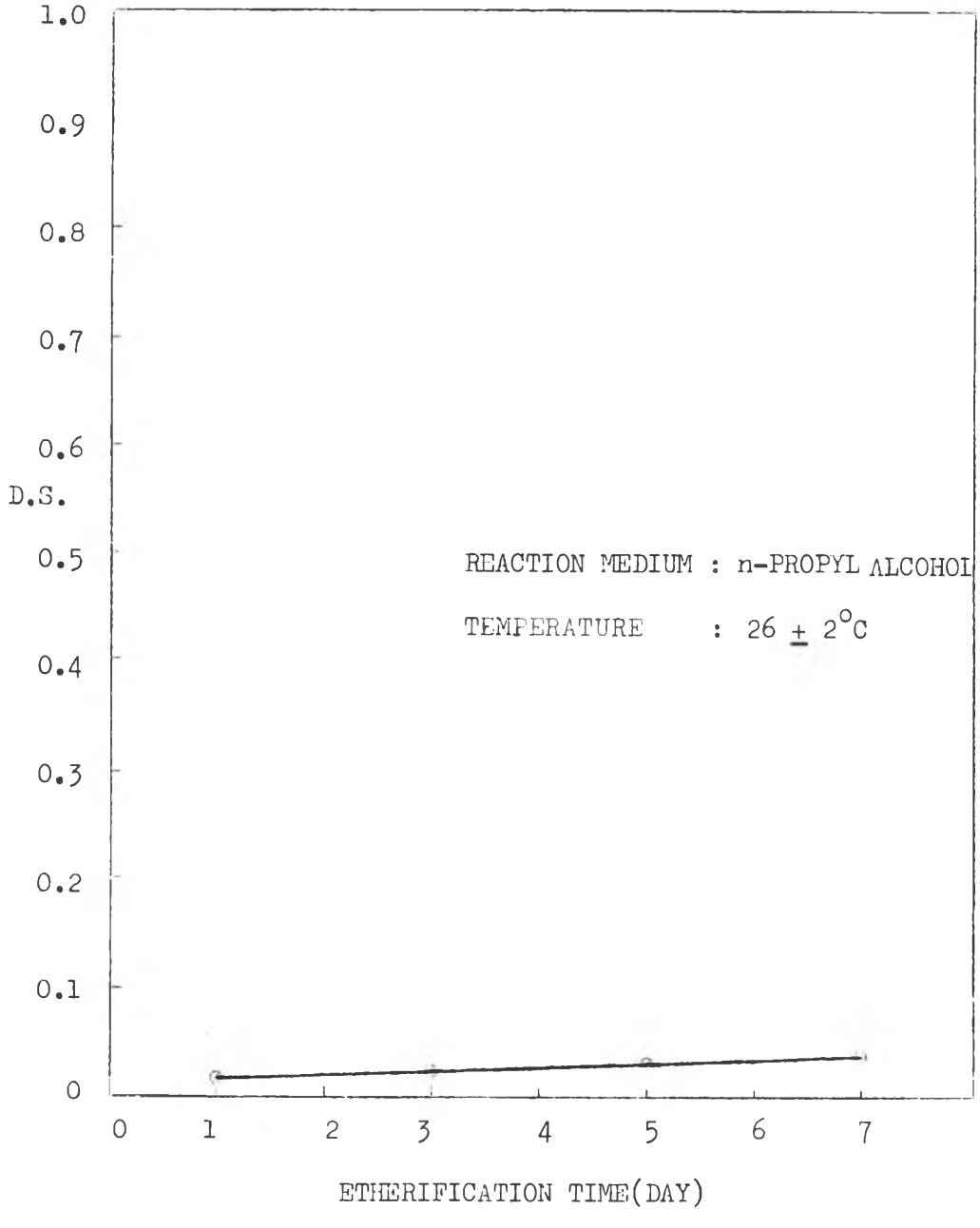

FIGURE 9 D.S. vs. ETHERIFICATION TIME

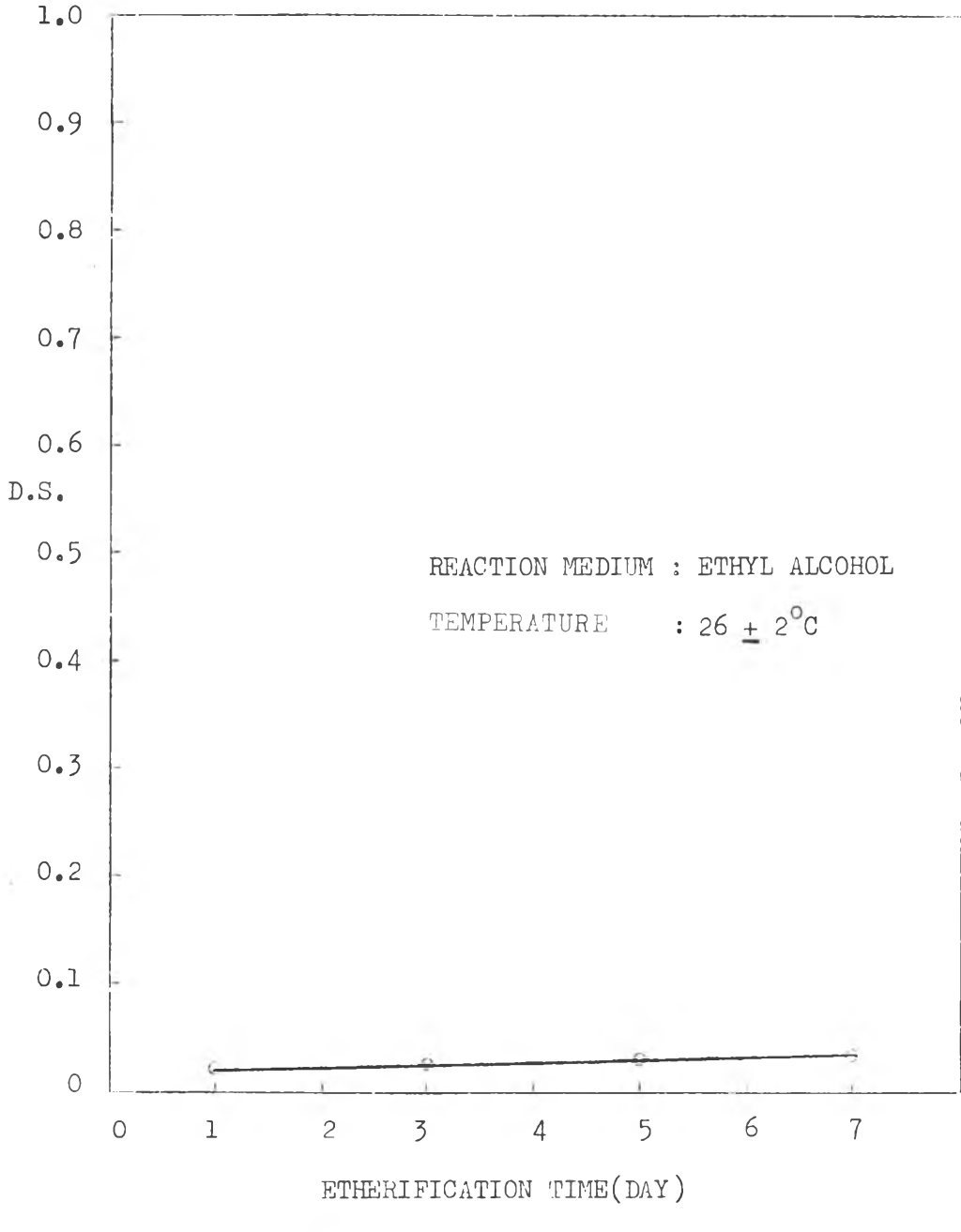

FIGURE 10 D.S. vs. ETHERIFICATION TIME

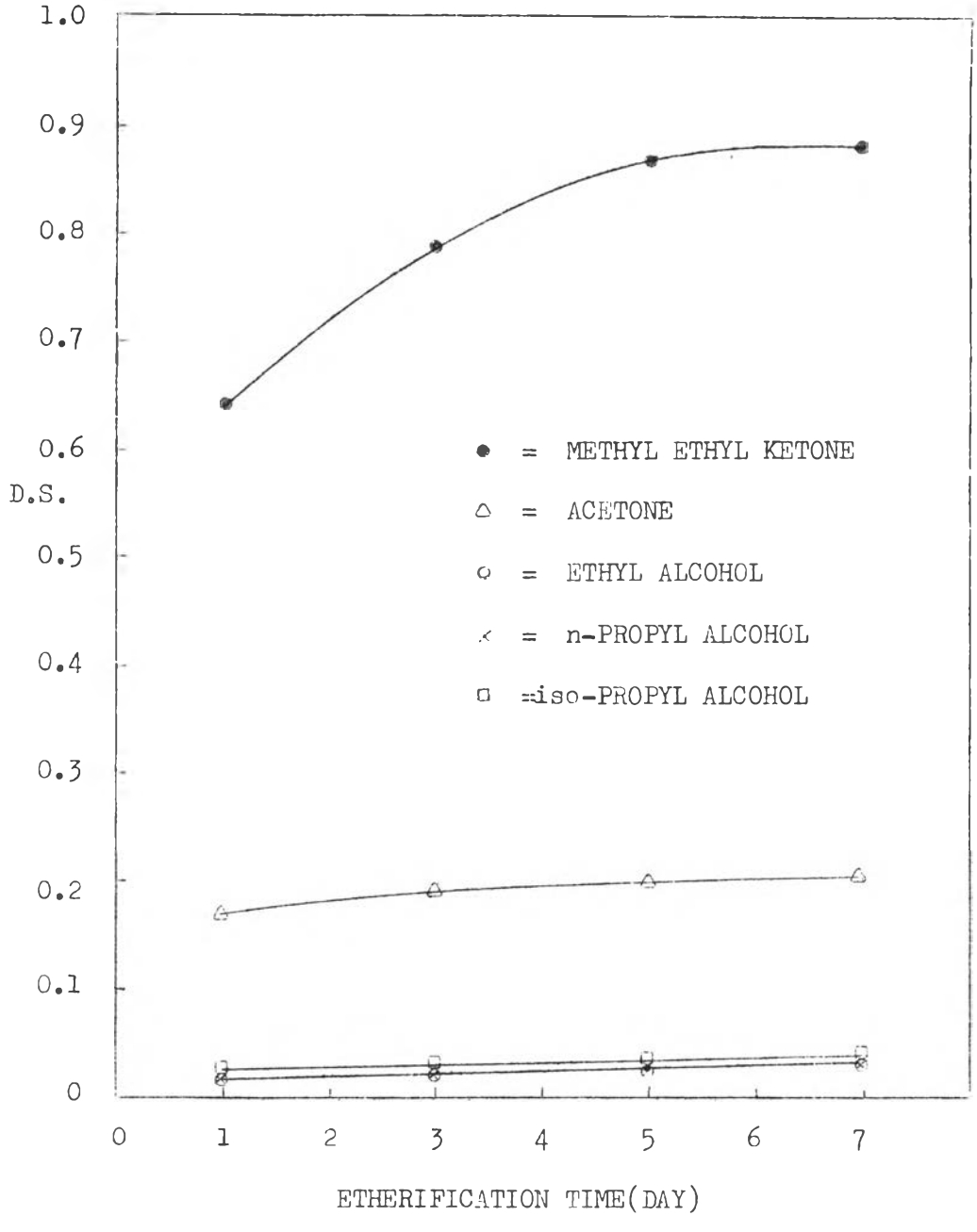

FIGURE 11 COMPARISON OF D.S.' s OF THE PRODUCTS OBTAINED BY USING POLAR SOLVENTS AS REACTION MEDIA, ETHERIFICATION AT 26 $\pm$ 2^{o}C

4.2 At 44 ± 2°C

4.2.1 Non-polar organic solvents as reaction media

Benzene, toluene, cyclohexane and n-hexane are also used to study the reactivity of sodium ions and the promotion of further etherification of cellulose at about 18°C higher than room temperature (26 ± 2°C). The D.S.'s of the products obtained from the various reaction media are shown in Table 3 and in graphical representations (see Figures 12-15). The reactivities of sodium ions are above 0.500 (except one from cyclohexane) and are clearly different from each other (see Figure 16), The extent of reactivities of sodium ions in various media are as follows: benzene (D.S. 0.642), toluene (D.S. 0.573), n-hexane (D.S. 0.531), cyclohexane (D.S. 0.494). From Figures 12-16, the inducing tendency of etherification decreases after 3 days except in toluene (decreases after 5 days). In benzene, n-hexane and cyclohexane media, the maximum value of D.S. are obtained on the third day of etherification whereas toluene gives maximum value of D.S. on the fifth day. The maximum values of D.S. are 0.664 (in benzene, 3 days), 0.594 (in toluene, 5 days), 0.580 (in n-hexane, 3 days) and 0.527 (in cyclohexane, 3 days).

Table 3 D.S.'s of the products obtained from experiment using non-polar organic solvents as reaction media and various reaction times at 44 ± 2°C

Reaction medium	D.S.*			
	Reaction time (day)			
	1	3	5	7
benzene	0.642	0.664	0.644	0.592
toluene	0.573	0.586	0.594	0.559
cyclohexane	0.494	0.523	0.527	0.513
n-hexane	0.531	0.580	0.564	0.551

* D.S. listed with 2.50% of overall experimental-error.

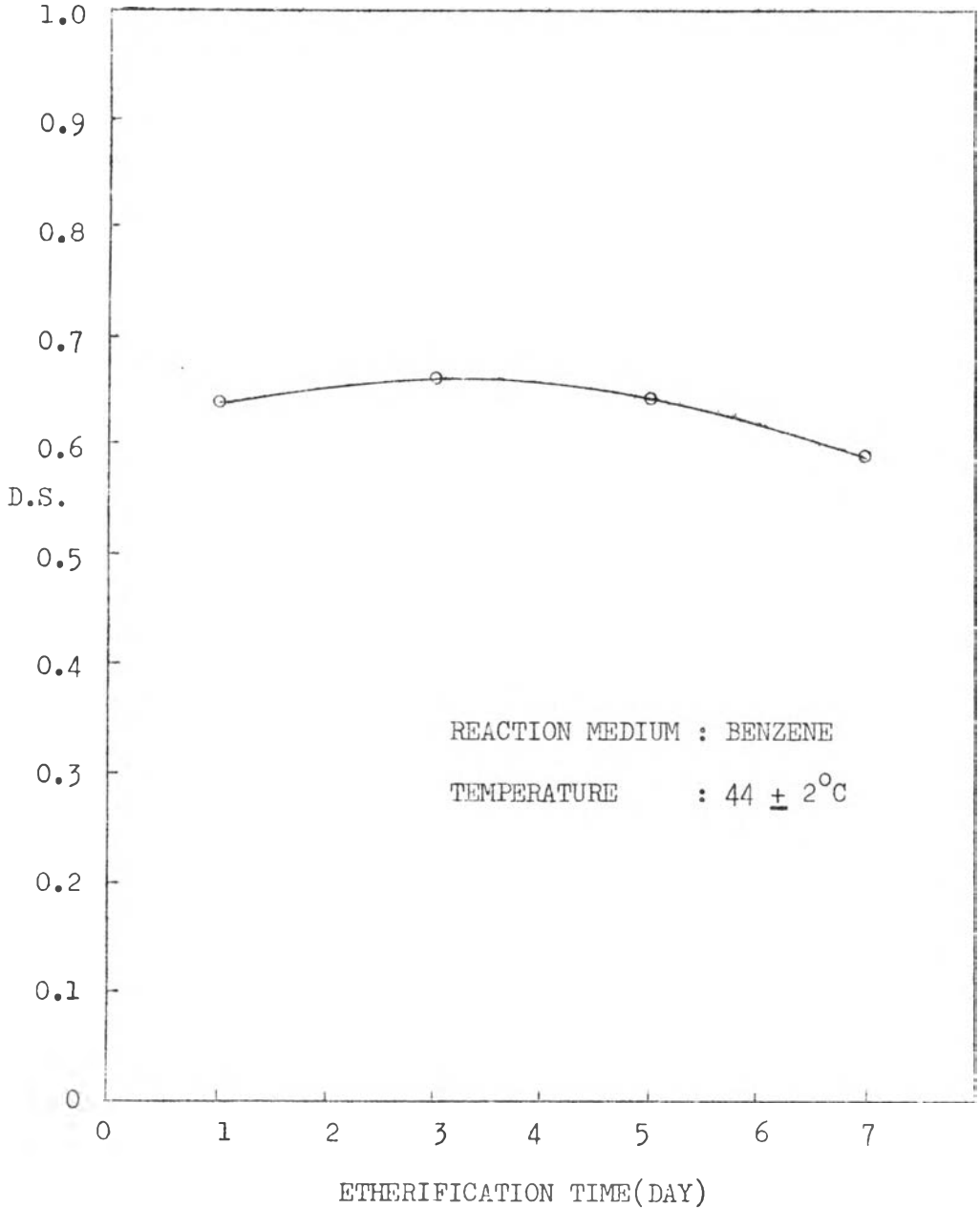

FIGURE 12 D.S. vs. ETHERIFICATION TIME

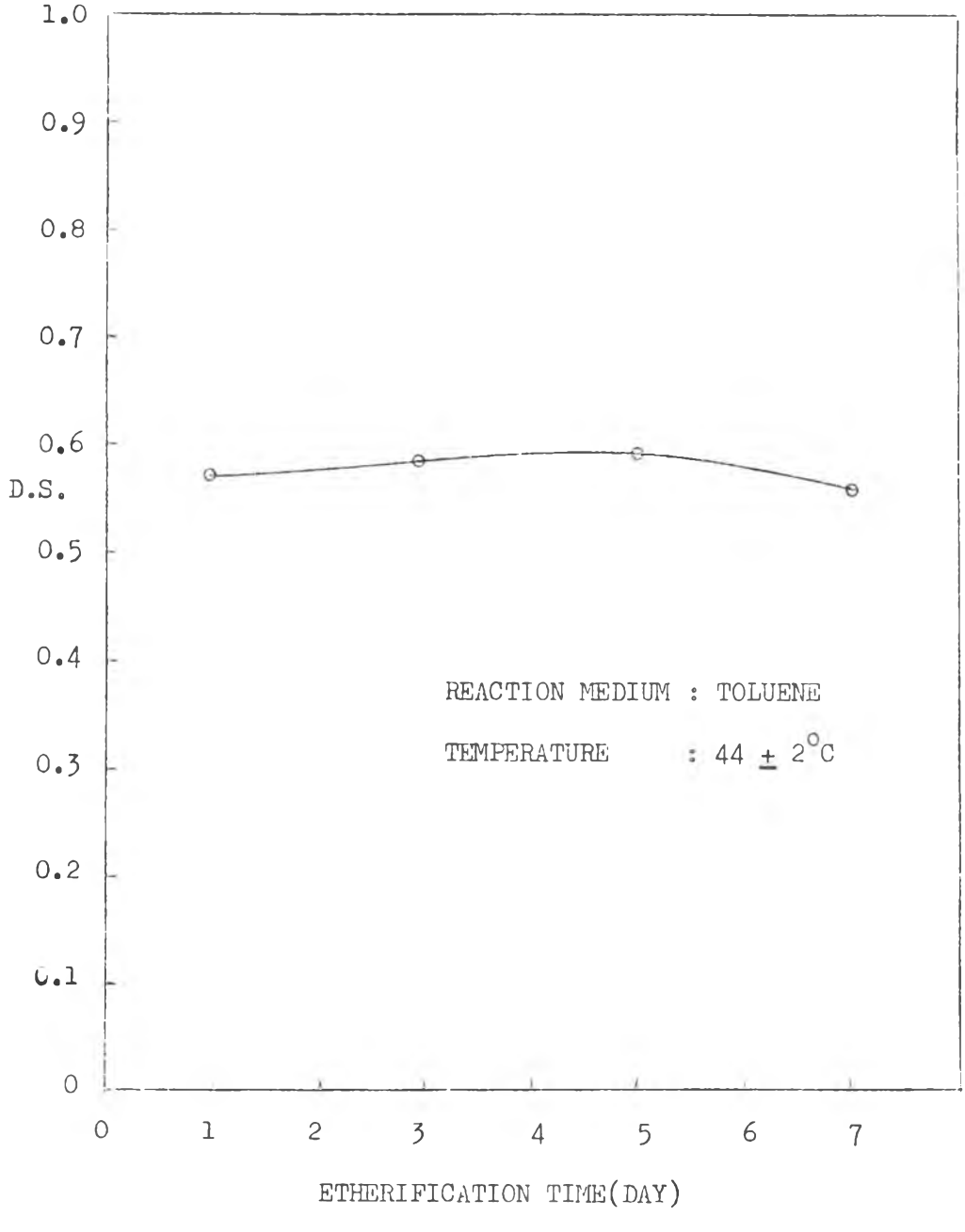

FIGURE 13 D.S. vs. ETHERIFICATION TIME

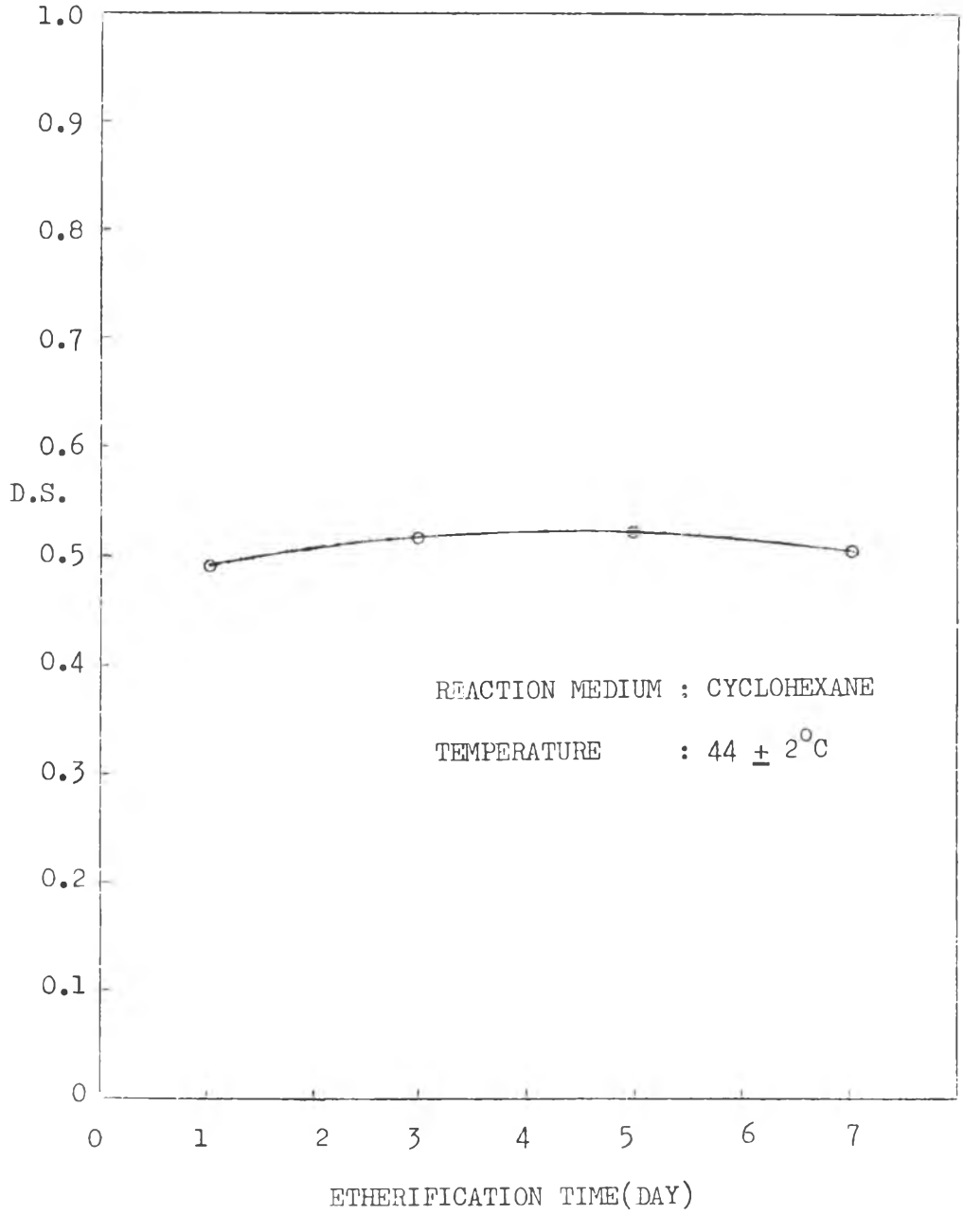

FIGURE 14 D.S. vs. ETHERIFICATION TIME

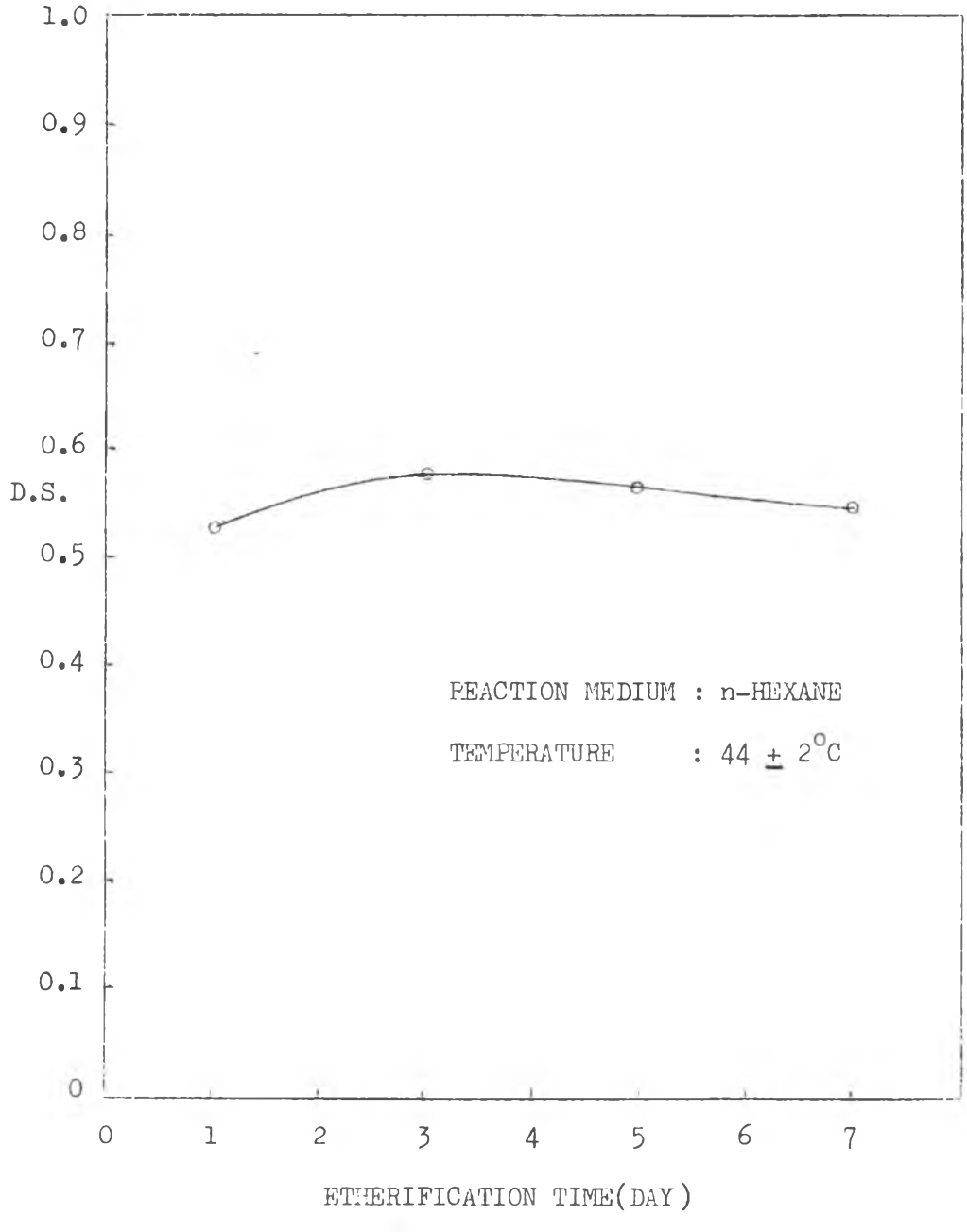

FIGURE 15 D.S. vs. ETHERIFICATION TIME

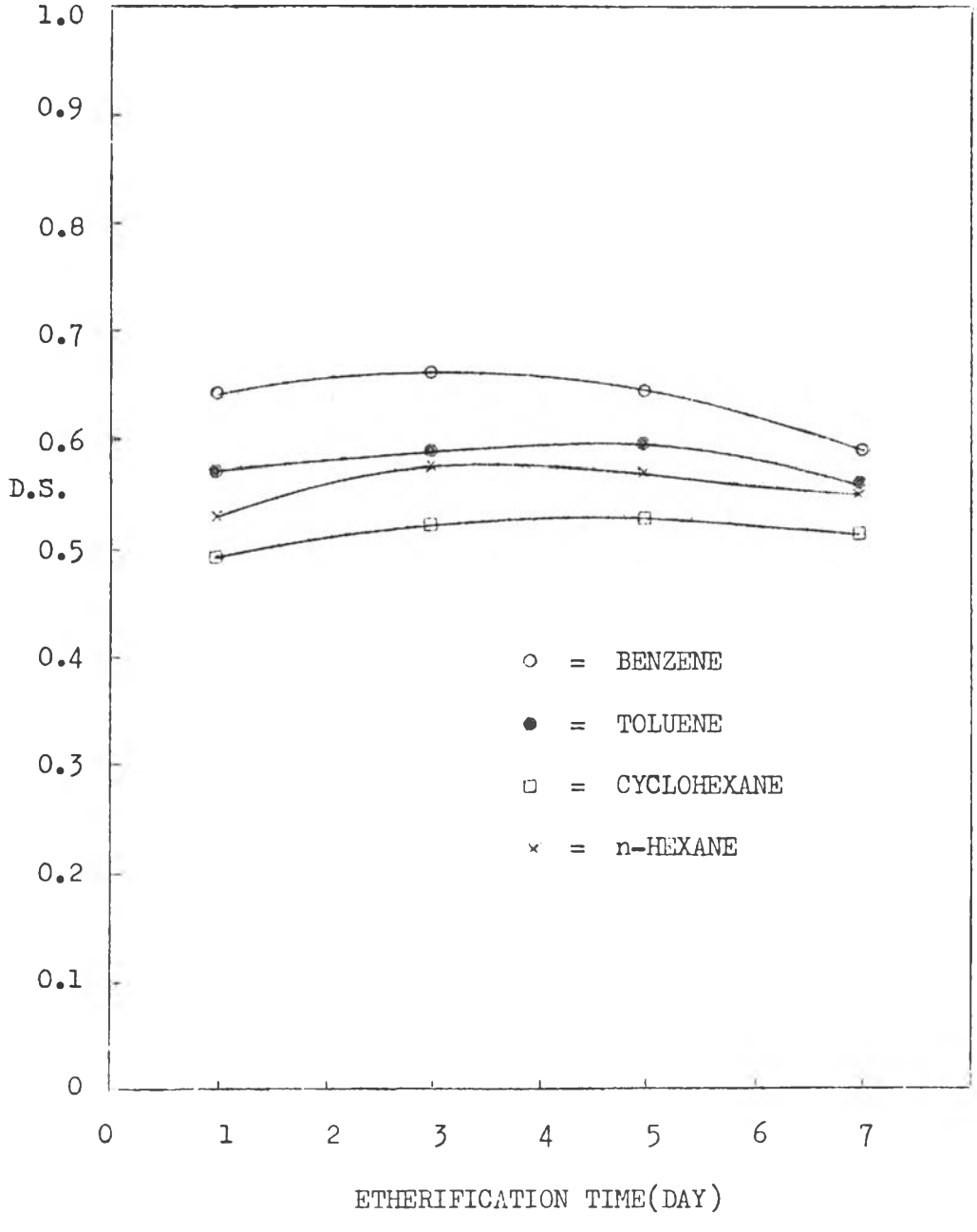

FIGURE 16 COMPARISON OF D.S.'s OF THE PRODUCTS OBTAINED BY USING NON POLAR SOLVENTS AS REACTION MEDIA, ETHERIFICATION AT 44 $\pm$ 2°C

4.2.2 Polar organic solvents as reaction media

Polar solvents (i.e. methyl ethyl ketone, acetone, iso-propyl alcohol, n-propyl alcohol and ethyl alcohol) are again used as reaction media. The D.S.'s of the products obtained are shown in Table 4 and their graphical representations are presented in Figures 17-22. The representations show that the reactivities of sodium ions in these reaction media are obviously different. From Figure 22, the reactivities of sodium ions in the ketones system are higher than ones in alcohols. For alcohols as reaction media, the appearances of graphs of n-propyl and iso-propyl alcohols are the same and the D.S.'s values from both systems slightly increase with increasing the reaction times. In ethyl alcohol, the D.S.'s of the products seem to increase rapidly with comparison to those in n-propyl and iso-propyl alcohols. For ketones as reaction media, the reactivity of sodium ions is high when methyl ethyl ketone is used as reaction medium. Acetone also gives higher D.S.values than alcohols but less than methyl ethyl ketone. The extent of reactivities of sodium ions are methyl ethyl ketone (D.S. 0.655) > acetone (D.S. 0.087) > ethyl alcohol (D.S. 0.083) > n-propyl alcohol (D.S. 0.029) > iso-propyl alcohol (D.S. 0.024).

From the result in Figure 22, the further etherification on the third day is sharply increased (about 7 times of the first day) when acetone is used though its D.S. on the first day is much lower (about 7.5 times) than one obtained from methyl ethyl ketone.

After 7 days of etherification, the D.S.'s of the products

are 0.738, 0.688, 0.378, 0.051 and 0.040 for methyl ethyl ketone, acetone, ethyl alcohol, n-propyl alcohol and iso-propyl alcohol respectively.

From 4.2.1 and 4.2.2, the reactivities of sodium ions in polar media excluding methyl ethyl ketone is lower than ones in non-polar solvents. For inducing tendency of further etherification of cellulose, it is, however, found that the methyl ethyl ketone and acetone are better reaction media than those non-polar solvents and the alcohols. In terms of the reactivity of sodium ions, benzene and methyl ethyl ketone are considered as good reaction media but the former gives less inducing tendency for further etherification of cellulose than the latter.

Table 4 D.S.'s of the products obtained from experiment using polar organic solvents as reaction media and various reaction times at 44 ± 2°C

Reaction medium	D.S.*			
	Reaction time (day)			
	1	3	5	7
methyl ethyl ketone	0.655	0.646	0.692	0.738
acetone	0.087	0.615	0.655	0.688
iso-propyl alcohol	0.024	0.032	0.035	0.040
n-propyl alcohol	0.029	0.036	0.035	0.051
ethyl alcohol	0.083	0.296	0.347	0.378

* D.S. listed with 2.81% of overall experimental-error.

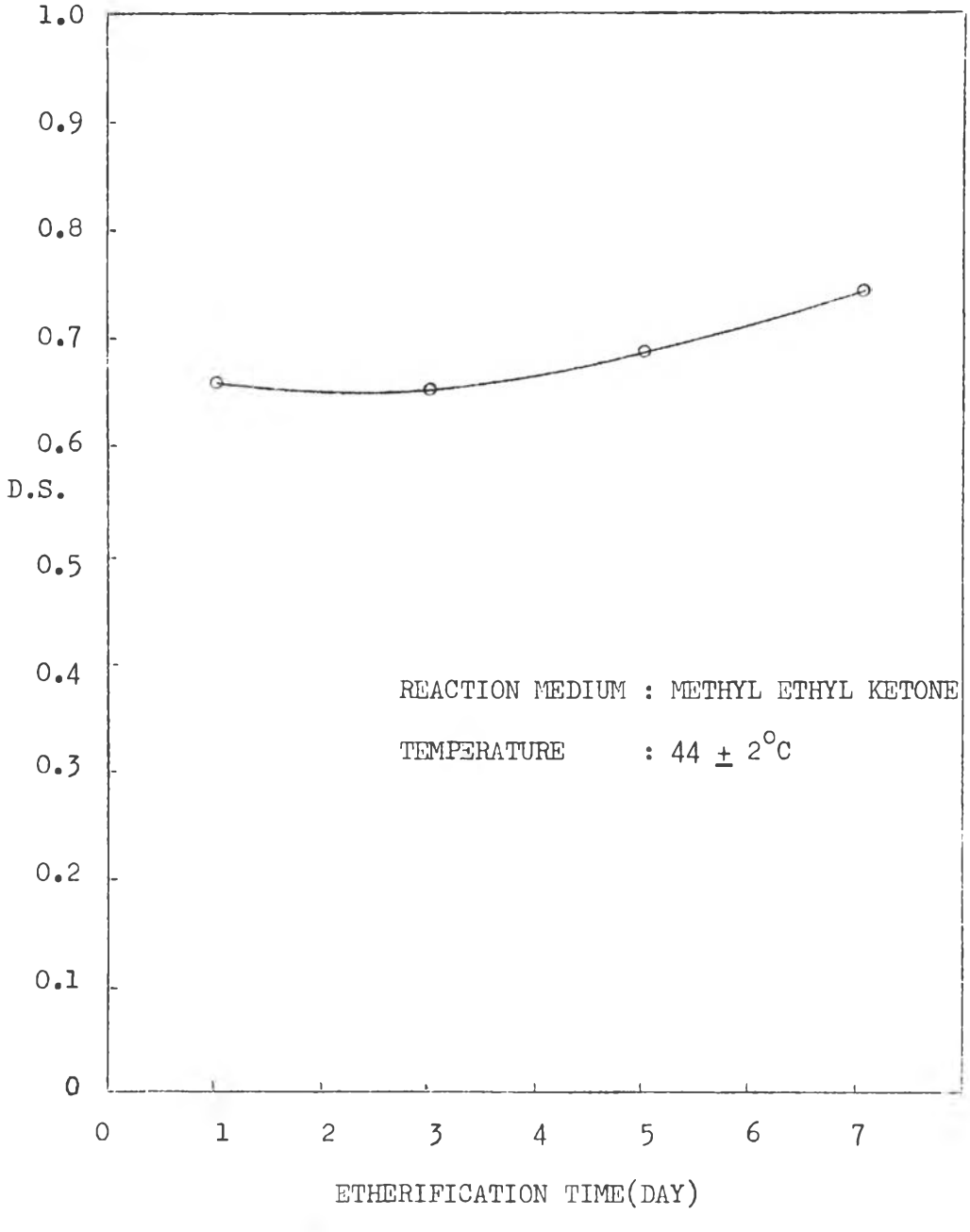

FIGURE 17 D.S. vs. ETHERIFICATION TIME

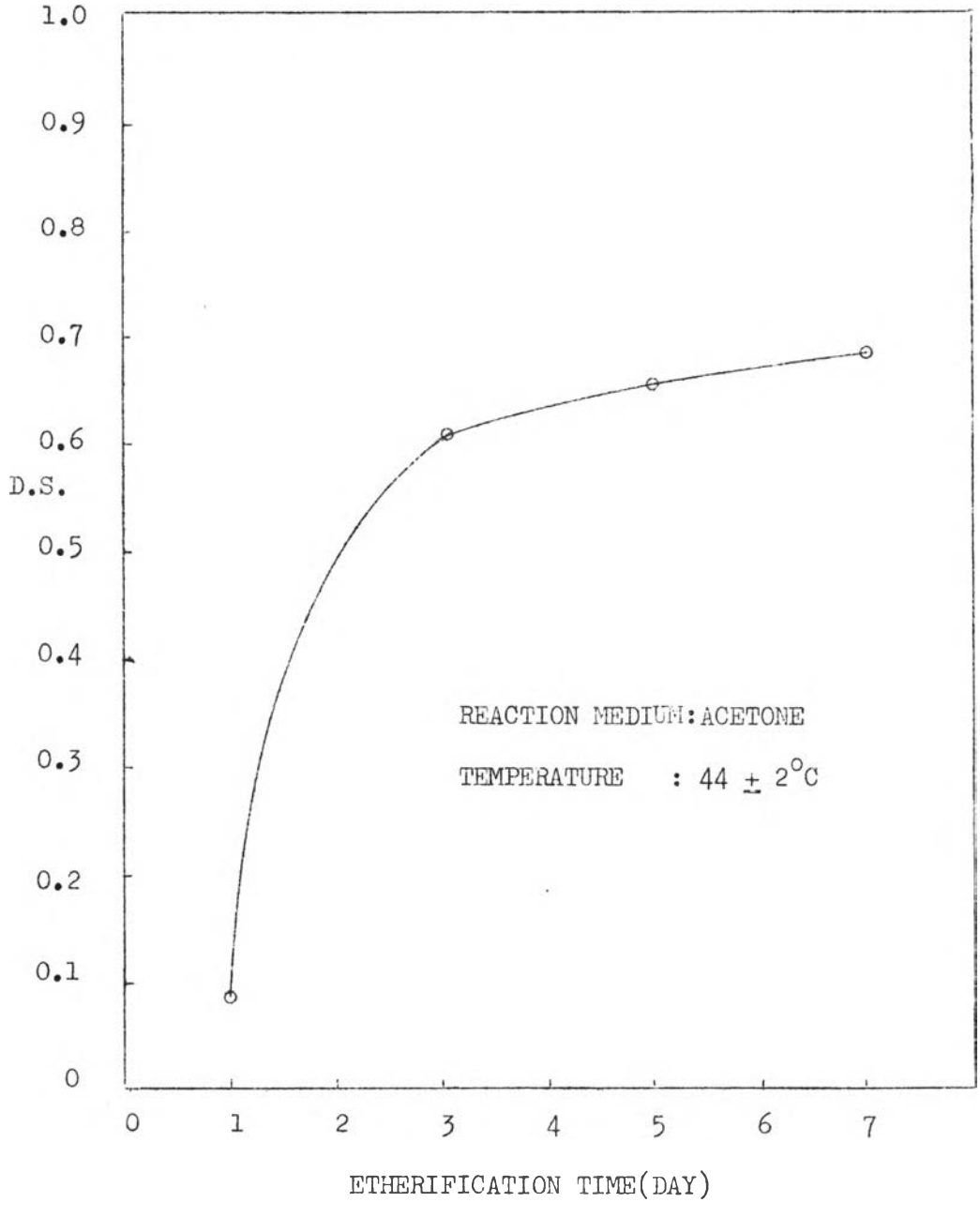

FIGURE 18 D.S. vs. ETHERIFICATION TIME

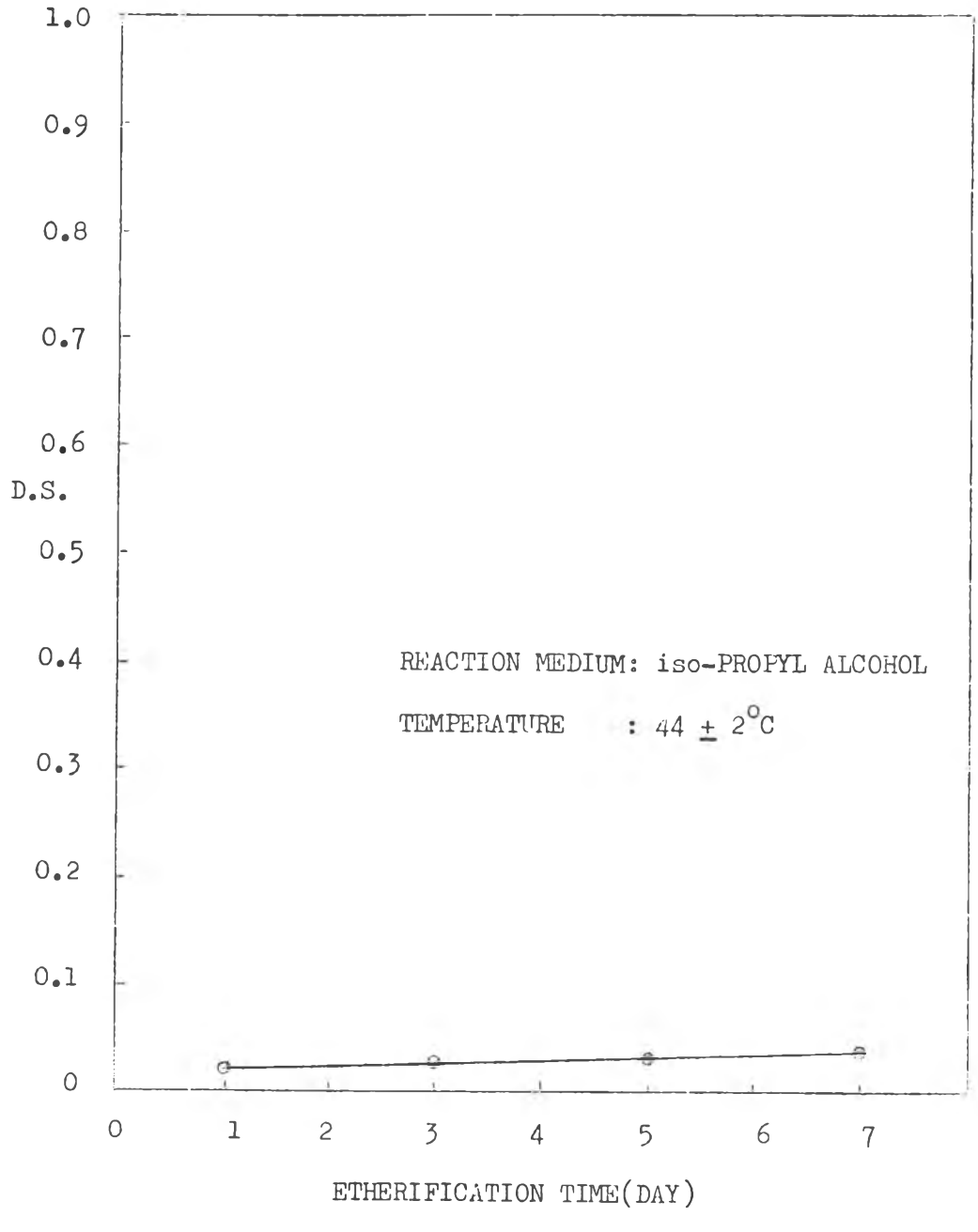

FIGURE 19 D.S. vs. ETHERIFICATION TIME

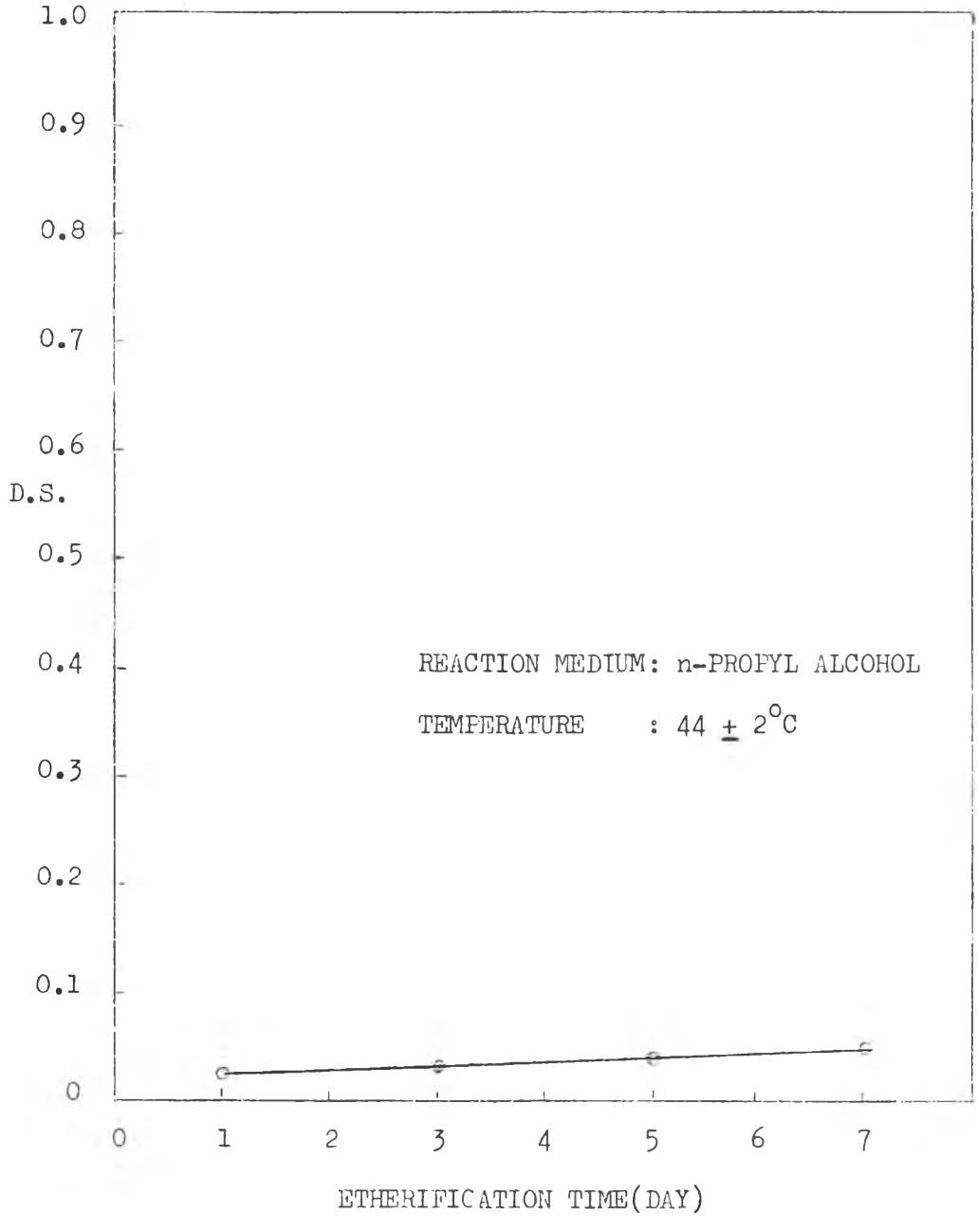

FIGURE 20 D.S. vs. ETHERIFICATION TIME

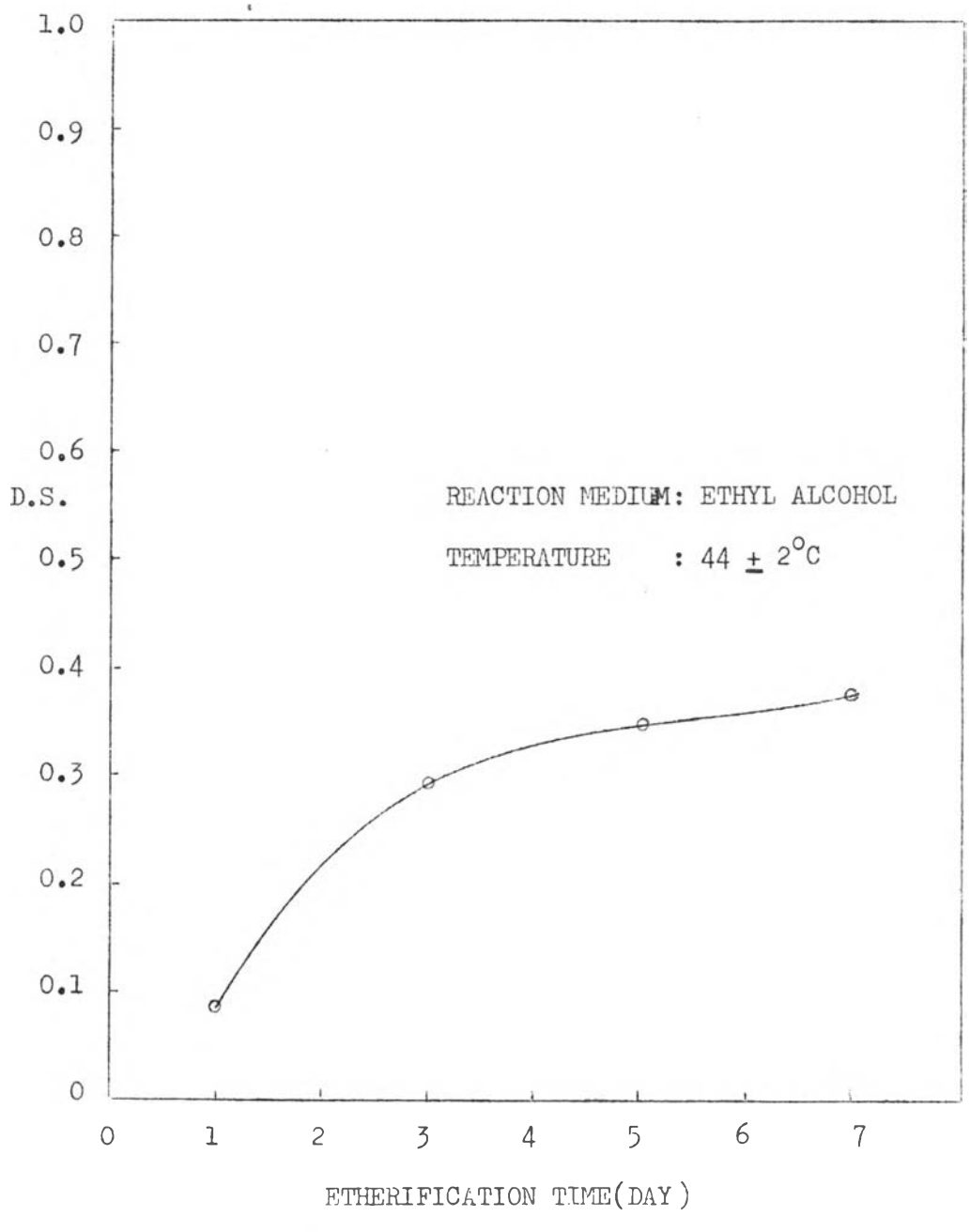

FIGURE 21 D.S. vs. ETHERIFICATION TIME

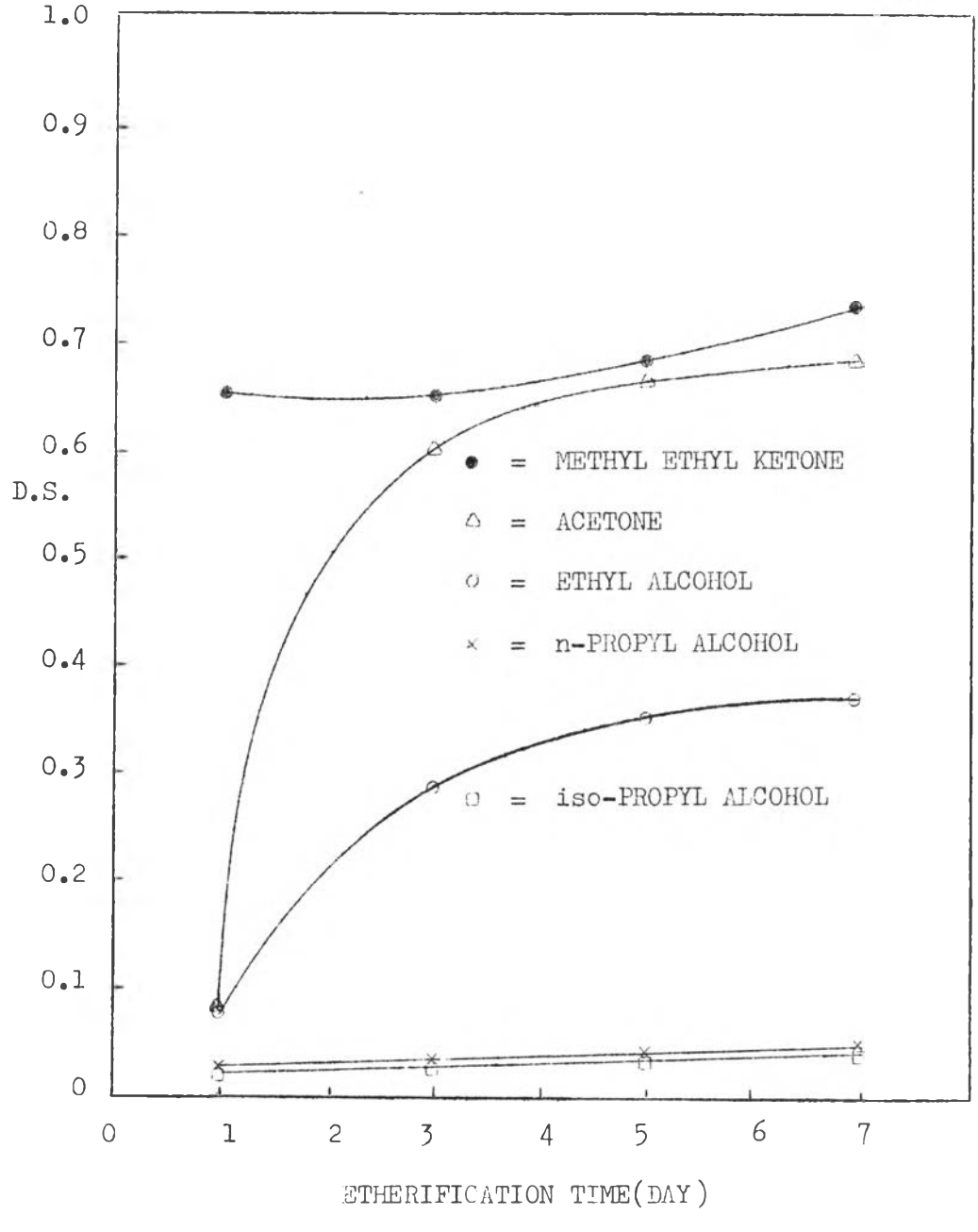

FIGURE 22 COMPARISON OF D.S.'s OF THE PRODUCTS OBTAINED BY USING POLAR SOLVENTS AS REACTION MEDIA, ETHERIFICATION AT 44 $\pm$ 2°C

4.3 Non-polar Organic Solvents vs. Polar Organic Solvents

Considering temperature as reaction variable for etherification using reaction media of the same characteristic nature (non-polar- or polar-), the results obtained can be discussed as follows :

4.3.1 Non-polar reaction media

Non-polar reaction media (benzene, toluene, cyclohexane and n-hexane) are used for etherification of cellulose. The effect of temperature on the reactivity of sodium ions as D.S.'s of the products are shown in Table 5 and their graphical representations are presented in Figures 23-26.

For benzene, the reactivity of sodium ions at 44 $\pm$ 2°C is higher than one at 26 $\pm$ 2°C (see Figure 23). However, the inducing tendency of further etherification at 26 $\pm$ 2°C is more than one at 44 $\pm$ 2°C. That is the D.S.'s of the products obtained at 26 $\pm$ 2°C increase with increasing reaction times whereas the D.S.'s of the products obtained at 44 $\pm$ 2°C drop after 3 days of etherification. At 44 $\pm$ 2°C, the maximum D.S. value (0.664) is obtained on the third day of etherification. After D.S.'s of the products are the same on about the fourth day, D.S.'s obtained at 26 $\pm$ 2°C are higher than one obtained at 44 $\pm$ 2°C.

A similar interpretation of the result is also obtained for toluene and n-hexane except the following differences (see Figures 24 and 26).

(1). The inducing tendencies of further etherification

at the two temperatures give the products of the same D.S.'s, 0.580 and 0.560 for approximately 2.2 and 1.8 days of etherification in toluene and n-hexane respectively.

(2). At 26 ± 2°C, the D.S.'s of the products increase with increasing reaction time, for both toluene and n-hexane.

The D.S.'s obtained at 44 ± 2°C also increase for certain period with increasing reaction time and decreasing in D.S.'s occur after 5 days of etherification in toluene and after 3 days in n-hexane.

(3). At 44 ± 2°C, the maximum D.S. values are obtained as 0.549 on the fifth day of etherification in toluene and 0.580 on the third day of etherification in n-hexane.

For cyclohexane, the reactivity of sodium ions at 44 ± 2°C and in cyclohexane medium is about 0.61% lower than one obtained at 26 ± 2°C. Since the decreasing of D.S. is, in fact, very insignicant, the result obtained can be possibly interpreted that there is no difference in reactivity of sodium ions due to the two different temperatures used for etherification of cellulose (see Figure 25). The appearance of graph when cyclohexane is used as reaction medium obviously differs from ones of benzene, toluene and n-hexane (see Figures 23 - 26). The inducing tendency of further etherification at 26 ± 2°C is better than ones at 44 ± 2°C, the maximum D.S. value of the product is 0.527 on the fifth day of etherification and the decreasing in D.S.'s occur after 5 days of etherification.

In short, the reactivities of sodium ions in etherification reaction at 44 ± 2°C in benzene, toluene and n-hexane are higher than ones at 26 ± 2°C whereas the reactivity of sodium ions in cyclohexane medium is approximately the same at the two different temperatures. However, the inducing tendencies of further etherifications at 26 ± 2°C in such systems are better than ones performed at 44 ± 2°C.

Table 5 Comparison of D.S.'s of the products obtained at 26 ± 2°C and at 44 ± 2°C for non-polar organic solvents as reaction media.

Recation medium	D.S.* obtained on the first day		Difference in D.S.
	Temperature (°C)		
	26 ± 2	44 ± 2	
benzene	0.515	0.642	0.127
toluene	0.502	0.573	0.071
cyclohexane	0.497	0.494	0.003
n-hexane	0.494	0.531	0.037

* D.S. listed with 2.46% of overall experimental-error.

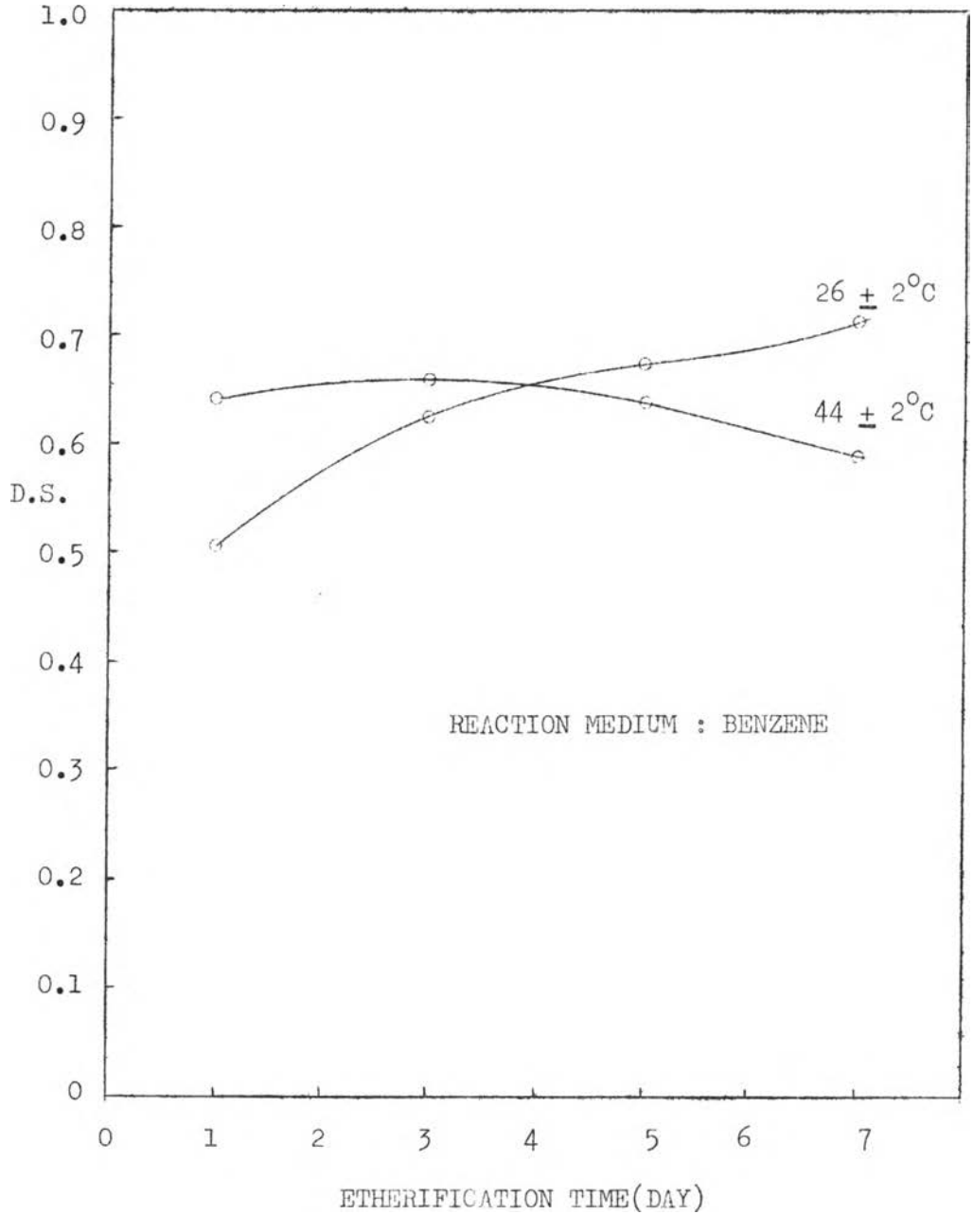

FIGURE 23 COMPARISON OF D.S.'s OF THE PRODUCTS OBTAINED AT 26 ± 2°C AND AT 44 ± 2°C

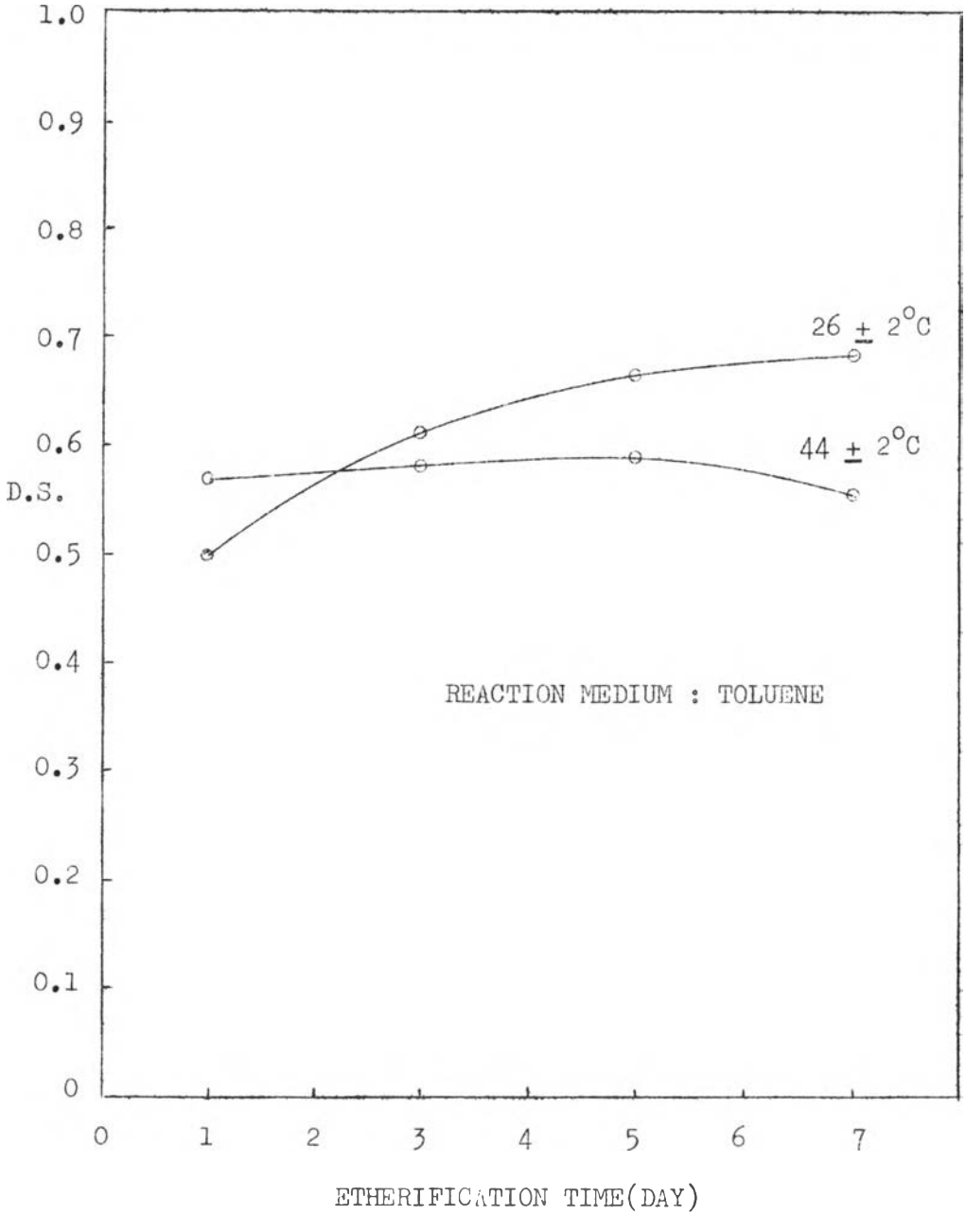

FIGURE 24 COMPARISON OF D.S.'s OF THE PRODUCTS OBTAINED AT 26 ± 2°C AND AT 44 ± 2°C

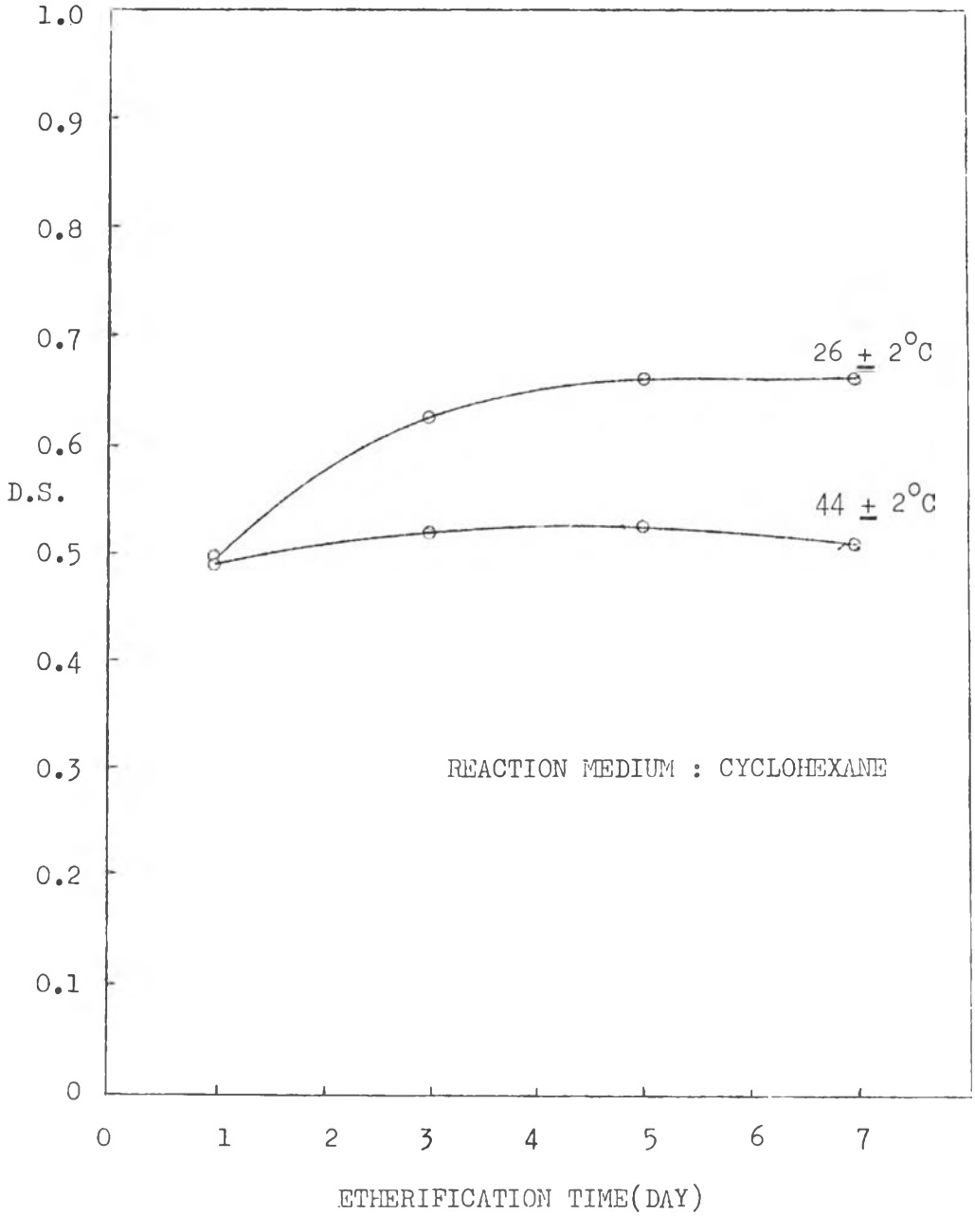

FIGURE 25 COMPARISON OF D.S.'s OF THE PRODUCTS OBTAINED AT 26 ± 2°C AND AT 44 ± 2°C

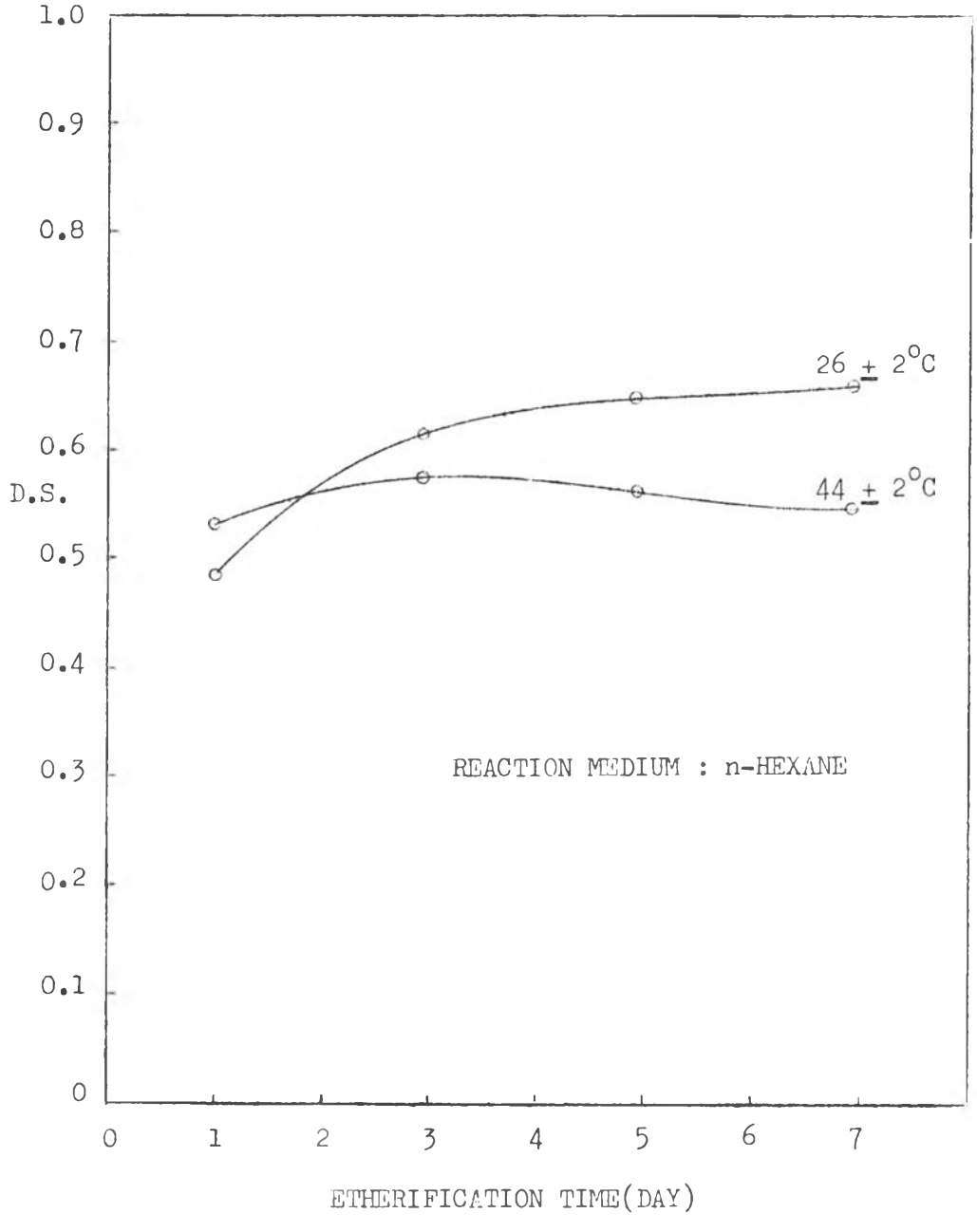

FIGURE 26 COMPARISON OF D.S.'s OF THE PRODUCTS OBTAINED AT 26 ± 2°C AND AT 44 ± 2°C

4.3.2 Polar reaction media

The same polar solvents as previously mentioned are used as reaction media. The reactivities of sodium ions represented by D.S.'s of the products obtained are shown in Table 6. The comparison of D.S.'s of the products obtained at 26 ± 2°C and at 44 ± 2°C are also shown by graphical representations (see Figures 27 - 31). From graphical representations obtained, the appearance of graphs obtained among various reaction media used are unique and individually characteristic.

For etherification of cellulose in methyl ethyl ketone, the reactivity of sodium ions at 44 ± 2°C is slightly higher than one at 26 ± 2°C (see Figure 27). The D.S.'s of the products obtained at 26 ± 2°C within the period of 7 days of etherification increase with increasing time. At 44 ± 2°C, the D.S. of the product with 3 days of etherification decreases from 0.655 to 0.646 and then increases with increasing time. It is, therefore, the curvature of the graphs obtained at 26 ± 2°C and at 44 ± 2°C are in opposite direction. This appearance is different from others obtained by this work especially the appearance of graph obtained at 44 ± 2°C is unique. Because of such unique appearance, the solution related to the extent of inducing tendency of further etherification is in question - that is how far D.S. of the product can be ended. An experiment for finding fact and for answering this question will be discussed later (see 4.4).

For acetone as reaction medium, the reactivity of sodium ions shows opposite phenomena from one in methyl ethyl ketone (see Figure 28). The reactivity of sodium ions at 26 ± 2°C is better than one at 44 ± 2°C but the inducing tendency of further etherification at 44 ± 2°C is better than ones at 26 ± 2°C. After 7 days of etherification at 44 ± 2°C, the D.S. is 0.688 which is the third of high D.S. obtained by this experiment whereas the first and second ones are 0.880, 0.738 obtained from methyl ethyl ketone at 26 ± 2°C and at 44 ± 2°C respectively.

For iso-propyl alcohol as reaction medium, the same values of D.S.'s of the products are obtained (see Figure 29). According to the same reaction time used, there is no effect of temperature on the change of the D.S.'s of etherification products.

For n-propyl alcohol as reaction medium, the D.S.'s have slightly affected inducing by different temperature and very slightly increase with increasing time (see Figure 30). The reactivity of sodium ions is, thus, almost the same.

For ethyl alcohol as reaction medium, the same appearance as in the propyl alcohols occurs when etherification was performed at 26 ± 2°C. As the temperature increases from 26 ± 2°C to 44 ± 2°C, the reactivity of sodium ions is increased about four times (from 0.021 to 0.083) and D.S.'s of the products increase rapidly. This increasing of D.S. is given the product with D.S. 0.378 after 7 days of etherification. The appearance of curve at 44 ± 2°C is similar to one of acetone

but the D.S.'s of the products slowly increase than those from acetone. The difference of D.S. values between 26 ± 2°C and 44 ± 2°C is in the following order acetone > ethyl alcohol > methyl ethyl ketone > n-propyl alcohol > iso-propyl alcohol (see Table 6).

Table 6 Comparison of D.S.'s of the products obtained at 26 ± 2°C and at 44 ± 2°C for polar organic solvents as reaction media.

Reaction medium	D.S.* obtained on the first day		Difference in D.S.
	Temperature (°C)		
	26±2	44±2	
methyl ethyl ketone	0.643	0.655	0.012
acetone	0.174	0.087	0.087
iso-propyl alcohol	0.029	0.024	0.005
n-propyl alcohol	0.020	0.029	0.009
ethyl alcohol	0.021	0.083	0.062

* D.S. listed with 2.61% of overall experimental-error.

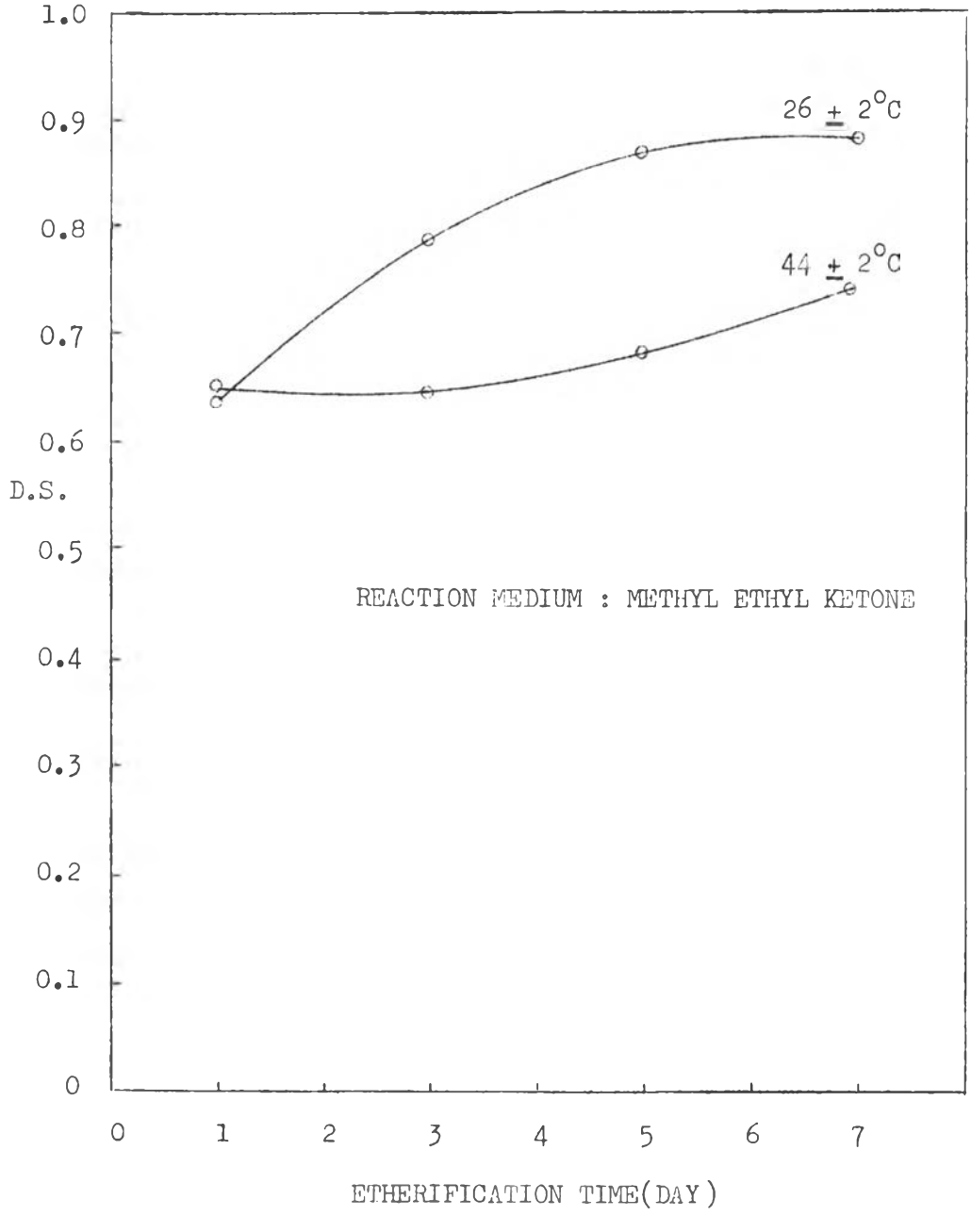

FIGURE 27 COMPARISON OF D.S.'s OF THE PRODUCTS OBTAINED AT 26 ± 2°C AND AT 44 ± 2°C

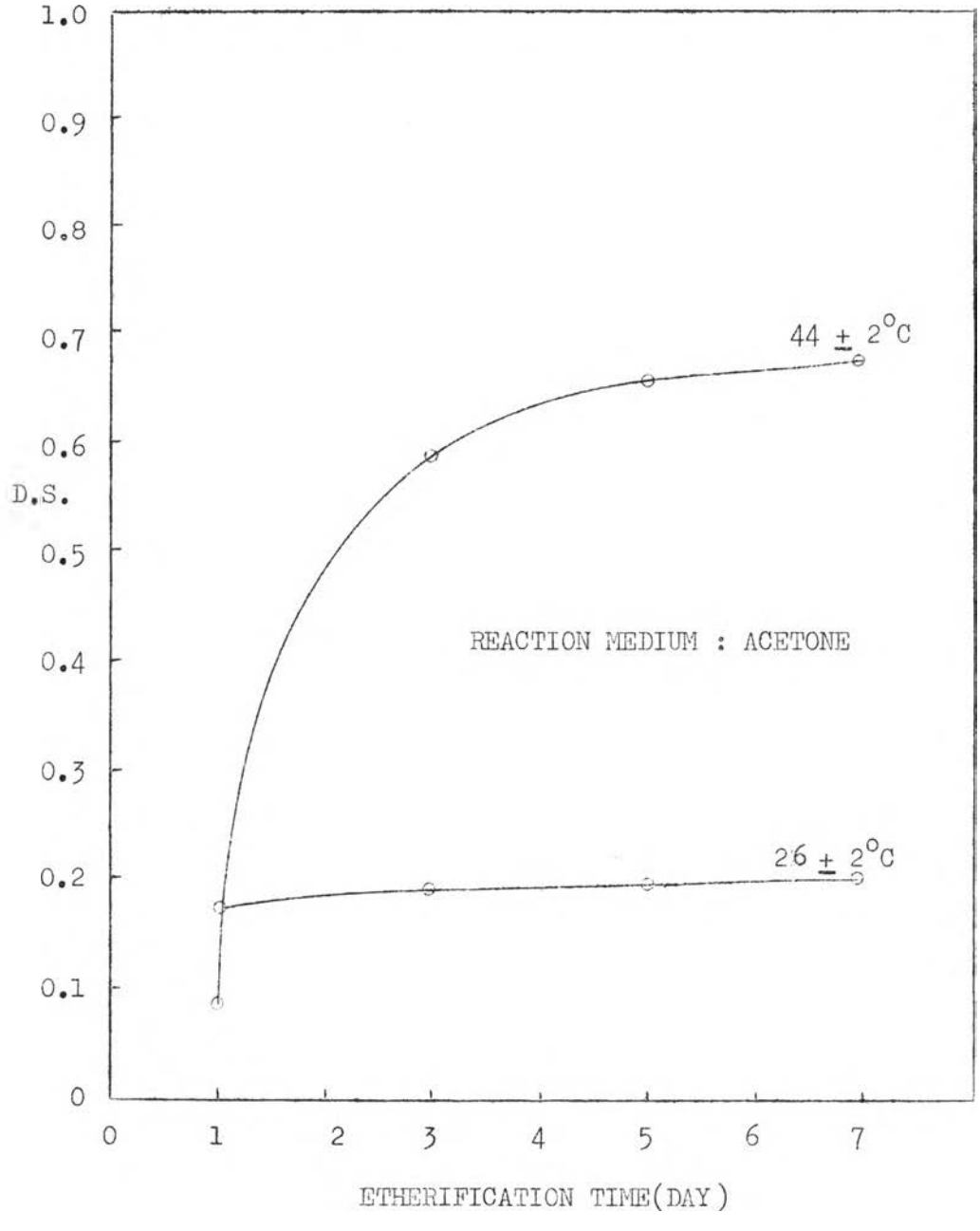

FIGURE 28 COMPARISON OF D.S.'s OF THE PRODUCTS OBTAINED AT 26 ± 2°C AND AT 44 ± 2°C

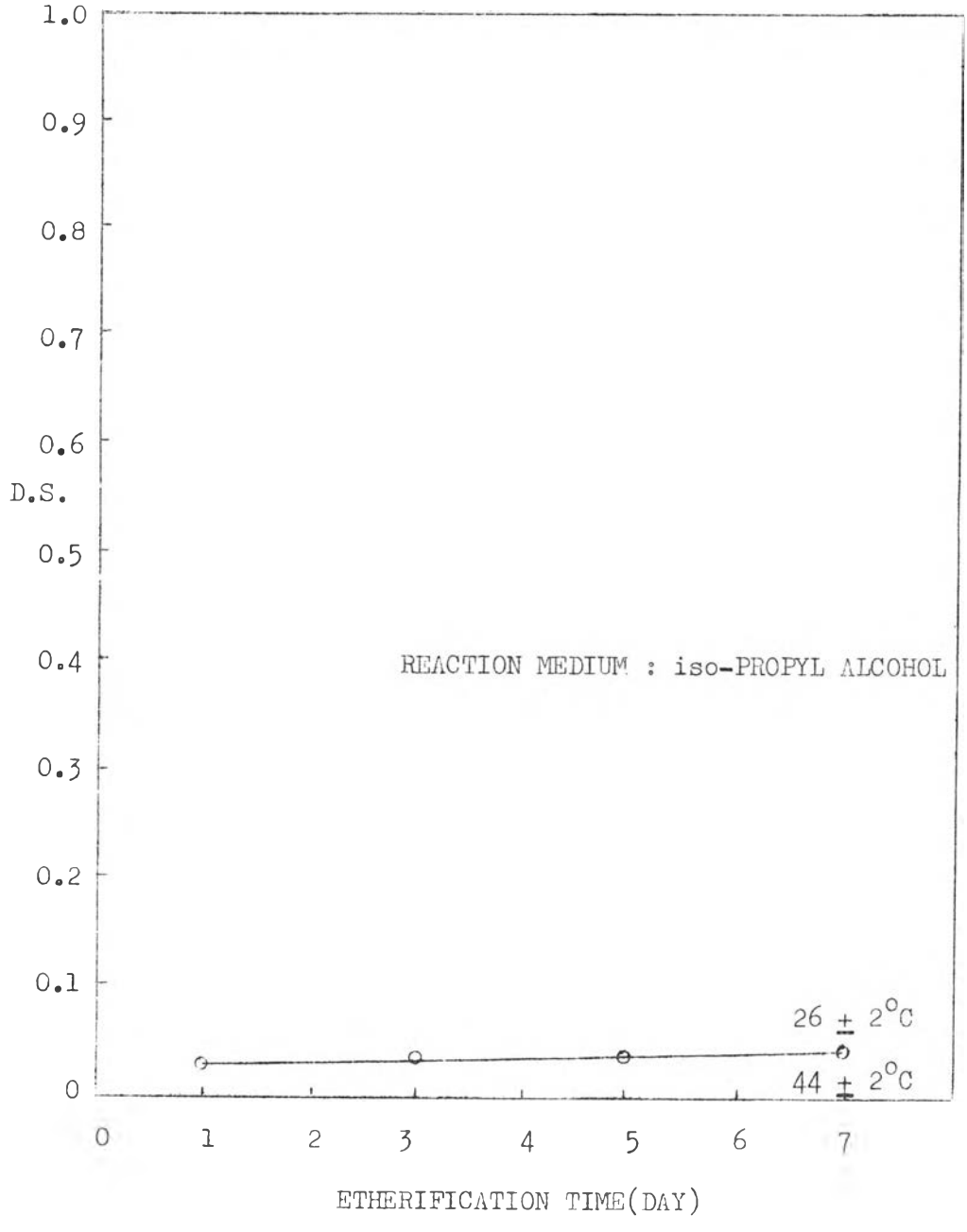

FIGURE 29 COMPARISON OF D.S.'s OF THE PRODUCTS OBTAINED AT 26 ± 2°C AND AT 44 ± 2°C

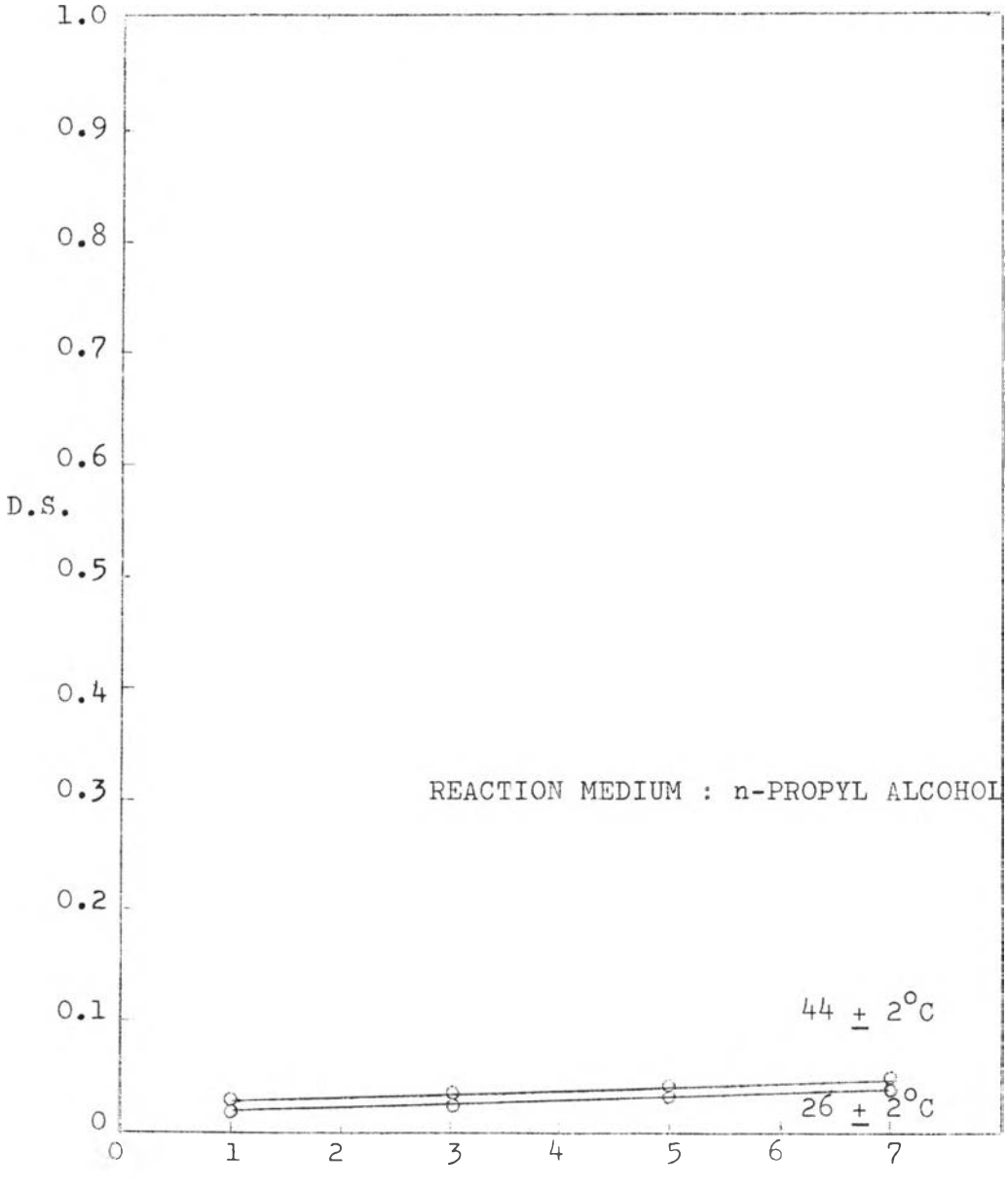

FIGURE 30 COMPARISON OF D.S.'s OF THE PRODUCTS OBTAINED AT 26 ± 2°C AND AT 44 ± 2°C

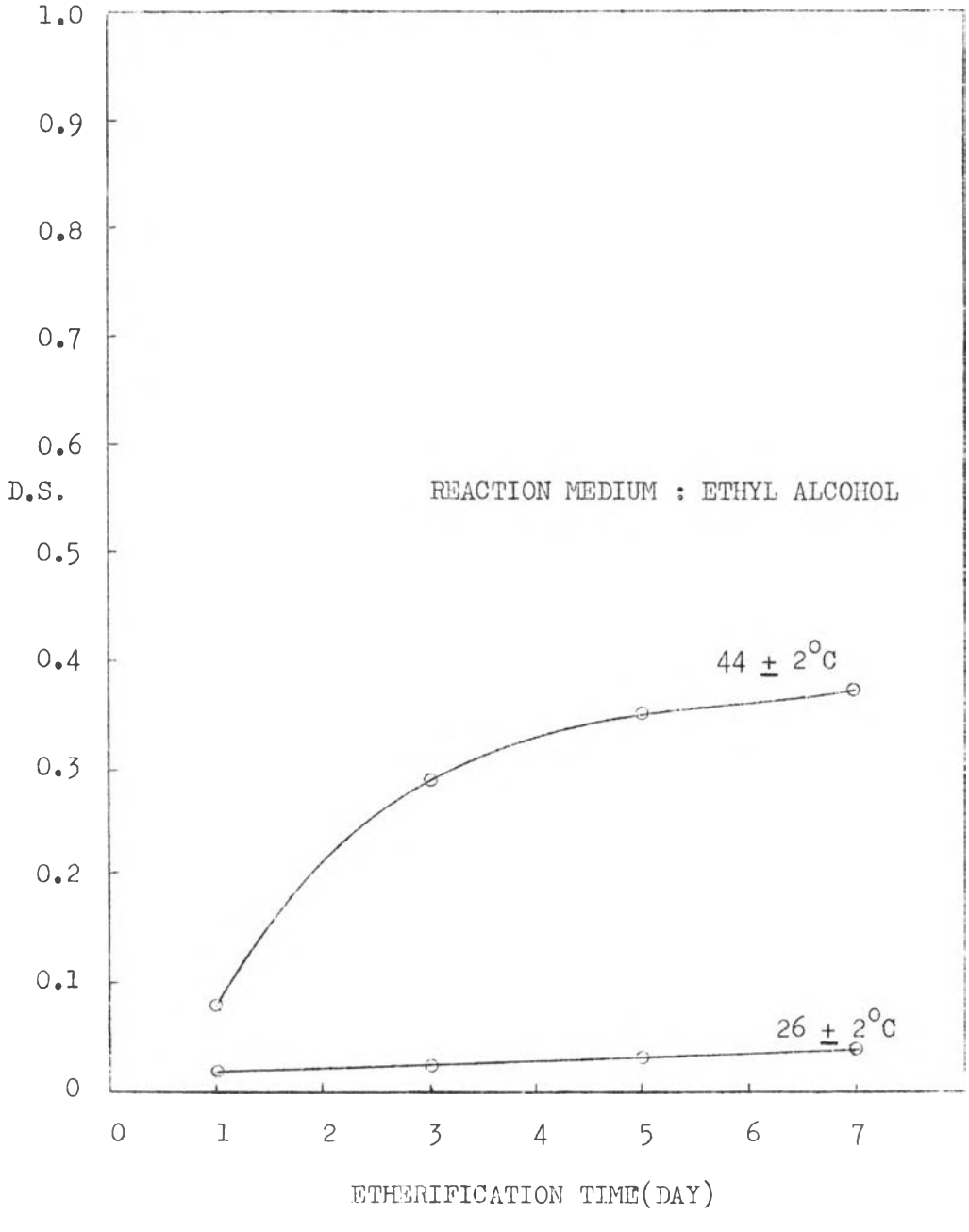

FIGURE 31 COMPARISON OF D.S.'s OF THE PRODUCTS OBTAINED AT 26 ± 2°C AND AT 44 ± 2°C

4.4 Maximum D.S. of the Product Obtained at 44 ± 2°C with Etherification in Methyl Ethyl Ketone.

As pointed out in 4.3.2, the appearance of graphical representation in Figure 27 is unique for one obtained at 44 ± 2°C with etherification in methyl ethyl ketone. According to such appearance, it is certainly drawn out two possibilities as follows:

(1). D.S. of the product will increase without dropping. This increasing should be less than 1.0 or possibly approach to 1.0.

(2). If there is dropping in D.S., its maximum is able to observe at any certain time.

As regards to the two possibilities, the extent of inducing tendency of further etherification at 44 ± 2°C is in question for how far D.S. of the product can be. To search for the fact, an other experiment was performed. Because of running out of the treated pulp formerly used, the new batch of treated pulp was, at this stage, used in the experiment conducted with the same manner as previously described. Since D.S. of the product depends on several factors including the nature of cellulose used as raw material. The experiment was also carried out at 26 ± 2°C for 1, 3, 5 and 7 days in order to check whether the new treated pulp maintains the same appearance of graphical representation as the previous result (Figure 27) or not.

By plotting the result in Table 7, the appearance of graph obtained from etherification of new treated pulp within the period of 7 days at 26 ± 2°C is similar to one previously obtained but with small difference in D.S. values (see Figure 32). These differences due to

nature of cellulose used as raw material. However, such differences does not condemn for the use of new treated pulp as raw material in etherification in this experiment. The similarity in appearance of graphical representation of D.S. values obtained from two different batches insure that each batch can be represented each other in reactivity of sodium ions and in extent of inducing tendency of further etherification excluding the consideration in D.S. quantity between them.

Table 7 D.S.'s of the products obtained from new treated pulp by using methyl ethyl ketone as reaction medium and etherification at 26 ± 2°C.

Reaction time (day)	D.S.*
1	0.702
3	0.838
5	0.886
7	0.897

* D.S. listed with 2.51% of overall experimental-error.

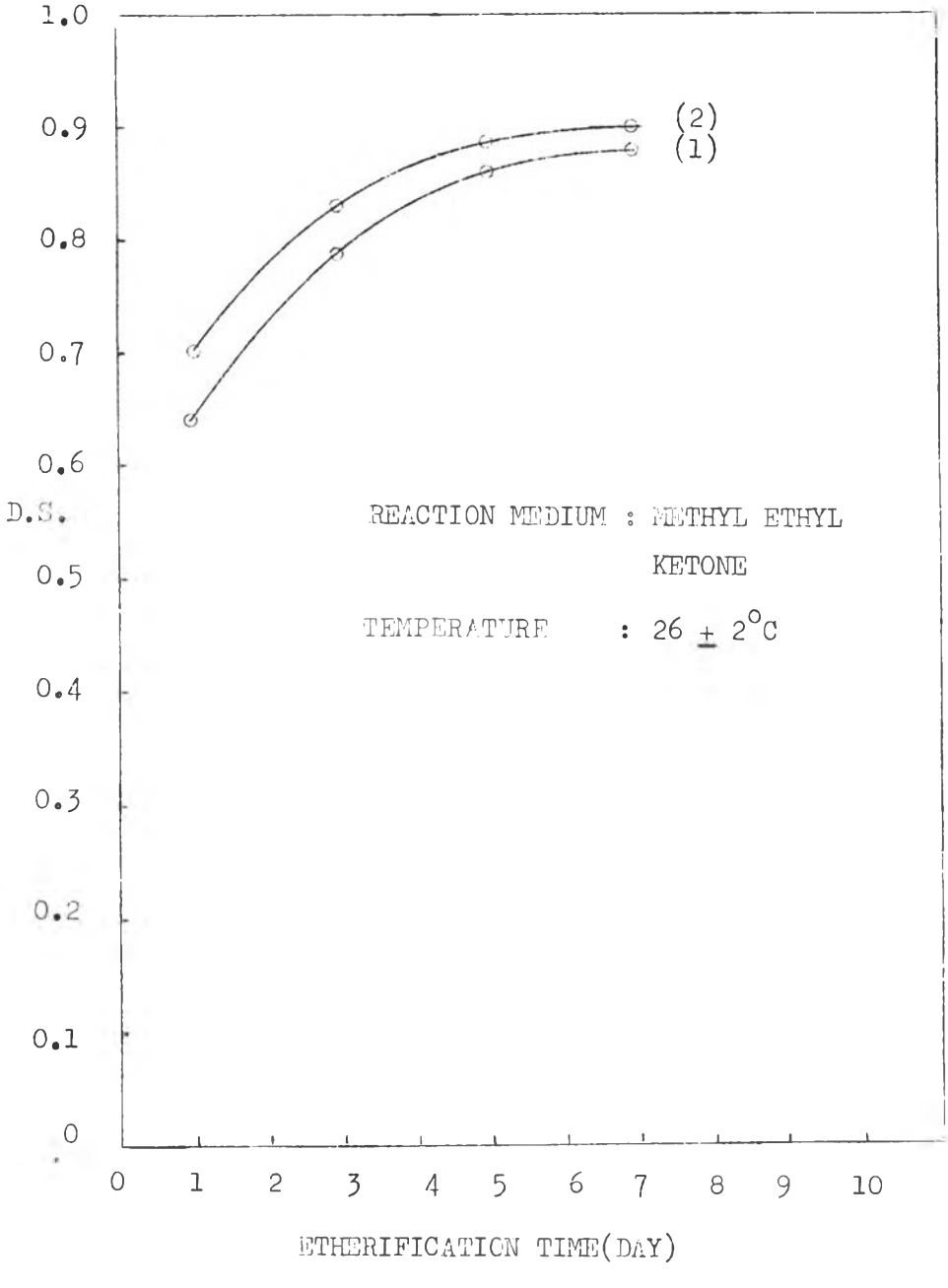

FIGURE 32 D.S. vs. ETHERIFICATION TIME

(1) = D.S.'s OF THE PRODUCTS OBTAINED FROM TREATED PULP OF FORMER BATCH

(2) = D.S.'s OF THE PRODUCTS OBTAINED FROM TREATED PULP OF NEW BATCH

The new treated pulp was, then, used as raw material in etherification at 44 ± 2°C for filling the gap derived from the above mentioned possibilities. The experiment was repeated the former procedure with reaction time 1, 3, 5, 7 days and so on. The etherification was allowed to proceed until either D.S. approaches to 1.0 or the dropping of D.S. occurs.

From the result, the reactivity of sodium ions at 44 ± 2°C is higher than an other at 26 ± 2°C as same as it occurs when former batch of treated pulp is used (see Tables 6 - 8). The D.S. of the products increases with reaction time during the first 8 days and then decreases with the reaction time (see Table 8 and Figure 33). The maximum D.S. is 0.860. It is possibly to say that the optimum reaction time for maximum D.S. when methyl ethyl ketone is used as reaction medium should not be longer than 8 days.

Table 8 D.S.'s of the products obtained from new treated pulp by using methyl ethyl ketone as reaction medium and etherification at 44 ± 2°C.

Reaction time (day)	D.S.*
1	0.736
3	0.728
5	0.747
7	0.783
8	0.860
9	0.792
10	0.760

* D.S. listed with 2.42% of overall experimental-error.

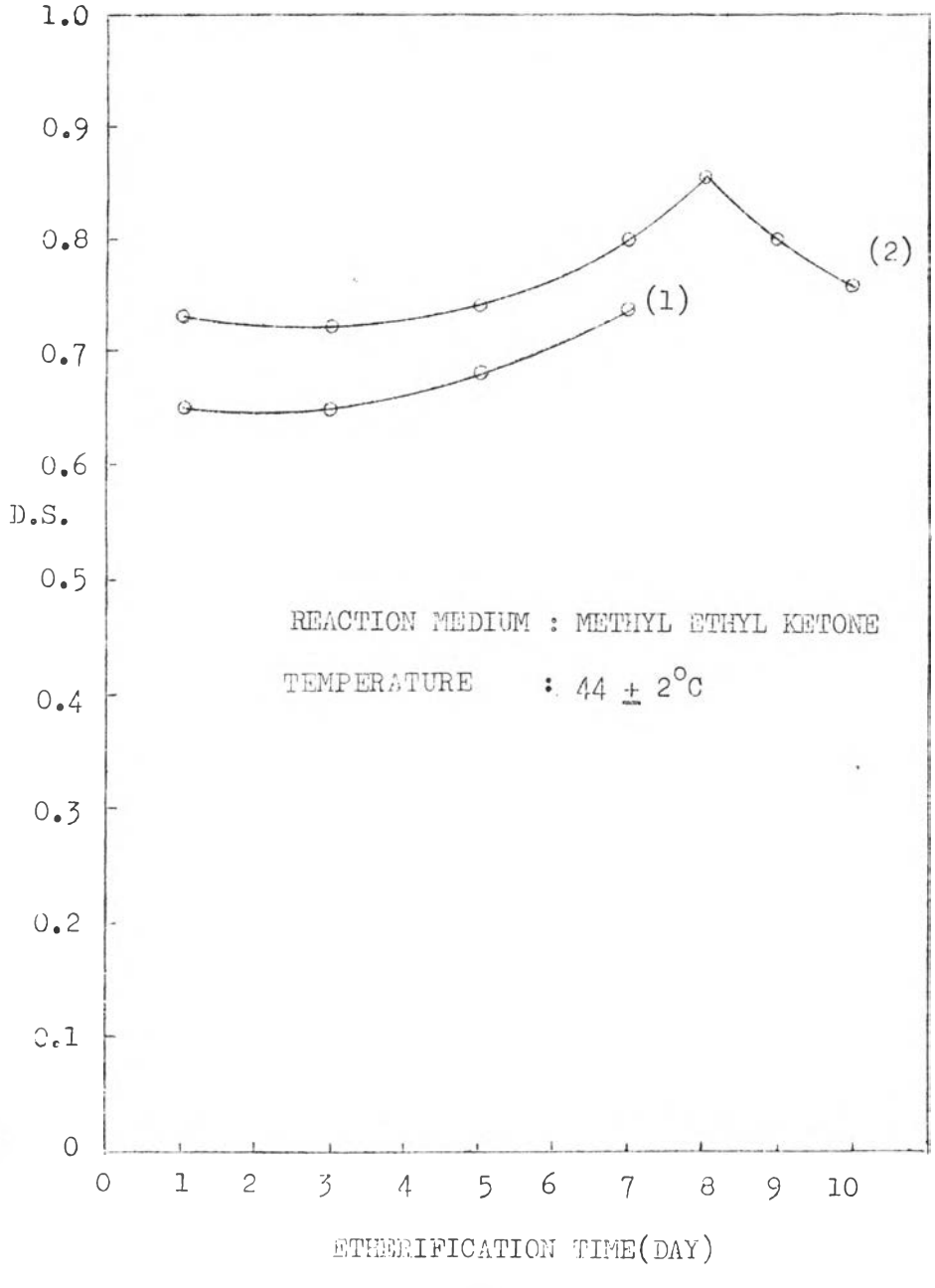

FIGURE 33 D.S. vs. ETHERIFICATION TIME

(1) = D.S.'s OF THE PRODUCTS OBTAINED FROM TREATED PULP OF FORMER BATCH

(2) = D.S.'s OF THE PRODUCTS OBTAINED FROM TREATED PULP OF NEW BATCH