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CHAPTER - IV

DISSOLUTION OF CALCITE IN ORGANIC ACIDS - I (effect of time and concentration)

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(Effect of etching time and concentration)

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4.1 INTRODUCTION

Applications of selective etching as a tool in the study of dislocation behaviour are well demonstrated (Johnston, 1962), but the basic mechanism of the process is still to be understood. Since the classical work of Gilman et al (1958) much work in this direction has appeared in the literature on alkali halides (Ives 1963, Ives and Hirth 1960, Urusovskaya 1963, Hari babu and Bansigir 1968, Bhagwan Raju and Bansigir 1971, Bhagwan Raju and Bansigir 1972, Sangwal et al 1978 etc.) as well as on metals (Popkova et al 1969, Popkova et al 1970, Bhatt et al 1974 etc.), in which attempts have been made to understand it.

Etching solutions of alkali halides consist of a solvent (usually some alcohol or organic acid) to which an inhibitor is added. The etchants for metals and semiconductors are relatively complicated and consist of at least two solutions. One of these solutions forms a compound with crystals while the other desorbs it by forming certain complexes. There is another class of etchants which consists of some pure solutions, for example mineral acids for etching of calcite, fluorite, barite, magnesium oxide etc. This class of etchants is suitable for the study of the etching process.

The shape of an etch pit is dependent on the nature, concentration, composition and temperature of etchant. Thus the earlier workers reported the occurrence of different shapes of etch pits on calcite cleavage faces due to various types of etchants. Even with the same etchant the change in concentration had a significant effect on the shape of etch pits (Watt, 1959 ; Stanley, 1959 ; Pandya and Pandya, 1961 ; Mehta, 1972 and Shah, 1976). In all cases the diluent used to change the concentration of an etchant was distilled water in which calcite is sparingly soluble (0.008 gm. per litre at 20^{o}C). It is thus clear that with the same etchant, either concentrated or diluted, the chemical reaction is not materially changed. However, the rate of reaction on cleavage face of calcite changes and this gives rise to production of etch pits of various shapes. This obviously points to the unusual characteristics of calcite cleavages. It was also reported that even with the same concentration of an etchant, the rate of stiring of the solution has a marked effect on the shape of etch figures (Hanke, 1961 ; Mehta, 1972).

Several workers have reported dislocation etchants for calcite cleavages and the present author has carried out a detailed systematic optical study of morphology of etch pits and etch rates on calcite cleavages by employing organic acids viz. Lactic (SM) and Formic (BDH) acids as etchants. The general information about these acids is presented in Appendix. The shapes of etch pits and etch rates as a function of etching time and concentration of the etchant are discussed in this chapter.

4.2 EXPERIMENTAL

Natural crystals of calcite were obtained from various localities in India (Shivrajpur, Pavagarh, Broach (Gujarat State) ; and Rajasthan etc.). The crystals are fairly big with their sizes ranges from 1 cm. to 15 cm. with cross sectional area of the order of 3 cm x 3 cm. A big crystal was selected and etching work was carried out on small pieces obtained by cleaving the crystal in the usual way i.e. by giving a sharp blow with a hammer on a razor blade kept in contact with the crystal along cleavage direction. The cleavage surface was fully immersed in a still etchant of known concentration for desired time of etching at a constant temperature. The temperature of the etchant was maintained to within ± 0.5°C by a regulator attached to constant temperature water bath for studies at higher temperature and by ice for studies at lower temperatures. After etching the crystal for a given period, it was kept in running water for some time. It was then dried by hot air blower. The samples etched were optically studied by CZ Vertival microscope described in Chapter 2. The variation of etch pit dimensions along direction [110] were carried out by using filar micrometer eyepiece (X 750) with least count of 0.2 microns. An accuracy of ± 0.1 μ can be achieved by this method. The surface dissolution rate was measured by usual weight loss method using a semi-microbalance. Electrical conductivity of etching solution was measured using a resistance bridge ($10^6 \Omega$) supplied by Phillips, India (Model PR-9500) described in Chapter 2. P_H of etching solution was measured by P_H meter (Elico Pvt. Ltd.) model LI-10.

4.3 OBSERVATIONS AND RESULTS

4.3.1 Effect of time on morphology of etch pits :

(a) Lactic acid :

Fig. 4.1, 4.2 and 4.3 show the photomicrographs of calcite cleavage face etched in 14.79 N (100 % by Vol.) lactic acid at 30°C for 8, 16 and 24 minutes respectively. It is clear that with the increase in etching time the number and location of etch pits remain same but the pits grow in size. Further, the internal structure of etch pits remains same i.e. point-bottomed etch pit remains point-bottomed and flat bottomed pit remains flat bottomed.

(b) Formic acid :

Fig. 4.4, 4.5 and 4.6 show the photomicrographs of cleavage face of calcite etched in 2.599 N (10% by vol.)

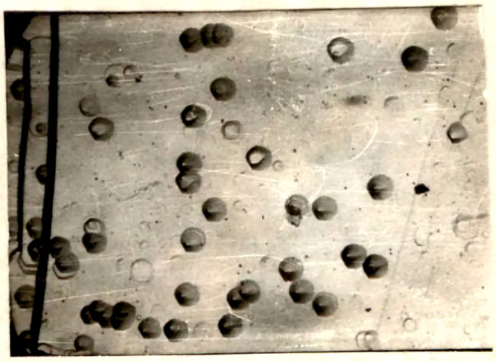


Fig. 4.1 x 126

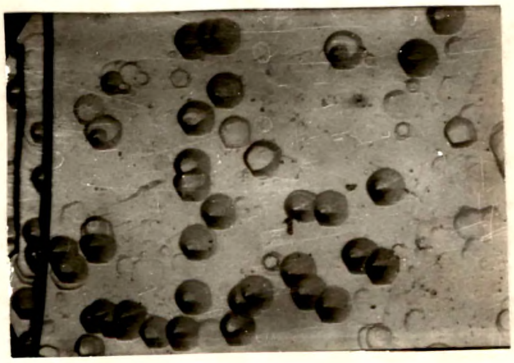


Fig. 4.2 x 126

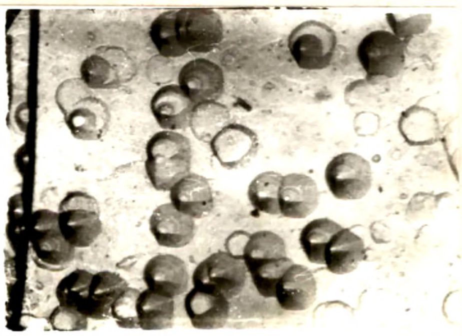


Fig. 4.3 x 126

Figures 4.1, 4.2 and 4.3 represent photomicrographs of calcite cleavage etched in 14.79N (100% by vol.) lactic acid at 30°C successively for 8, 16 and 24 minutes respectively.

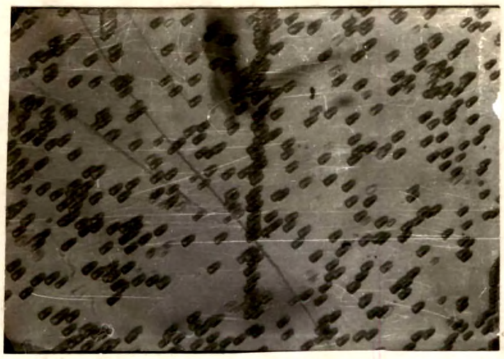


Fig. 4.4 x 126

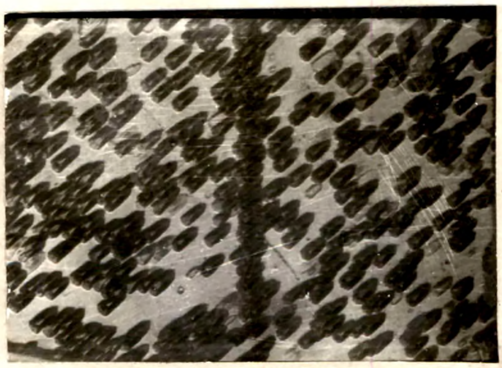


Fig. 4.5 x 126

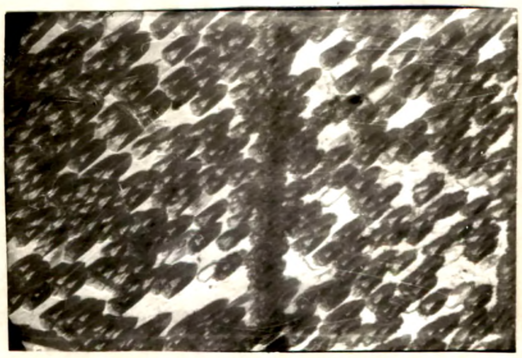


Fig. 4.6 x 126

Figures 4.4, 4.5 and 4.6 show photomicrographs of calcite cleavage etched in 2.599N (10% by vol.) formic acid at 30°C successively for 3, 6 and 9 seconds respectively.

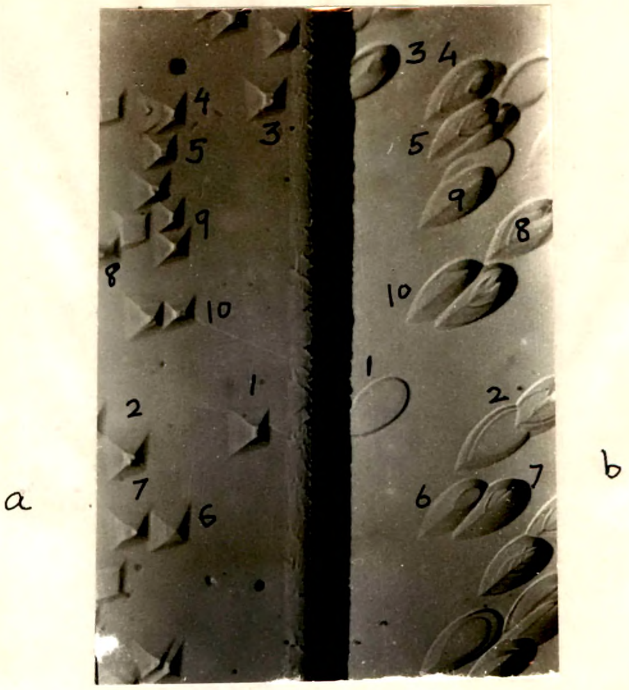
formic acid at 30°C successively for 3, 6 and 9 seconds respectively. In this case also the etch pit density remains constant and the internal structure of pits do not change with etching time. Further, the cleavage lines (fig. 4.4) are eaten away by successive etching (fig. 4.5 and 4.6). As a result there is a shifting of cleavage line from its original position on the virgin unetched cleavage surface.

4.3.2 Effect of concentration on morphology of etch pits :

(a) Lactic acid :

It is known that calcite reacts with lactic acid to form highly soluble reaction products, calcium lactate, water and gaseous carbon dioxide. The later goes to the atmosphere.

In order to assess the influence of concentration of lactic acid on shape of etch pits, it is desirable to keep temperature of etching constant and vary the concentration systematically. In the present report temperature of etching is kept constant and effect of acid concentration on shape of etch pits is investigated in detail. Fig. 4.7(a) shows the photomicrograph of freshly cleaved surface etched by 0.1479N (1 % by vol.) lactic acid for 45 seconds at 35°C whereas its counterpart (fig. 4.7b) was etched by 1.479 N (10% by vol.) lactic acid for 15 seconds.



x 300

Fig. 4.7 a and b show the photomicrographs of calcite cleavage counterparts etched in 0.1479N (1% by vol.) and 1.479N (10% by vol.) for 45 and 15 seconds at 35°C respectively.

(a) (b)

x 200

Fig. 4.8 a and b show the photomicrographs of calcite cleavage counterparts etched in 0.1479N (1% by vol.) and 10.353N (70% by vol.) lactic acid at 35°C for 45 and 90 seconds respectively.

Certain characteristic features of these photomicrographs of oppositely matched cleavage faces of calcite are as follows :-

(i) The etch pits produced by 0.1479 N (1 % by vol.) lactic acid have rhombic outlines whereas pits produced by 1.479 N (10% by vol.) lactic acid have leaf-like (oval) shape. The etch pits on both counterparts of fig. 4.7 are eccentric.

(ii) Although the concentration of etchant is different in both cases, there is one-to-one correspondence of etch pit position in both photomicrographs. However, there is not complete correspondence of etch pits so far as characteristics of these patterns are concerned. In order to bring out these features, correspondence of individual pits on both photomicrographs was made by numbering them and presented in the following table :-

Concentration Induced morphology of etch pits

Correspondence of etch pits of different structures on oppositely matched cleavage counterparts.

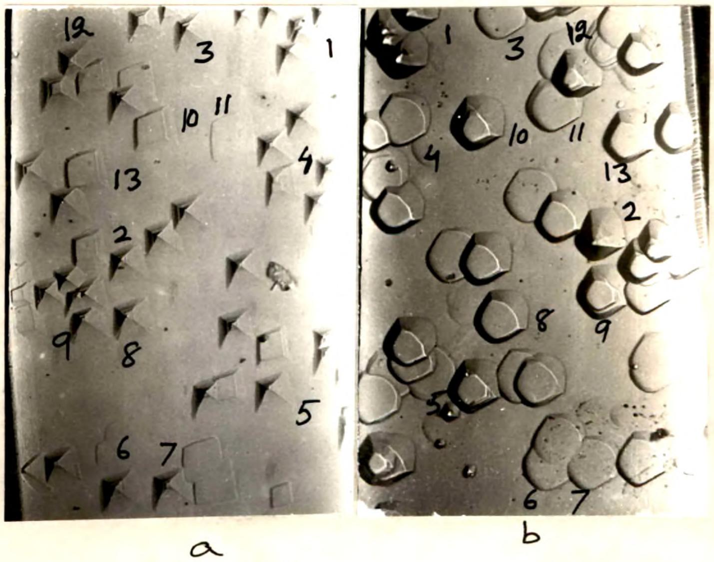
Etchant : Lactic acid

Structure of etch pits	Structure of etch pits
A 0.1479 N Conc. 45 seconds time (fig. 4.7a).	1.479 N Conc. (fig. 4.7b) 15 seconds etching time.
Plane shape of pit : Rhombic	Plane shape of pit : leaflike
(i) Point-bottomed pits 1, 2, 3, 6 and 7	(i) Flat bottomed pits 1, 2, 3, 6 and 7.
(ii) Flat-bottomed pit 8	(ii) Terraced pit 8
(iii) Point bottomed pits 9 and 10	(iii) Point-bottomed pits 9 and 10
(iv) Point-bottommed pits 4 and 5	(iv) Terraced pits 4 and 5
B Conc : 0.1479 N (fig. 4.9a) time : 45 seconds.	Conc : 14.79 N (fig. 4.9b) time : 20 ~~Seconds~~ minutes.
Plane shape of pit : Rhombic	Plane shape of pit : Curvilinear pentagon
(i) Point-bottomed 1 and 2	(i) Point-bottomed pits 1 and 2
(ii) Point-bottomed 3, 4, 5, 6, 7, 8 and 9	(ii) Flat-bottomed pits 3, 4, 5, 6, 7, 8 and 9.
(iii) Flat-bottomed pits 10, 11, 12 and 13.	(iii) Flat-bottomed pits 10, 11, 12 and 13.

It should be remarked here that the present author has carefully studied several matched cleavage counterparts and almost all characteristics mentioned in above table were observed. Further, rhombic outline of etch pit could be observed for concentrations less than 0.1479 N (1 % by vol.). As the concentration increases, the shape of etch pit changes to leaf-like shape. Leaf-like shape of an etch pit could be observed upto 5.1765 N (35% by vol.) concentration of lactic acid.

Fig. 4.8a and 4.8b represent photomicrographs of oppositely matched cleavage counterparts etched in 0.1479 N (1 % by vol.) lactic acid at 35°C for 45 seconds and 10.353 N (70% by vol.) lactic acid at 35°C for 90 seconds. It should be noted here that almost all the characteristics mentioned for fig. 4.7 (a,b) are observed in fig. 4.8 (a,b). The shape of an etch pit produced by 10.353 N (70% by vol.) (fig. 4.8b) tends to be curvilinear elongated pentagon. These pits are also eccentric.

Fig. 4.9 (a and b) show the photomicrographs of oppositely matched faces etched in 0.1479 N (1 % by vol.) lactic acid and 14.79 N (100% by vol.) lactic acid at 35°C for 45 seconds and 20 minutes respectively. In addition to the correspondence of etch pits of different structures at identical places on cleavage counterparts (cf, table above) the only noticeable feature is curvilinear pentagonal (almost circular) shape of an etch pit.



x 200

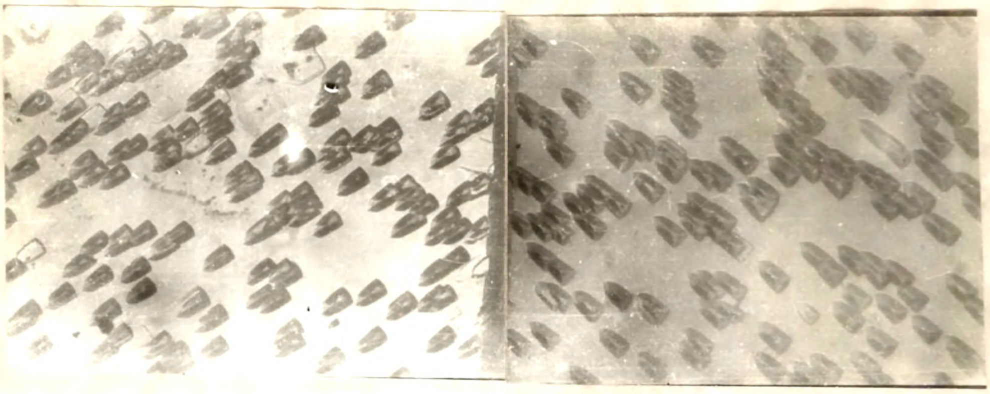
Fig. 4.9 a and b show photomicrographs of calcite cleavage counterparts etched in 0.1479N (1% by vol.) and 14.79N (100% by vol.) lactic acid at 35°C for 45 seconds and 20 minutes respectively.

(b) Formic acid :

Fig. 4.10a and 4.10b represent the photomicrographs of appositely matched surfaces etched in 2.599 N (10% by vol.) formic acid at 35°C for 5 seconds. It can be seen that almost all pits are point-bottomed and exhibit excellent one-to-one correspondence. The pits have elongated pentagonal shape on the cleavage surface.

Fig. 4.11a and 4.11b represent the matched counterparts etched in 2.599 N (10% by vol.) formic acid at 35°C for 5 seconds and 10.396 N (40% by vol.) formic acid at 35°C for 5 seconds respectively. The pits are point-bottomed and show one-to-one correspondence. The rate of attack in 2.599 N (10% by vol.) is less than that of 10.396 N (40% by vol.) formic acid, since the etch pits (fig. 4.11b) are bigger in size than those on its counterpart (fig. 4.11a). The cleavage line A is affected by etching showing a clear shift in accordance with the observations reported by earlier workers (Patel and Tolansky, 1957, Pandya and Pandya 1959, Shah 1976).

Fig. 4.12a and 4.12b show the photomicrographs of identical regions on freshly cleaved counterparts etched in 2.599 N (10% by vol.) formic acid at 35°C for 5 seconds and 15.494 N (60% by vol.) formic acid at 35°C for 10 seconds respectively. Unlike figures 4.10 and 4.11 there is a



x 126

a b

Fig. 4.10 a and b show the photomicrographs of calcite cleavage counterparts etched in 2.599N (10% by vol.) formic acid at 35°C for 5 seconds.

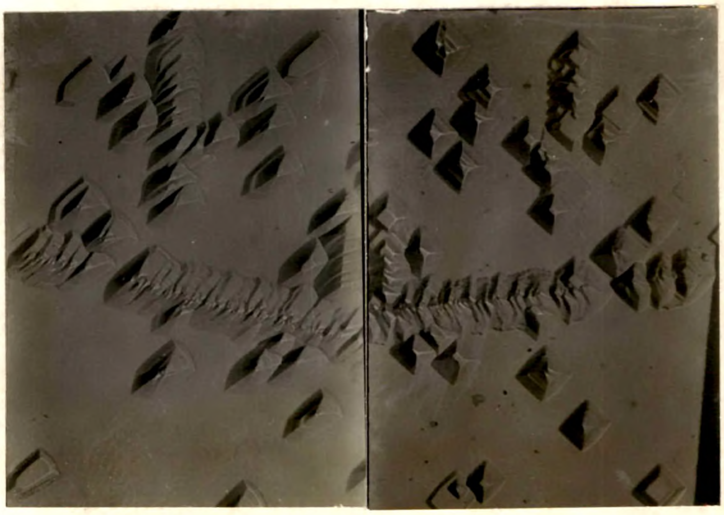
a b

x 126

Fig. 4.11 a and b show the photomicrographs of calcite cleavage counterparts etched in 2.599N (10% by vol.) and 10.396N (40% by vol.) formic acid at 35°C for 5 seconds each respectively.

x 200

Fig. 4.12 a and b show the photomicrograph of calcite cleavage counterparts etched in 2.599N (10% by vol.) and 15.494N (60% by vol.) formic acid at 35°C for 5 & 10 seconds respectively.



x 200

Fig. 4.13 a and b show the photomicrographs of calcite cleavage counterparts etched in 2.599N (10% by vol.) & 20.692N (80% by vol.) formic acid at 35°C for 7 and 25 seconds respectively.

difference in the internal structure of pits in fig. 4.12. The characteristics of pits produced by lactic acid (fig. 4.7, 4.8 and 4.9) are observed in fig. 4.12. The geometrical outline of etch pits on surface is pentagonal. This shape persists for a range of concentration from 0.2599 N (1% by vol.) to 15.494 N (60% by vol.) formic acid. However, the tip of the pentagon (depth point) tends to disappear in 15.494 N (60% by vol.) acid. Although there is excellent matching of linear correspondence of etch pits (fig. 4.12 a and b), the internal structures are noticeably different.

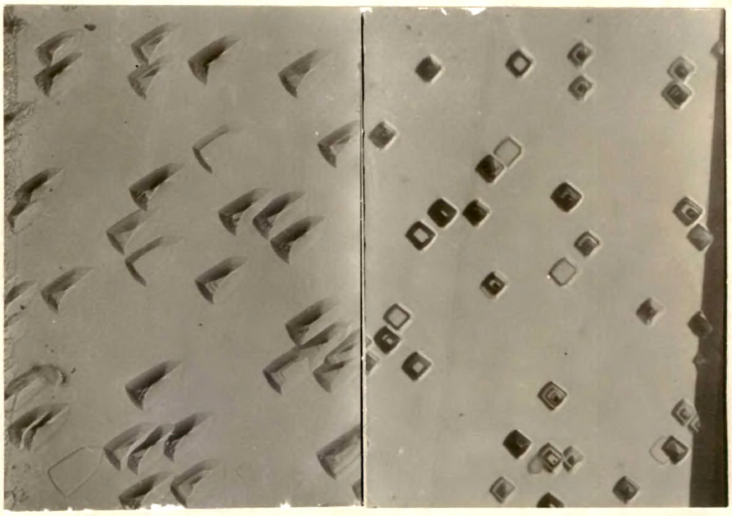
Fig. 4.13a and 4.13b represent the cleavage counterparts etched in 2.599 N (10% by vol.) formic acid at 35°C for 5 seconds and 20.692 N (80% by vol.) formic acid at 35°C for 25 seconds respectively. It should be noted that the rate of attack decreases with concentration as more etching time is needed to get same size of an etch pit. The pits produced by 20.692 N (80% by vol.) formic acid have rectangular outline. The rectangular shape of an etch pit is observed within the concentration range 18.093 N (70% by vol.) to 25.99 N (100% by vol.) acid. The etch pit shape also changes the appearance and structure of linear arrays on identical portions of both the counterparts. Further these arrays are structurally different from those observed in the earlier photomicrographs (fig. 4.12 a and b).

Fig. 4.14a and 4.14b show the photomicrographs of counterparts etched in 2.599 N (10% by vol.) formic acid at 35°C for 5 seconds and 25.99 N (100% by vol) formic acid at 35°C for 150 seconds respectively. Here also almost all characteristics described for pits (fig. 4.7) are reflected. There is good one-to-one correspondence of etch pits on the corresponding region of cleavage counterparts. However, the plane shape of etch pits in these photomicrographs are different.

It should be noted that in case of formic acid, the internal structure of etch pits for lower concentrations upto 10.396 N (40% by vol.) does not change significantly (fig. 4.10 and 4.11) but as the concentration is increased further, the dissimilarity in the internal structure of etch pits becomes obvious (fig. 4.12, 4.13 and 4.14).

4.3.3 Effect of time on etch rates :

Several sets of observations of etch pit lengths along [110] for different times of etching for various etching temperatures were taken. Table 4.1 and 4.2 present a typical set of observations on variation of length of an etch pit (L) measured along [110] direction and weight-loss per cm^2. with etching time at various temperatures of etching using 14.79 N (100% by vol.) lactic acid and 2.599 N



x 200

Fig. 4.14 a and b show the photomicrographs of calcite cleavage counterparts etched in 2.599N (10% by vol.) & 25.99N (100% by vol.) formic acid at 35°C for 7 and 150 seconds respectively.

TABLE 4.1

Etchant : 14.79 N (100% by Vol.) Lactic acid

Temp. of etching	40°C		50°C		
Time in minutes	L x 10^{-4} cm.	Wt. loss per cm^2 gm x 10^{-4}	Time in minutes	L x 10^{-4} cm.	Wt. loss per cm^2 gm x 10^{-4}
4	11.96	2.76	2	9.36	1.80
8	24.96	5.52	4	18.72	3.60
12	38.48	8.28	8	39.00	7.20
16	50.96	11.04	12	60.84	10.80
20	65.00	13.80	16	80.60	14.40

TABLE 4.1 Cont...

Temp. of etching	60°C			70°C	
Time in minutes	L x 10^{-4} cm.	Wt. loss per cm^2 gm x 10^{-4}	Time in minutes	L x 10^{-4} cm	Wt. loss per cm^2 gm x 10^{-4}
2	24.44	3.00	1	29.64	2.40
3	35.00	4.50	2	55.64	4.80
4	47.84	6.00	3	79.56	7.20
5	55.00	7.50	-		
6	66.04	9.00	-		

TABLE 4.2

Etchant : 2.599 N (10% by Vol.) Formic acid

Temp. of etching	$10^{o}C$		$20^{o}C$		
Time in seconds	L x 10^{-4} cm.	Wt. loss per cm^{2} gm x 10^{-5}	Time in minutes	L x 10^{-4} cm	Wt. loss per cm^{2} gm x 10^{-5}
5	17.35	39.97	5	25.65	53.93
10	34.00	79.94	10	51.40	107.86
15	41.40	119.91	15	77.05	161.78
20	67.90	159.89	20	103.00	215.72

TABLE 4.2 Cont...

Temp. of etching	30°C		50°C		
Time in seconds	$L \times 10^{-4}$ cm.	Wt. loss per cm^2 gm $\times 10^{-5}$	Time in minutes	$L \times 10^{-4}$ cm.	Wt. loss per cm^2 gm $\times 10^{-5}$
5	38.40	71.81	3	46.95	75.85
10	77.90	143.63	6	93.90	151.70
15	116.30	215.44	9	141.00	227.56
20	155.60	287.26			

(10% by vol.) formic acid respectively as etchants. Length of an etch pit along [110] is plotted against etching time (fig. 4.15 and 4.16). It is clear from these plots that length of an etch pit varies linearly with etching time and the straight line passes through origin. The slopes of these lines give the rate of tangential dissolution, V_t, along direction [110] at corresponding temperatures of etching. Similarly, weight loss per cm^2. is plotted against etching time (fig. 4.17 and 4.18) ; the plots are again straight lines passing through origin. The slopes of these plots give the rate of surface dissolution, V_s, in gm. per cm^2 per unit time. On dividing this quantity by density of calcite (2.71 gm/c.c.) we get the rate of surface dissolution, V_s, in cm/sec. It should be mentioned here that the plots of length of an etch pit (L) and weight loss per cm^2 are always straight lines for all concentrations and temperatures of etching of lactic and formic acids. Straight line plots clearly indicate that rates of tangential as well as surface dissolution are independent of etching time but depend on temperature and concentration of the etchant.

4.3.4 Effect of concentration on etch rates :

(a) Lactic acid :

The dependence of tangential (V_t) and surface

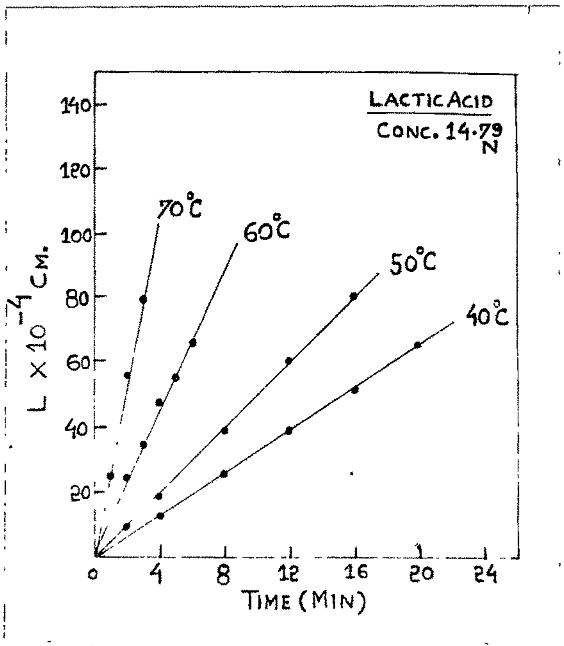


Fig. 4.15 Plot of length versus time for 14.79 N (100% by vol.) lactic acid at different temperatures.

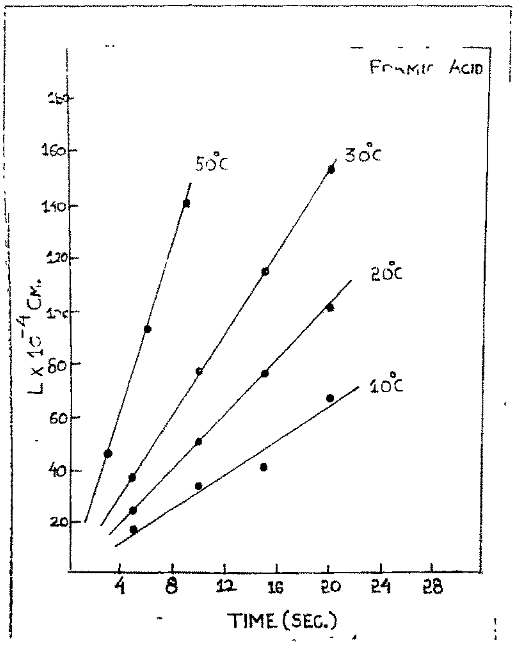


Fig. 4.16 Plot of length versus time for 2.599N (10% by vol.) formic acid at different temperatures.

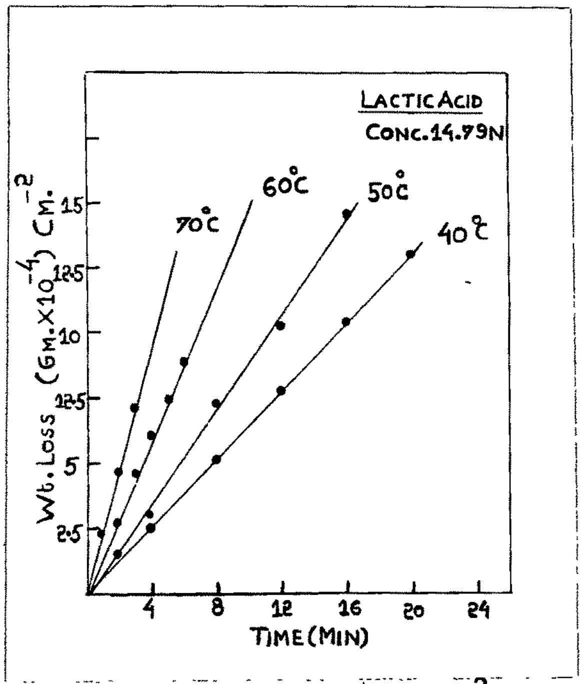


Fig. 4.17 Plot of weight-loss per cm^2 versus time for 14.79N (100% by vol.) lactic acid and at different temperatures.

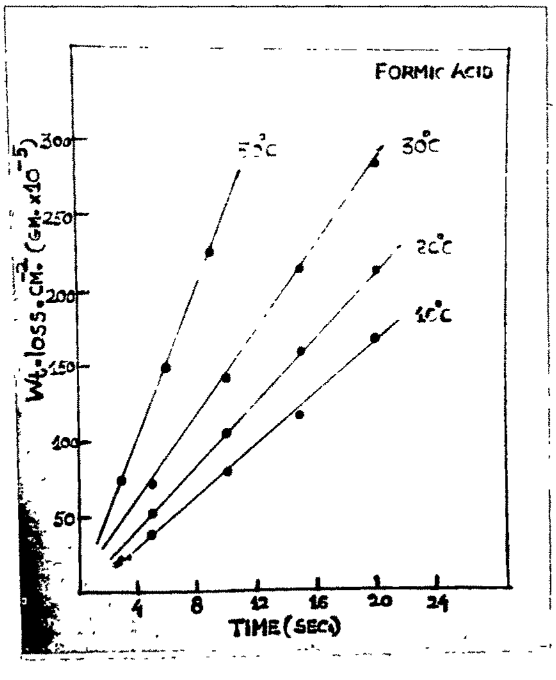


Fig. 4.18 Plot of weight-loss per cm^2 versus time for 2.599N (10% by vol.) formic acid at different temperatures.

dissolution rate (V_s) on concentration of lactic acid at various temperatures is illustrated by fig. 4.19 and 4.20 respectively. The values of V_t and V_s for various concentrations and temperatures are listed in Table 4.3. The diluent used was distilled water. A careful examination of fig. 4.19 and 4.20 shows that the rate of tangential dissolution and that of surface dissolution increases intially with the increase in the concentration of an acid. After an initial increase, the rate of dissolution decreases with further increase in the concentration of an acid showing a sharp maximum. The nature of V_t - C and V_s - C curves is similar. The maximum is observed at 1.479N (10% by vol.) concentration of lactic acid. But at 80°C, it shifts to 2.958 N (20% by vol.).

(b) Formic acid :

The rates of tangential as well as surface dissolution at various concentrations of formic acid and at various temperatures ranging from 10°C to 60°C are listed in table 4.4. The concentration dependence of V_t and V_s is shown in fig. 4.21 and 4.22. The rate of dissolution shows a sharp maximum at 7.797 N (30% by vol.) concentration. In case of formic acid also the concentration corresponding to maximum rate of dissolution is same for surface and tangential dissolution. The concentration corresponding to maximum rate of reaction, C_{max}, does not depend upon temperature of etching.

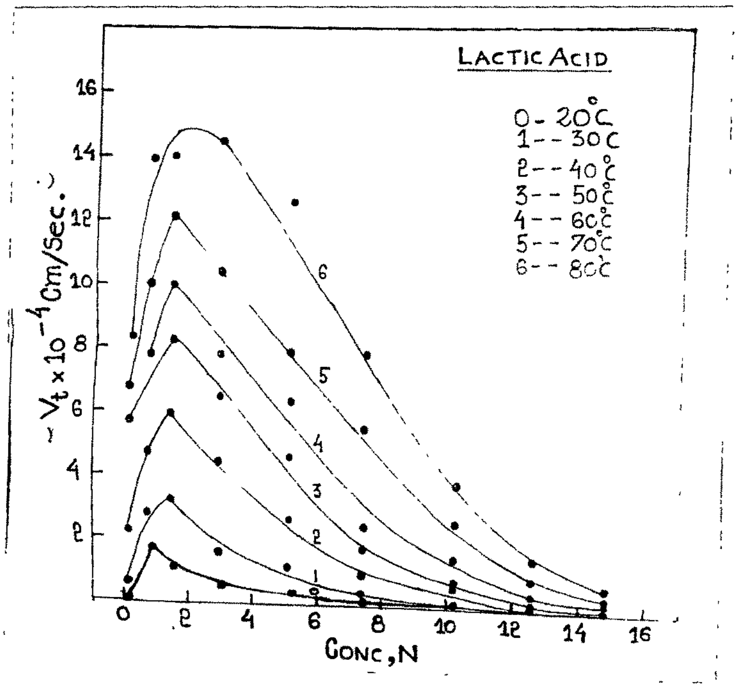


Fig. 4.19 Plot of V_t versus concentration of lactic acid for different temperatures.

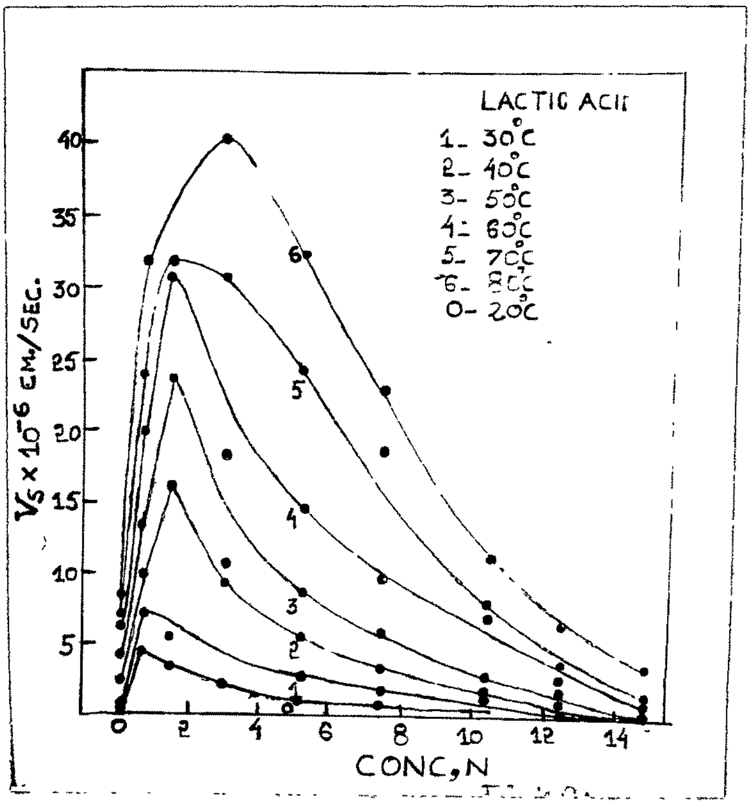


Fig. 4.20 Plot of V_5 versus concentration of lactic acid for different temperatures.

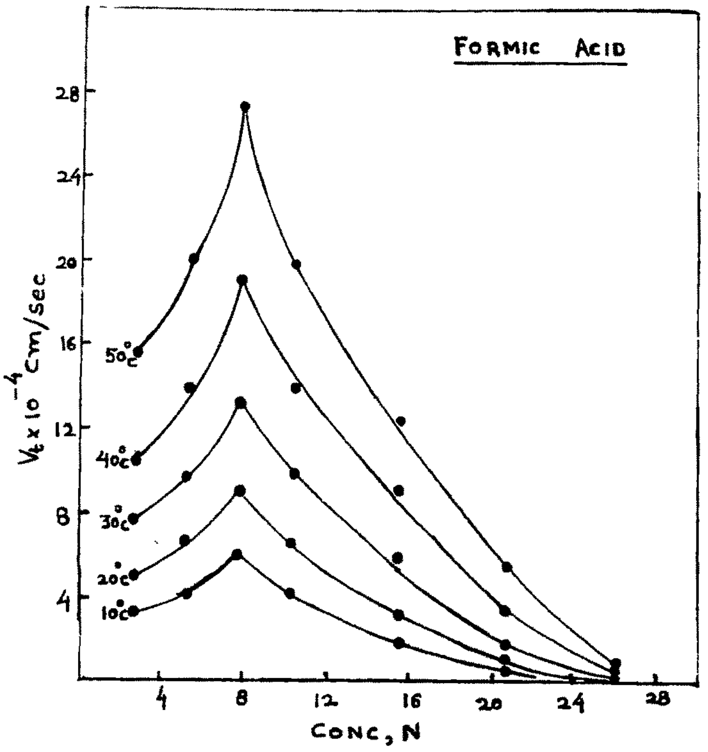


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Fig. 4.21 Plot of V_t versus concentration of formic acid for different temperatures.

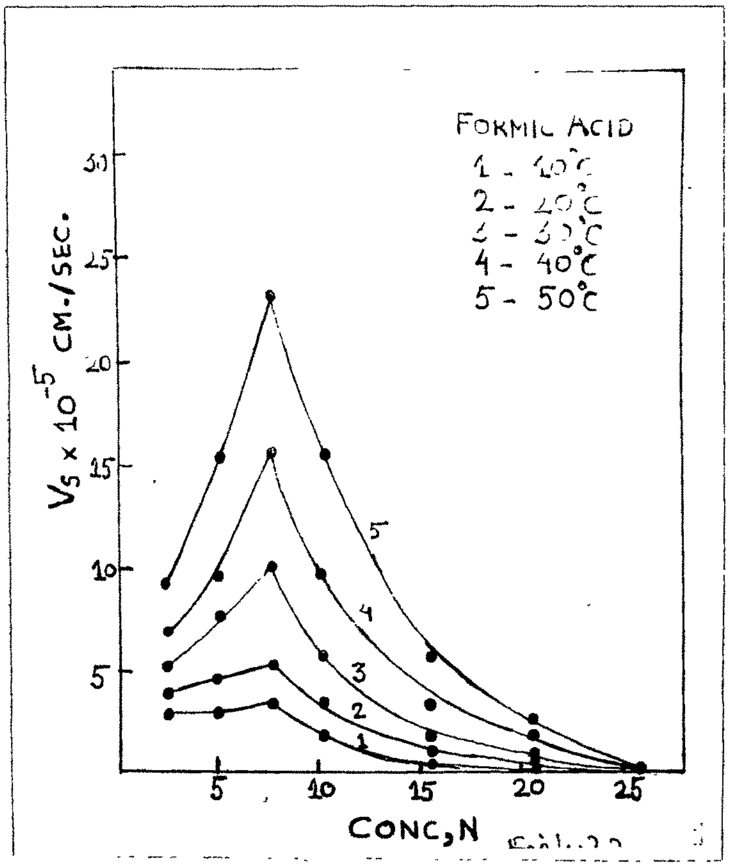


Fig. 4.22 Plot of V_s versus concentration of formic acid for different temperatures.

TABLE 4.3

Etchant ; DL-Lactic acid (SM)   Diluent : Distilled water

Conc. N 1	Temp ^{o}C 2	Tangential rate $V_t \times 10^{-4}$ cm/sec 3	log V_t 4	Surface dissolution rate $V_s \times 10^{-6}$ 5	log V_s 6	1/T 7	$\frac{V_t}{V_s}$ 8
0.1479 (1% by Vol)	30	0.572	$\bar{5}.7574$	0.70	$\bar{7}.8451$	3.30	81.71
	40	2.23	$\bar{4}.3483$	2.45	$\bar{6}.3899$	3.19	91.02
	50	5.72	$\bar{4}.7574$	4.43	$\bar{6}.6463$	3.09	129.11
	60	5.19	$\bar{4}.7160$	7.38	$\bar{6}.8681$	3.008	70.32
	70	6.76	$\bar{4}.8299$	6.09	$\bar{6}.7849$	2.91	111.00
	80	8.32	$\bar{4}.9201$	8.67	$\bar{6}.9381$	2.83	95.96
	20*	0.16	$\bar{5}.2000$	0.25	$\bar{7}.4000$	3.41	64.00

* Values estimated from graph.

TABLE 4.3 Cont...

1	2	3	4	5	6	7	8
	20	1.85	$\bar{4}.2672$	4.80	$\bar{6}.6810$	3.41	38.54
	30	2.86	$\bar{4}.4564$	7.38	$\bar{6}.8681$	3.30	38.75
	40	4.68	$\bar{4}.6702$	10.25	$\bar{5}.0111$	3.19	45.65
0.7395 (5% by vol)	50	5.20	$\bar{4}.7160$	13.65	$\bar{5}.1353$	3.09	38.09
	60	7.80	$\bar{4}.8921$	19.95	$\bar{5}.3000$	3.00	39.09
	70	10.14	$\bar{3}.0060$	23.99	$\bar{5}.3800$	2.91	42.26
	80	14.04	$\bar{3}.1473$	31.62	$\bar{5}.5000$	2.83	44.40

TABLE 4.3 Cont....

1	2	3	4	5	6	7	8
	20	1.04	$\bar{4}.0170$	3.14	$\bar{6}.4965$	3.41	33.12
	30	3.38	$\bar{4}.5289$	5.54	$\bar{6}.7432$	3.30	61.01
	35	4.42	$\bar{4}.6454$	9.23	$\bar{6}.9650$	3.24	47.88
	40	5.98	$\bar{4}.7767$	16.61	$\bar{5}.2203$	3.19	36.00
	45	-	-	20.30	$\bar{5}.3074$	3.14	-
1.4790 (10% by vol)	50	8.32	$\bar{4}.9201$	23.98	$\bar{5}.3800$	3.09	34.69
	55	9.36	$\bar{4}.9713$	27.68	$\bar{5}.4421$	3.04	33.81
	60	10.00	$\bar{3}.0000$	31.37	$\bar{5}.4965$	3.00	31.88
	70	12.22	$\bar{3}.0870$	31.37	$\bar{5}.4965$	2.91	38.95
	80	14.04	$\bar{3}.1473$	32.29	$\bar{5}.5091$	2.83	43.48

TABLE 4.3 cont...

1	2	3	4	5	6	7	8
	20	0.52	$\bar{5}.7160$	2.21	$\bar{6}.3452$	3.41	23.52
	25	1.04	$\bar{4}.0170$	2.95	$\bar{6}.4702$	3.35	35.25
	35	2.51	$\bar{4}.4000$	8.49	$\bar{6}.9288$	3.24	29.56
	40	4.47	$\bar{4}.6503$	9.23	$\bar{6}.9640$	3.19	48.42
	45	3.64	$\bar{4}.5611$	11.07	$\bar{5}.0442$	3.14	32.88
2.9580 (20% by volume)	50	6.50	$\bar{4}.8129$	10.15	$\bar{5}.0064$	3.09	64.03
	55	6.50	$\bar{4}.8129$	18.45	$\bar{5}.2661$	3.04	35.23
	60	7.80	$\bar{4}.8921$	18.45	$\bar{5}.2661$	3.00	42.27
	70	10.40	$\bar{3}.0170$	31.37	$\bar{5}.4965$	2.91	33.15
	75	14.04	$\bar{3}.1473$	35.37	$\bar{5}.5486$	2.87	44.75
	80	14.45	$\bar{3}.1600$	40.97	$\bar{5}.6112$	2.83	30.12

TABLE 4.3 Cont...

1	2	3	4	5	6	6	8
	20	0.40	$\bar{5}.6021$	1.77*	$\bar{6}.2500$	3.41	22.5
	25	0.71	$\bar{5}.8513$	-	-	3.35	-
	30	1.30	$\bar{4}.0000$	3.00*	$\bar{6}.4771$	3.30	43.33
	40	2.70	$\bar{4}.4314$	5.70*	$\bar{6}.7558$	3.19	47.36
5.1765 (35% by volume)	50	4.68	$\bar{4}.6702$	9.00*	$\bar{6}.9542$	3.09	52.00
	60	6.30	$\bar{4}.8000$	15.00*	$\bar{5}.1760$	3.00	42.00
	70	7.94	$\bar{4}.9000$	25.00*	$\bar{5}.3979$	2.91	31.76
	80	12.58	$\bar{3}.1000$	32.50*	$\bar{5}.5118$	2.83	38.70

TABLE 4.3 cont...

1	2	3	4	5	6	7	8
7.3950 (50% by volume)	20	0.25	$\bar{5}.4000$	1.29	$\bar{6}.1110$	3.41	19.37
	30	0.50	$\bar{5}.7000$	2.03	$\bar{6}.3074$	3.30	24.63
	40	1.00	$\bar{4}.0000$	3.69	$\bar{6}.5671$	3.19	27.10
	50	1.82	$\bar{4}.2600$	6.09	$\bar{6}.7846$	3.09	29.88
	55	2.24	$\bar{4}.3502$	7.38	$\bar{6}.8681$	3.04	30.35
	60	2.52	$\bar{4}.4014$	10.00	$\bar{5}.0000$	3.00	25.20
	65	4.68	$\bar{4}.6702$	-	-	2.95	-
	70	5.62	$\bar{4}.7500$	18.45	$\bar{5}.2661$	2.91	30.46
	80	7.943	$\bar{4}.8999$	23.06	$\bar{5}.3630$	2.83	34.75

TABLE 4.3 cont....

1	2	3	4	5	6	7	8
10.3530 (70% by volume)	20	0.213	$\bar{5}.3284$	1.845	$\bar{6}.2661$	3.41	11.54
	30	0.224	$\bar{5}.3502$	1.480	$\bar{6}.1581$	3.30	15.13
	40	0.560	$\bar{5}.7500$	1.845	$\bar{6}.2661$	3.19	30.35
	50	0.946	$\bar{5}.9761$	2.950	$\bar{6}.4702$	3.09	32.03
	60	1.660	$\bar{4}.2201$	8.490	$\bar{6}.8288$	3.00	19.55
	70	2.756	$\bar{4}.4402$	6.830	$\bar{6}.8343$	2.91	40.26
	80	3.900	$\bar{4}.5911$	11.620	$\bar{5}.0654$	2.83	33.56

TABLE 4.3 contd...

1	2	3	4	5	6	7	8
12.5715 (85% by volume)	20	0.060	$\bar{6}.7800$	-	-	3.41	-
	30	0.075	$\bar{6}.8921$	0.55	$\bar{6}.0400$	3.30	14.18
	35	0.083	$\bar{6}.9191$	1.29	$\bar{6}.1111$	3.24	6.43
	40	0.140	$\bar{5}.1461$	1.29	$\bar{6}.1111$	3.19	10.85
	50	0.260	$\bar{5}.4000$	2.03	$\bar{6}.3074$	3.09	12.80
	60	0.500	$\bar{5}.7000$	2.95	$\bar{6}.4702$	3.00	16.94
	70	1.040	$\bar{4}.0170$	3.69	$\bar{6}.5671$	2.91	28.18
	80	1.585	$\bar{4}.2000$	6.900	$\bar{6}.8400$	2.83	22.97

TABLE 4.3 Cont....

1	2	3	4	5	6	7	8
	30	0.052	$\bar{6}.7160$	0.369	$\bar{7}.5671$	3.41	14.09
	40	0.057	$\bar{6}.7574$	0.420	$\bar{7}.6278$	3.19	13.57
	45	0.062	$\bar{6}.7952$	0.420	$\bar{7}.6278$	3.14	14.76
14.7900 (100% by volume)	50	0.088	$\bar{6}.9465$	0.550	$\bar{7}.7432$	3.09	16.00
	60	0.1768	$\bar{5}.2475$	0.920	$\bar{7}.9650$	3.00	19.21
	70	0.416	$\bar{5}.6191$	1.480	$\bar{6}.1691$	2.91	28.10
	80	0.832	$\bar{5}.9201$	4.430	$\bar{6}.6463$	2.83	18.78

TABLE 4.4

Etchant : Formic Acid. H.COOH (BDH 98-100%) Diluent : Distilled water

Concentration (Normality)	Temp. ^{o}C	Tangential Rate of dissolution $V_t \times 10^{-4}$ cm/sec.	$\log V_t$	Surface dissolution Rate. $V_s \times 10^{-5}$ cm/sec.	$\log V_s$	$\frac{1}{T} \times 10^{-3}$	$\frac{V_t}{V_s}$
1	2	3	4	5	6	7	8
2.599	10	3.47	$\bar{4}.5400$	2.95	$\bar{5}.4699$	3.53	11.76
	15	4.23	$\bar{4}.6259$	3.46	$\bar{5}.5400$	3.47	12.22
	20	5.13	$\bar{4}.7101$	3.98	$\bar{5}.6000$	3.41	12.88
	25	6.46	$\bar{4}.8101$	4.67	$\bar{5}.6700$	3.35	13.83
	30	7.68	$\bar{4}.8850$	5.30	$\bar{5}.7243$	3.30	14.49
	35	9.55	$\bar{4}.9800$	6.31	$\bar{5}.7993$	3.24	15.13
	40	10.44	$\bar{3}.0187$	7.07	$\bar{5}.8500$	3.19	14.76
	45	13.34	$\bar{3}.1252$	8.31	$\bar{5}.9200$	3.14	16.05
	50	15.65	$\bar{3}.1945$	9.33	$\bar{5}.9700$	3.09	16.77
	60	20.89	$\bar{3}.3200$	-	-	3.00	-

TABLE 4.4 Contd...

1	2	3	4	5	6	7	8
5.198	10	4.24	$\bar{4}.6269$	2.88	$\bar{5}.4594$	3.53	14.72
	15	5.46	$\bar{4}.7370$	3.39	$\bar{5}.5302$	3.47	16.10
	20	6.71	$\bar{4}.7370$	4.58	$\bar{5}.6609$	3.41	14.65
	25	8.51	$\bar{4}.9300$	5.62	$\bar{5}.7497$	3.35	15.14
	30	9.84	$\bar{4}.9930$	6.92	$\bar{5}.8401$	3.30	14.21
	35	12.02	$\bar{3}.0799$	8.71	$\bar{5}.9400$	3.24	13.80
	40	14.03	$\bar{3}.1470$	9.77	$\bar{5}.9900$	3.19	14.36
	45	17.18	$\bar{3}.2350$	12.59	$\bar{4}.1000$	3.14	13.64
	50	19.95	$\bar{3}.3000$	15.49	$\bar{4}.1900$	3.09	12.87
	60	27.54	$\bar{3}.4400$	22.91	$\bar{4}.3600$	3.00	12.02

TABLE 4.4 Contd....

1	2	3	4	5	6	7	8
7.797	10	5.96	$\bar{4}.7750$	4.46	$\bar{5}.6493$	3.53	13.36
	15	7.44	$\bar{4}.8715$	5.49	$\bar{5}.7400$	3.47	13.55
	20	9.12	$\bar{4}.9600$	5.49	$\bar{5}.7400$	3.41	16.66
	25	11.22	$\bar{3}.0500$	8.71	$\bar{5}.9400$	3.35	12.88
	30	13.40	$\bar{3}.1271$	10.47	$\bar{4}.0200$	3.30	12.79
	35	16.60	$\bar{3}.2201$	13.18	$\bar{4}.1199$	3.24	12.59
	40	19.28	$\bar{3}.2851$	15.85	$\bar{4}.2001$	3.19	12.16
	45	23.60	$\bar{3}.3729$	19.50	$\bar{4}.2900$	3.14	12.10
	50	27.54	$\bar{3}.4399$	23.49	$\bar{4}.3699$	3.09	11.74
	60	38.02	$\bar{3}.5800$	31.62	$\bar{4}.5000$	3.00	12.02

TABLE 4.4 Contd...

1	2	3	4	5	6	7	8
	10	4.24	$\bar{4}.6269$	1.95	$\bar{5}.2900$	3.53	21.74
	15	5.46	$\bar{4}.7370$	2.69	$\bar{5}.4298$	3.47	20.29
	20	6.71	$\bar{4}.8270$	3.54	$\bar{5}.5490$	3.41	18.95
	25	8.51	$\bar{4}.9300$	4.67	$\bar{5}.6700$	3.35	18.22
10.396	30	9.84	$\bar{4}.9390$	5.88	$\bar{5}.7700$	3.30	16.73
	35	12.02	$\bar{3}.0799$	7.76	$\bar{5}.8900$	3.24	15.48
	40	14.03	$\bar{3}.1470$	9.77	$\bar{5}.9900$	3.19	14.36
	45	17.18	$\bar{3}.2350$	12.59	$\bar{4}.1000$	3.14	13.64
	50	19.95	$\bar{3}.3000$	15.49	$\bar{4}.1900$	3.09	12.84
	60	27.54	$\bar{3}.4400$	22.91	$\bar{4}.3600$	3.00	12.02

TABLE 4.4 Contd....

1	2	3	4	5	6	7	8
15.594	10	1.90	$\bar{4}.2795$	0.56	$\bar{6}.7499$	3.53	33.92
	15	2.50	$\bar{4}.3979$	0.77	$\bar{6}.8900$	3.47	32.46
	20	3.35	$\bar{4}.5250$	1.04	$\bar{5}.0200$	3.41	32.21
	25	4.30	$\bar{4}.6335$	1.46	$\bar{5}.1650$	3.35	29.45
	30	6.02	$\bar{4}.7800$	1.90	$\bar{5}.2799$	3.30	31.68
	35	7.54	$\bar{4}.8774$	2.66	$\bar{5}.4249$	3.24	28.34
	40	9.20	$\bar{4}.9638$	3.39	$\bar{5}.5302$	3.19	27.13
	45	11.89	$\bar{3}.0752$	4.46	$\bar{5}.6500$	3.14	26.65
	50	12.59	$\bar{3}.1000$	5.80	$\bar{5}.7634$	3.09	21.70
	60	-	-	8.50	$\bar{5}.9300$	3.00	-

TABLE 4.4 Contd...

1	2	3	4	5	6	7	8
20.792	10	0.63	$\bar{5}.8000$	0.316	$\bar{6}.5000$	3.53	19.93
	15	0.84	$\bar{5}.9255$	0.417	$\bar{6}.6200$	3.47	20.14
	20	1.20	$\bar{4}.0800$	0.575	$\bar{6}.7600$	3.41	20.86
	25	1.58	$\bar{4}.2000$	0.794	$\bar{6}.9100$	3.35	19.89
	30	1.95	$\bar{4}.2900$	1.000	$\bar{5}.0000$	3.30	19.50
	35	2.83	$\bar{4}.4520$	-	-	3.24	-
	40	3.55	$\bar{4}.5500$	2.09	$\bar{5}.3200$	3.19	16.98
	45	4.70	$\bar{4}.6721$	2.51	$\bar{5}.4000$	3.14	18.72
	50	5.70	$\bar{4}.7500$	2.75	$\bar{5}.4411$	3.09	20.72
	60	7.80	$\bar{4}.8900$	3.98	$\bar{5}.6000$	3.00	19.59

TABLE 4.4 Cont...

1	2	3	4	5	6	7	8
25.990	20	0.065	$\bar{6}.8101$	0.0437	$\bar{7}.6404$	3.41	14.87
	25	0.096	$\bar{6}.9800$	-	-	3.35	-
	30	0.129	$\bar{5}.1120$	0.079	$\bar{7}.8976$	3.30	16.32
	35	0.195	$\bar{5}.2913$	0.100	$\bar{6}.0000$	3.24	19.5
	40	0.257	$\bar{5}.4100$	0.169	$\bar{6}.2278$	3.19	15.20
	45	0.355	$\bar{5}.5501$	0.194	$\bar{6}.2900$	3.14	18.29
	50	0.529	$\bar{5}.7234$	0.263	$\bar{6}.4199$	3.09	20.11
	60	0.933	$\bar{5}.9701$	0.416	$\bar{6}.6200$	3.00	22.27

4.4 DISCUSSION :

4.4.1 Morphology of etch pits :

On going through the various shapes of etch pits produced by lactic and formic acids on calcite cleavage faces, it is clear that all the shapes are symmetrical about [110] direction which is usually passing through the centre of plane figure of a pit, projected on a cleavage surface. Further, for a given range of concentration all pits usually exhibit same geometrical outlines irrespective of their origin on the cleavage surface. All these observations regarding shapes of etch pits produced by different concentrations of lactic and formic acids at 35°C are summarized in Table 4.5.

It is worthwhile to discuss following characteristic features of etch pits revealed by both etchants.

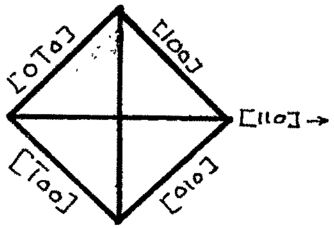
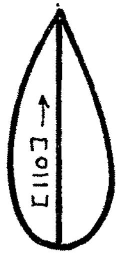
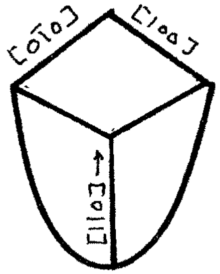
(a) Observation of fixed shape at certain concentration (range) of an etchant.

(b) Change of shape with change in concentration (range) of an etchant.

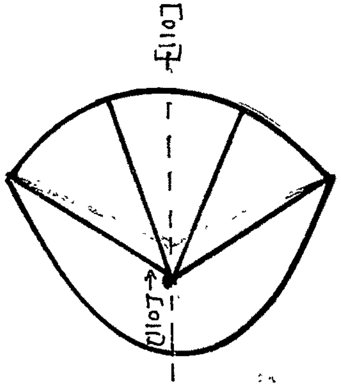
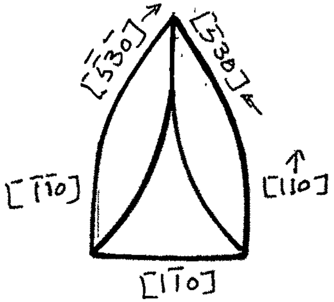
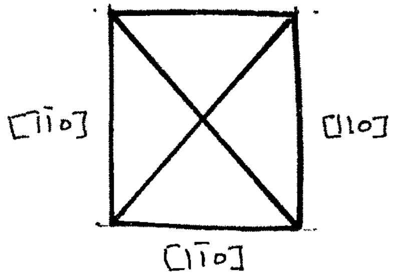
(a) Observation of fixed shape at certain concentration of an etchant :

Different shapes of etch pits are produced due to different chemical reaction rates along various directions

TABLE - 4.5

Sr.No.	Etchant	Conc, Range, N.	Shape	Quality of pit shape
1	Lactic acid	$<$ 0.1479 (<1% by vol.)		1. Well defined Rhombic 2. Finite eccentricity 3. Poor quality
2	Lactic acid	0.1479 - 5.1765 (10% - 35%)		1. Leaf-like 2. Good quality 3. High eccentricity
3	Lactic acid	7.395 - 12.5715 (50% - 85%)		1. Curvilinear elongated pentagon 2. Good quality 3. High eccentricity

cont..

4	Lactic acid	12.5715 - 14.79 (85% - 100%)		1. Curvilinear pentagon 2. Very good quality 3. High eccentricity
5	Formic acid	1.2599 - 15.494 (1% - 60%)		1. Elongated pentagon with slightly curvilinear lines 2. Good quality 3. Nearly zero eccentricity
6	Formic acid	15.494 - 25.99 (60% - 100%)		1. Rectangles with slightly curivilinear lines 2. Finite eccentricity 3. Good quality.

on a crystal surface ; several factors such as composition of etchant, concentration of etchant, etching period, condition of etching (static or dynamic), temperature of the etchant and a crystal, anisotropic character of a crystal surface, surface imperfections, imperfections terminating on a surface and strength of imperfections and their interactions may change the magnitude or direction or both of chemical rates on a crystal surface. In what follows the shape of an etch pit means the plane geometrical outlines of an etch pit on a crystal surface. The pyramidal or flat-bottomed nature of an etch pit is not taken into account. The observations presented above clearly indicate that a change in magnitude of reaction rates within a definite range of concentration does not change the shape of an etch pit, it simply accelarates or retards the growth of pits without introducing a change in shape.

(b) Change of shape with change in concentration (range) of an etchant :

From the whole spectrum of etch pit shapes, it is clear that the pits are usually bound by directions of low indices. Since the shapes of etch pits remain nearly same, when they are produced at line defects or at point defects, the normal rate of dissolution for these pits does not affect the shape noticeably. The factor governing the shape of etch pits is the tangential rate of dissolution, V_t, along different directions on the surface. From a study of changes of pit shapes with progressive change in the concentration of an etchant, it can be conjectured that there is a systematic change in the direction of reaction rates on the surface. This in turn suggests the creation of new directions of reaction rates and elimination or modification of old directions. This view is supported by the fact that when a pit shape changes from elongated pentagon to rectangle (fig. 4.13 and 4.14) motion of ledges along $[530]$ and $[\bar{5}\bar{3}0]$ reduces to zero. Similarly the dissolution along $[100]$ reduces when shape changes from rhombic to leaf-like shape (fig. 4.7). Again when concentration is further increased, the rate along $[0\bar{1}0]$ and $[100]$ becomes prominent and the pit-shape changes from leaf-like to pentagon with curvilinear sides (fig. 4.8 and 4.9). It should be noted that direction of reaction rates which are making equal angles with the line of symmetry $[110]$ are simultaneously eliminated or produced by a systematic change in concentration of an etchant. Due to production or anihilation of pairs of reaction rates along $[110]$, the point-bottomed or flat-bottomed pit with any geometrical outline on the surface remains symmetrical about the line of symmetry $[110]$.

For each etchant the following experiments were carried out :-

(i) Matching of identical areas on cleavage counterparts etched by the same etchant or different etchants for equal or unequal period of etching at constant temperature.

(ii) Successive etching of the same cleaved surface by the same etchant for different etching times.

(iii) Very thin cleavage flake etched by an etchant.

The observations on matching of etch pits produced by an etchant on oppositely matched cleavage counterparts had shown complete one-to-one correspondence so far as the location, number and orientations of etch pits were concerned. Further, when a cleavage surface was etched by an etchant (Say lactic acid) and its counterparts by another etchant, the matching of etch pits on identical areas of these counterparts was fairly good. Successive etching of the same cleaved surface by an etchant had produced the growth of etch pits at unchanged positions on the cleavage surface and that no new pits were formed. When thin flakes (thickness $\sim$ 0.01 mm) were etched, good correspondence of etch pits on the front and reverse faces was also noticed. All these experiments indicate that pits were produced at dislocations terminating on the surface of observation ; hence all etchants reveal dislocations. Whether they reveal all dislocations or not is not considered in the present report. It was reported earlier while considering the matching of etch pits on cleavage counterparts that flat-bottomed etch pits on one cleavage surface had correspondence with point bottomed etch pits on the counterpart. This suggests that a few of dislocations of insufficient strength etch out at a faster rate ; hence the flat-bottomed pits are produced at these places. ~~It should be remarked.~~ It should be remarked that these points were not studied in detail in the present work.

4.4.2 Requirements of a good etchant :

It is well known that the etchant should have following characteristics :-

(i) It should~~b~~ be of such a composition that it will give good all round results and reveal the greatest number and variety of structural defects, characteristics and irregulaties present. At the same time, it should be able to distinguish its effect from those produced by any of the etchants which can attack only definite types of defects. Thus this selective etching should enable one to a study only specific defects.

(ii) It should be simple in composition and stable so that its concentration will not change appreciably upon standing or during use at room temperature and also if possible at moderately higher or lower temperatures.

(iii) It should have constant characteristics at a particular temperature so that the conditions of etching can be easily reproduced. The important conditions of etching are as follows :-

(a) Temperature of etching : The rate at which the etchant attacks a specimen depends upon the temperature at which etching takes place. The precise influence of temperature, however, varies according to the composition (amount of impurity present and previous history of the specimen). It is, therefore, desirable for reproducible results to carry out etching experiments only at a definite temperature.

(b) Time of etching : The time of etching is perhaps one of the important factors contributing to successful etching and attendent appearance of the structure enabling their detailed study possible with the help of optical techniques. For example, if the time of etching is short as compared to that appropriate for a particular material, the etch structure will not be completely developed nor will there be sufficient details revealed to permit accurate interpretation of the etched area. However, too long time of etching is just as unsatisfactory as one too short, owing to details of surface structure being thereby obscured to varying degrees and frequently some parts of the structure being completely obliterated. The time of etching depends upon the conditions of the surface (freshly cleaved surface, heat treated surface etc.) and the temperature and nature of etchant.

(iv) While etching a specimen etchant should not form products which will precipitate on the surface of the specimen considered, but must have such a composition that reaction products are immediately dissolved chemically or physically in the solution. They must possess closer affinity with the etchant than with the specimen.

(v) It should be non-injurious and non-toxic to the person conducting work.

(vi) For orientation determination, the etchant should develop etch pits or facets with plane faces accurately parallel to the crystallographic planes of low indices.

The above presents, in general, the requirements for the development of a good etchant. In view of these requirements and the discussion of following points, the characteristics of the etchants used in the present investigation will now be considered.

(i) Matching of etch patterns on oppositely matched cleavage faces of calcite.

(ii) Internal structure of etch pits on matched faces.

(iii) Quality of etch pits.

(iv) Change of shape due to change from one concentration range to another.

In addition to these there are also few noticeable features of each dislocation etchant, which will now be considered.

4.4.2 (a) Characteristics of lactic acid as the etchant :

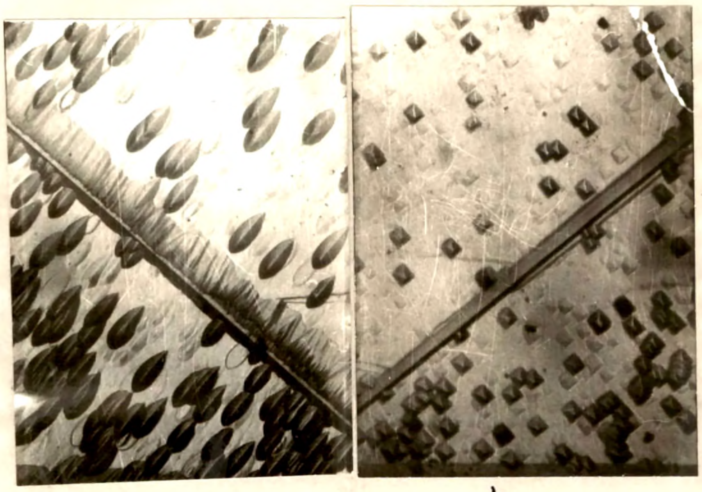
As far as the location of etch pits is concerned, there is perfect matching. However, the internal structure of pits on either cleavage parts are not fully reflected. Since temperature of etching is kept constant, the concentration of the etchant is going to be deciding factor in resolving this anomaly of mismatching of internal structures of etch pits on the matched cleavage faces. Further, the shape of an etch pit is not changed by the etching time (fig. 4.1, 4.2 and 4.3). The quality of etch pits improves with the increase in the concentration of lactic acid. Further, the number of dislocations revealed by lactic acid is independent of concentration of lactic acid.

4.4.2 (b) Characteristics of formic acid as the etchant :

The matching of etch pits on cleavage counterparts is perfect as far as location of etch pits is concerened. The number of dislocations revealed by formic acid is also independent of concentration of formic acid. The etch pit shape is also independent of etching time (fig. 4.4, 4.5 and 4.6). Further, it is interesting to note that for concentrations less than 15.494 N (60% by vol.) there is a good matching of internal structures of etch pits (fig. 4.10 and 4.11). As the concentration increases, the mismatching of internal structures of etch pits also increases (fig. 4.12, 4.13 and 4.14).

4.4.2 (c) Matching of cleavage counterparts etched in lactic and formic acids :

Fig. 4.23a represents photomicrograph of calcite cleavage face etched in 1.479N (10% by vol.) lactic acid



a b

x 126

Fig. 4.23 a and b show the photomicrographs of calcite cleavage counterparts etched 1.479N (10% by vol.) lactic acid and 25.99N (100% by vol.) formic acid at 30^{o}C for 5 and 150 seconds respectively.

at $30^{\circ}C$ for 5 seconds and fig. 4.23b represents photomicrograph of its counterpart etched in 25.99 N (100% by vol.) formic acid at $30^{\circ}C$ for 150 seconds. It is clear that the matching is perfect. Thus lactic and formic acids reveal equal number of dislocations irrespective of the concentration of the etchant.

4.4.2 (d) Quality of etch pits :

The quality of etch pit includes consideration of the shape, size, symmetrical nature and contrast of the pits with respect to the surface (depth etc.). For a given etchant (lactic or formic acid) etch pits produced on a cleavage surface are almost of equal sizes.

The conditions for the formation of visible etch pits on a crystal surface subjected to etching are (i) $V_n / V_t > 0.1$ (ii) $V_n / V_s > 1$ (Robinson, 1968). Later, Shah (1976) reported that for the formation of visible etch pits, in addition to the above conditions, the ratio of tangential rate of dissolution, V_t, to that of surface dissolution, V_s, i.e. V_t / V_s should be greater than 10 and higher the ratio V_t / V_s better is the quality of etch pits. A critical study of tables 4.3 and 4.4 show that the ratio V_t / V_s is greater than 10. Further, the quality of pits improves with the increase in the concentration of lactic acid (fig. 4.7b, 4.9b) ; however, the ratio V_t / V_s decreases with the concentration. In case of formic acid, this ratio does not change noticeably. Thus, the ratio V_t / V_s alone can not account for the quality of etch pits. It is therefore obvious that the combination of V_t, V_s and V_n is likely to enhance the understanding of the quality of etch pits.

4.4.3 Nature of etch rate versus concentration plots :

The nature of V - C plots is illustrated in fig. 4.19, 4.20, 4.21 and 4.22. The rate of chemical reaction, after an initial increase, decreases considerably with an increase in the etchant concentration. Sangwal and Arora (1978) reported the occurrence of such peaks in their studies on dissolution of MgO in HCl, HNO_3 and H_2SO_4 solutions. The nature of V - C curves was explained on the basis of adsorption phenomena. The equation of the rate (Sangwal and Arora 1978, Sangwal et al 1979, Gerasimov et al, 1974) is given by

$$V = \frac{K\,C_a}{1 + K_a\,C_a} \qquad \ldots\ldots (4.1)$$

for moderate adsorption of the reactant and weak adsorption of reaction product where K, K_a are constants and C_a is the acid concentration. It was claimed that equation 4.1 explains the nature of V - C plots. If eqn. 4.1 explains the nature of V - C plots, then, mathematically the condition for obtaining an extremum viz.

$$\left(\frac{dv}{dC_a}\right)_{C_a=0} = 0$$

must be satisfied. Now differentiating equation 4.1 with respect to C_a, we get,

$$\frac{dv}{dC_a} = \frac{(1 + K_aC_a)K - KC_aK_a}{(1 + K_aC_a)^2}$$

$$= \frac{K\ (1 + K_aC_a - K_aC_a)}{(1 + K_aC_a)^2}$$

or $$\frac{dv}{dC_a} = \frac{K}{(1 + K_aC_a)^2} \qquad \ldots\ldots (4.2)$$

Now,

$$\left(\frac{dv}{dC_a}\right)_{C_a = 0} = \frac{K}{(1 + K_aC_a)^2} \qquad \ldots\ldots (4.3)$$

or $K = 0$

This is not possible in view of the finite value of V (Equation 4.1). Thus equation 4.1 is incapable of explaining the nature of V - C plots.

Let us now analyse the factors reponsible for observed decrease in the rate of reaction after an initial increase in its value. The rate of chemical reaction can decrease due to following :

(a) decrease in the availability of ions,

(b) decrease in the ionic mobility,

(c) increase in the viscosity of the etchant with increasing concentration,

(d) Inhibition by reaction products.

The factors mentioned above will now be discussed in detail.

(a) Availability of ions :

Generally, the concentration of ions in the solution increases with the increase in the concentration of acid. To confirm this fact, P_H of the etching solutions for various concentration was measured at room temperature (30°C) and the values are listed in table 4.6. A glance at this table shows that P_H of lactic as well as formic acid decreases with the increase in the concentration of acids. P_H is given by,

$$P_H = - \log [H^+] \qquad \ldots\ldots. \ (4.4)$$

Therefore, the concentration of acidic ions increases with the increase in the acid concentration. Thus, the initial increase in the rate of chemical reaction may be understood

TABLE - 4.6

Lactic Acid			Formic Acid		
Conc, N	Conc, % by vol.	P_H	Conc, N	Conc, % by vol.	P_H
0.1479	1	2.30	2.599	10	2.75
0.7395	5	2.20	5.198	20	2.40
1.4790	10	2.10	7.797	30	2.09
2.9580	20	1.88	10.396	40	1.65
5.1765	35	1.55	15.494	60	1.00
7.3950	50	1.20	20.692	80	-
10.3530	70	0.85	25.990	100	-
12.5715	85	0.50			
14.7900	100	0.05			

in terms of increase in the concentration of ions. However, if the rate of chemical reaction depends only on the concentration of ions, it should increase continuously with the concentration of etchant. The observed decrease in the rate after certain concentration cannot be explained on basis of density of ions since the concentration of ions increases with the increasing concentration of etchants.

(b) Ionic mobility :

The dissolution of a crystal in etchant depends upon the availability and mobility of ions. It is well known that electrical conductivity of the solution also depends upon availability and mobility of ions. It is therefore necessary to analyze the dependence of ionic mobility on concentration of the etchant by measuring electrical conductivity of etching solutions of different concentrations at different temperatures ranging from room temperature to 80°C. The electrical conductivity, σ_c, of lactic and formic acids of various concentrations at different temperatures is shown in tables 4.7 and 4.8 respectively.

The dependence of electrical conductivity on concentrations of lactic and formic acids is illustrated by graphs 4.24 and 4.25 which indicate that electrical conductivity of lactic and formic acids initially increases

TABLE 4.7 (LACTIC ACID)

Temp.	0.1479 N		0.7395 N		1.479 N	
^{o}C	$\sigma_c \times 10^{-3}$	$\log \sigma_c$	$\sigma_c \times 10^{-3}$	$\log \sigma_c$	$\sigma_c \times 10^{-3}$	$\log \sigma_c$
32	4.700	$\bar{3}.6720$	8.545	$\bar{3}.9317$	10.444	$\bar{2}.0188$
40	4.860	$\bar{3}.6866$	9.096	$\bar{3}.9588$	10.846	$\bar{2}.0352$
45	5.030	$\bar{3}.7015$	9.400	$\bar{3}.9731$	11.280	$\bar{2}.0523$
50	5.220	$\bar{3}.7176$	9.724	$\bar{3}.9878$	11.280	$\bar{2}.0523$
55	5.420	$\bar{3}.7339$	9.929	$\bar{3}.9969$	11.750	$\bar{2}.0700$
60	5.640	$\bar{3}.7512$	10.217	$\bar{2}.0093$	11.750	$\bar{2}.0700$
65	5.760	$\bar{3}.7604$	10.217	$\bar{2}.0093$	12.260	$\bar{2}.0885$
70	5.870	$\bar{3}.7686$	10.444	$\bar{2}.0188$	12.589	$\bar{2}.1000$
75	6.000	$\bar{3}.7781$	10.444	$\bar{2}.0188$	12.818	$\bar{2}.0178$
80	6.130	$\bar{3}.7874$	10.444	$\bar{2}.0188$	12.818	$\bar{2}.1078$

TABLE 4.7 contd....

Temp.	2.9580 N		5.1765 N		7.3950 N	
	σ_c x 10^{-3}	log σ_c	σ_c x 10^{-3}	log σ_c	σ_c x 10^{-3}	log σ_c
32	10.444	$\bar{2}.0188$	8.812	$\bar{3}.9450$	5.875	$\bar{3}.7690$
40	10.846	$\bar{2}.0352$	-	-	6.266	$\bar{3}.7970$
45	11.280	$\bar{2}.0523$	9.400	$\bar{3}.9731$	6.558	$\bar{3}.8167$
50	12.051	$\bar{2}.0810$	9.724	$\bar{3}.9878$	7.050	$\bar{3}.8481$
55	12.589	$\bar{2}.1000$	10.071	$\bar{2}.0030$	7.421	$\bar{3}.8704$
60	12.818	$\bar{2}.1078$	10.444	$\bar{2}.0188$	7.833	$\bar{3}.8939$
65	13.055	$\bar{2}.1157$	10.846	$\bar{2}.0352$	8.057	$\bar{3}.9061$
70	13.055	$\bar{2}.1157$	10.846	$\bar{2}.0352$	8.294	$\bar{3}.9187$
75	13.055	$\bar{2}.1157$	10.846	$\bar{2}.0352$	8.545	$\bar{3}.9317$
80	13.055	$\bar{2}.1157$	10.846	$\bar{2}.0352$	8.545	$\bar{3}.9317$

TABLE 4.7 contd...

Temp. °C	10.353 N		12.5715 N		14.79 N	
	$\sigma_c \times 10^{-3}$	$\log \sigma_c$	$\sigma_c \times 10^{-3}$	$\log \sigma_c$	$\sigma_c \times 10^{-3}$	$\log \sigma_c$
32	2.238	$\bar{3}.3498$	0.829	$\bar{4}.9188$	0.142	$\bar{4}.1523$
40	2.473	$\bar{3}.3933$	0.940	$\bar{4}.9732$	0.156	$\bar{4}.1932$
45	2.660	$\bar{3}.4249$	1.007	$\bar{3}.0030$	0.174	$\bar{4}.2406$
50	2.877	$\bar{3}.4590$	1.084	$\bar{3}.0352$	0.198	$\bar{4}.2967$
55	3.098	$\bar{3}.4912$	1.175	$\bar{3}.0700$	0.227	$\bar{4}.3561$
60	3.279	$\bar{3}.5157$	1.281	$\bar{3}.1075$	0.256	$\bar{4}.4083$
65	3.397	$\bar{3}.5311$	1.410	$\bar{3}.1492$	0.284	$\bar{4}.4534$
70	3.481	$\bar{3}.5417$	1.484	$\bar{3}.1714$	0.313	$\bar{4}.4956$
75	3.569	$\bar{3}.5526$	1.566	$\bar{3}.1949$	0.335	$\bar{4}.5251$
80	3.569	$\bar{3}.5526$	1.659	$\bar{3}.2198$	0.361	$\bar{4}.5582$

TABLE 4.8 (FORMIC ACID)

Temp. °C	1.299 N (1%)		2.599 N (10%)		5.198 N (20%)	
	$\sigma_c \times 10^{-3}$	$\log \sigma_c$	$\sigma_c \times 10^{-3}$	$\log \sigma_c$	$\sigma_c \times 10^{-3}$	$\log \sigma_c$
32	11.90	$\bar{2}.0755$	14.84	$\bar{2}.1715$	19.32	$\bar{2}.2860$
40	13.05	$\bar{2}.1155$	15.48	$\bar{2}.1900$	20.14	$\bar{2}.3040$
45	13.55	$\bar{2}.1319$	16.59	$\bar{2}.2198$	20.43	$\bar{2}.3102$
50	14.10	$\bar{2}.1492$	17.19	$\bar{2}.2352$	21.36	$\bar{2}.3296$
55	-	-	17.85	$\bar{2}.2516$	22.03	$\bar{2}.3430$
60	14.84	$\bar{2}.1715$	17.84	$\bar{2}.2519$	23.50	$\bar{2}.3711$
65	15.32	$\bar{2}.1853$	19.32	$\bar{2}.2860$	23.89	$\bar{2}.3282$
70	15.66	$\bar{2}.1948$	19.32	$\bar{2}.2860$	23.89	$\bar{2}.3282$
75	16.02	$\bar{2}.2045$	20.43	$\bar{2}.3102$	23.89	$\bar{2}.3782$
80	16.20	$\bar{2}.2095$	21.04	$\bar{2}.3230$	23.89	$\bar{2}.3782$

TABLE 4.8 Contd...

Temp. °C	7.797 N (30%)		10.396 N (40%)		15.499 N (60%)	
	$\sigma_c \times 10^{-3}$	log σ_c	$\sigma_c \times 10^{-3}$	log σ_c	$\sigma_c \times 10^{-3}$	log σ_c
32	20.00	$\bar{2}.3010$	18.31	$\bar{2}.2627$	11.75	$\bar{2}.0701$
40	20.00	$\bar{2}.3010$	19.18	$\bar{2}.2828$	12.70	$\bar{2}.1038$
45	20.43	$\bar{2}.3101$	19.86	$\bar{2}.2980$	13.06	$\bar{2}.1159$
50	21.14	$\bar{2}.3251$	20.29	$\bar{2}.3073$	13.56	$\bar{2}.1323$
55	22.43	$\bar{2}.3508$	21.04	$\bar{2}.3230$	13.96	$\bar{2}.1449$
60	23.50	$\bar{2}.3710$	21.36	$\bar{2}.3296$	14.39	$\bar{2}.1580$
65	23.89	$\bar{2}.3782$	21.86	$\bar{2}.3397$	14.85	$\bar{2}.1730$
70	24.00	$\bar{2}.3802$	21.86	$\bar{2}.3397$	14.84	$\bar{2}.1730$
75	24.00	$\bar{2}.3802$	22.03	$\bar{2}.3430$	14.84	$\bar{2}.1730$
80	24.00	$\bar{2}.3802$	22.03	$\bar{2}.3430$	14.84	$\bar{2}.1730$

TABLE 4.8 contd....

Temp.	20.692N (80%)		25.99 N (100%)	
$^{\circ}C$	$\sigma_c \times 10^{-3}$	$\log \sigma_c$	$\sigma_c \times 10^{-3}$	$\log \sigma_c$
32	6.75	$\bar{3}.8293$	0.618	$\bar{4}.7910$
40	6.88	$\bar{3}.8376$	0.671	$\bar{4}.8267$
45	7.05	$\bar{3}.8482$	0.705	$\bar{4}.8482$
50	7.23	$\bar{3}.8591$	0.742	$\bar{4}.8704$
55	7.50	$\bar{3}.8751$	0.775	$\bar{4}.8893$
60	7.50	$\bar{3}.8751$	0.806	$\bar{4}.9063$
65	7.83	$\bar{3}.8938$	0.829	$\bar{4}.9186$
70	8.06	$\bar{3}.9063$	0.870	$\bar{4}.9395$
75	8.20	$\bar{3}.9138$	0.887	$\bar{4}.9479$
80	8.29	$\bar{3}.9186$	0.910	$\bar{4}.9590$

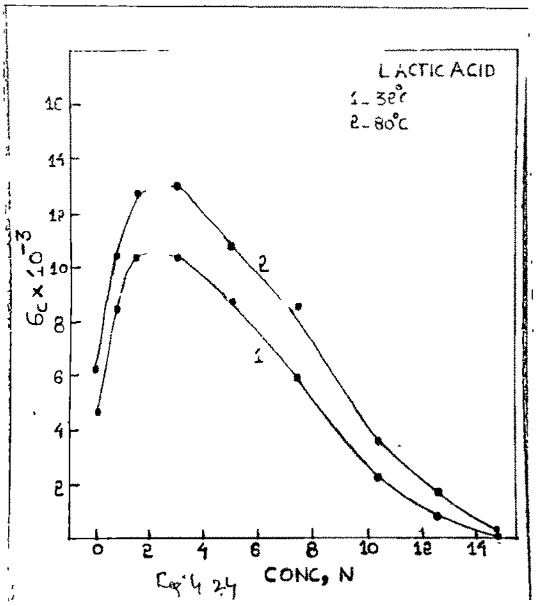


Fig. 4.24 Plot of electrical conductivity, σ_c, versus concentration of lactic acid at room temperature and 80°C.

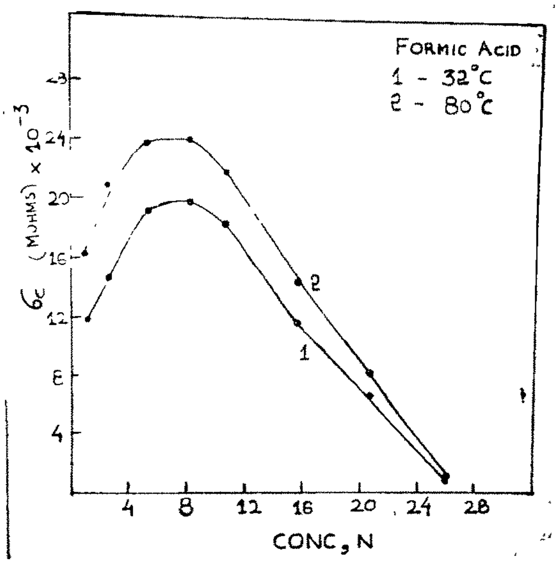


Fig. 4.25 Plot of electrical conductivity, σ_c, versus concentration of formic acid at room temperature and 80°C.

with the concentration, attains a maximum value at a particular concentration , and decreases thereafter. The nature of graph of electrical conductivity versus etchant concentration is similar to that of etch rate versus etchant concentration (fig. 4.19, 4.20, 4.21 and 4.22). It is interesting to note that the maximum in conductivity plots (fig. 4.24 and 4.25) is obtained exactly at the same cencentrations of lactic and formic acids viz. 1.479 N (10% by vol.) and 7.797 N (30% by vol.) respectively. Further, the maximum in conductivity plots for lactic acid has shifted to 2.958 N (20% by vol.) at 80°C. Similar shift was observed in V-C plots of lactic acid. (fig. 4.19, 4.20).

Thus it can be concluded that the maximum observed in V-C plots is the property of the etchant and not of the crystal surface as it has been reported by earlier workers (Sangwal et al 1978). The rate of a chemical reaction decreases with the decrease in the ionic mobility. This can be verified by determining the order of a chemical reaction in the present work.

The order of a chemical reaction, n, is given by

$$V = K\,C^{n} \qquad \ldots\ldots\ldots \qquad (4.5)$$

Where K is a constant and C is the concentration of the etchant. Taking logarithms on both sides of equation 4.5, we get,

$$\log V = \log K + n \log C \qquad \ldots\ldots. (4.6)$$

Thus, the slope of log V versus log C plots gives the order of a reaction. Graphs of log V versus log C for tangential and surface dissolution for concentrations greater than 1.479 N (10% by vol.) lactic acid are shown in fig. 4.26 and 4.27. Similar graphs for concentration of formic acid greater than 7.797 N (30% by vol.) are shown in fig. 4.28 and 4.29. The slopes of these graphs give the order of tangential reaction, n_t, and that of surface dissolution, n_s. The values of n_t and n_s in different concentration regions of lactic and formic acids are shown in tables 4.9 and 4.10 respectively.

Further, similar plots for electrical conductivity, σ_c, viz. $\log \sigma_c$ versus log C for lactic and formic acids are shown in fig. 4.30 and 4.31 respectively.

The values of slopes of these graphs, n_c, are also listed in tables 4.9 and 4.10.

The values of n_t, n_s and n_c are almost comparable for higher concentrations of lactic acid. This is also true for higher concentrations of formic acid. The study of tables 4.9 and 4.10 shows that the rate of chemical reaction decreases with the increase in the concentration of acids due to decrease in the ionic mobility of lactic and formic acids.

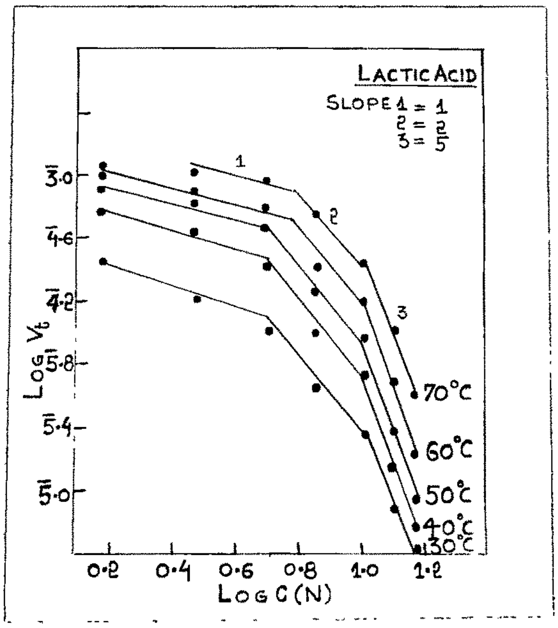


Fig. 4.26 Plot of log V_t versus log C for lactic acid

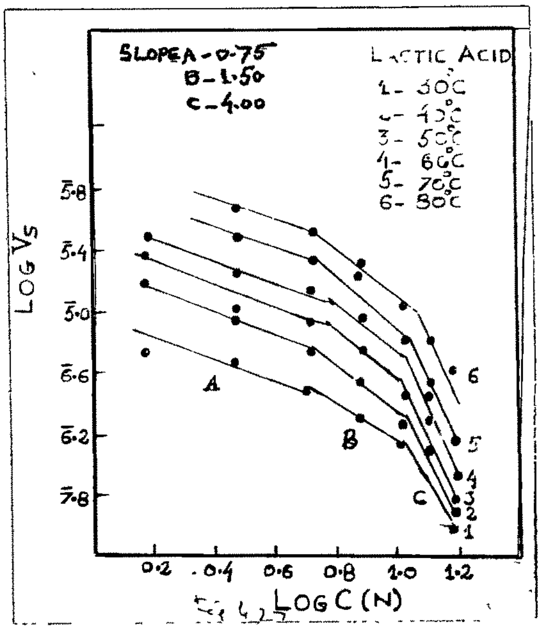
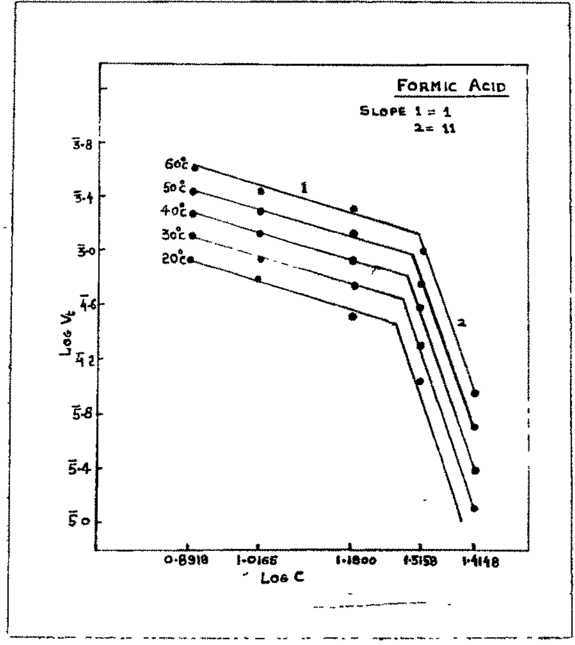


Fig. 4.27 Plot of log V_s versus log C for lactic acid.



4.28

Fig. 4.28 Plot of log V_t versus log C for formic acid.

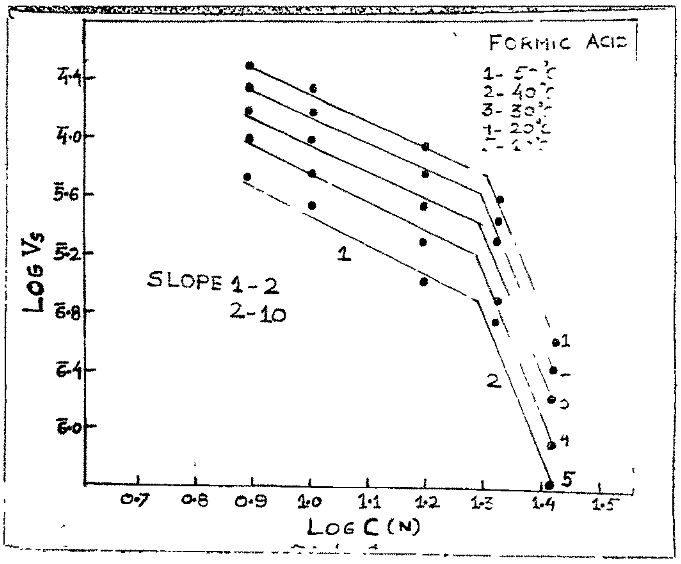


Fig. 4.29 Plot of log V_s versus log C for formic acid.

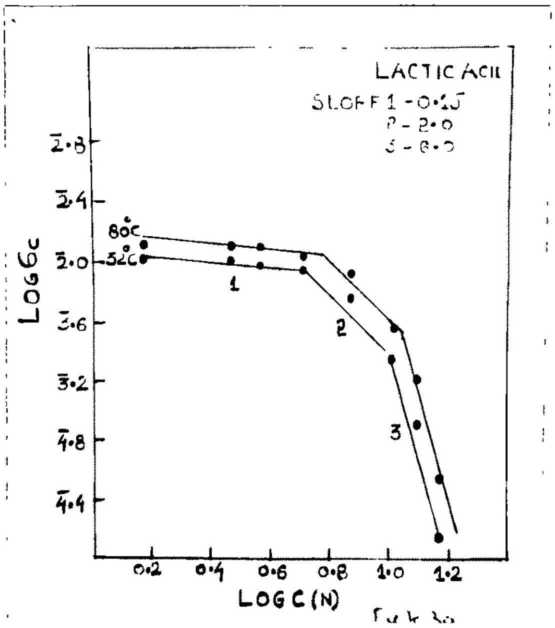


Fig. 4.30 Plot of log σ_c vs log C for lactic acid.

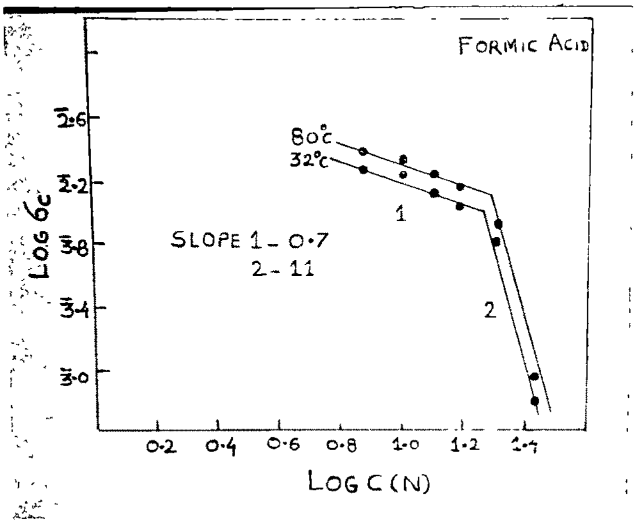


Fig. 4.31 Plot of log σ_c versus log C for formic acid.

TABLE - 4.9 (Lactic acid)

Conc, Range N	η_t	η_s	η_c	η_δ	$\frac{\eta_t}{\eta_s}$
1.479 - 5.1765	0.60	0.75	0.15	0.40	0.80
5.1765 - 10.353	2.00	1.50	2.00	2.30	1.33
10.353 - 14.79	5.00	4.00	6.00	5.20	1.25

TABLE - 4.10 (Formic acid)

Conc, Range N	η_t	η_s	η_c	η_δ	$\frac{\eta_t}{\eta_s}$
Less than 5	-	-	-	.90	-
7.797 - 15	1	2	0.70	0.22	0.5
15 - 25	11	10	11	0.92	1.1

(c) Analysis of viscosity effects :

Table 4.11 shows the viscosity of DL-Lactic acid at 25°C. (Kirk and oth~~er~~mer, 1967)

TABLE - 4.11

Conc., % by vol.	Viscosity (σ)	Conc, C N	log C	log σ
9.16	1.15	1.35	0.1303	0.0607
24.35	1.67	3.60	0.5563	0.2227
45.48	3.09	6.72	0.8273	0.4900
64.33	13.03	11.14	1.0468	1.1149
85-32	28.50	12.62	1.1010	1.4548

Graphs of log σ versus log C are shown in fig. 4.32 and the slope of this graph in a particular range of concentration of lactic acid gives the value n_σ . The values of n_σ are listed in table 4.9. A glance at this table shows that the values of n_t, n_s, n_c and n_σ are comparable. Thus, the reason for decrease in the ionic mobility with the increase in the concentration of lactic acid may be increasing viscosity of lactic acid with acid concentration.

Table 4.12 shows the relative viscosity of formic acid ($\frac{\eta}{\eta_0} \simeq \sigma$) at 20°C where η = absolute viscosity, η_0 = absolute viscosity of water at 20°C (= 1.002 Cp)

TABLE 4.12

Relative viscosity of formic acid at 20°C.

Acid Conc. % by Wt.	n/no	Acid Conc. (N)	log C(N)	log n/no
1.00	1.009	0.2130	$\bar{1}.3284$	0.0037
3.00	1.023	0.6430	$\bar{1}.8082$	0.0098
5.00	1.037	1.0755	0.0135	0.0157
10.00	1.068	2.1708	0.3365	0.0286
14.00	1.092	3.0616	0.4858	0.0382
18.00	1.117	3.9656	0.5982	0.0479
24.00	1.154	5.3470	0.7281	0.0622
32.00	1.201	7.2381	0.8596	0.0795
36.00	1.225	8.205	0.9141	0.0881
40.00	1.251	9.1877	0.9631	0.0972
44.00	1.278	10.1853	1.0076	0.1064
48.00	1.306	11.1986	1.0486	0.1158
52.00	1.337	12.2280	1.0874	0.1262
56.00	1.371	13.2739	1.1229	0.1370
60.00	1.4071	14.3366	1.1562	0.1482
70.00	1.508	17.0697	1.2319	0.1783
100.00	1.800	25.9900	1.4148	0.2253

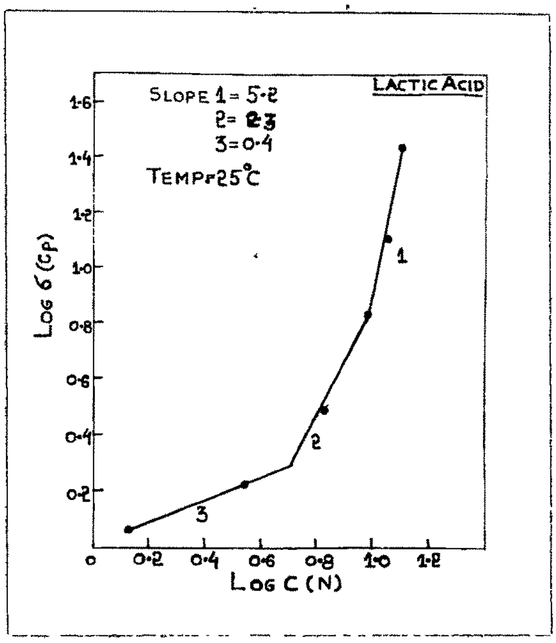


Fig. 4.32 Plot of log σ versus log C for lactic acid.

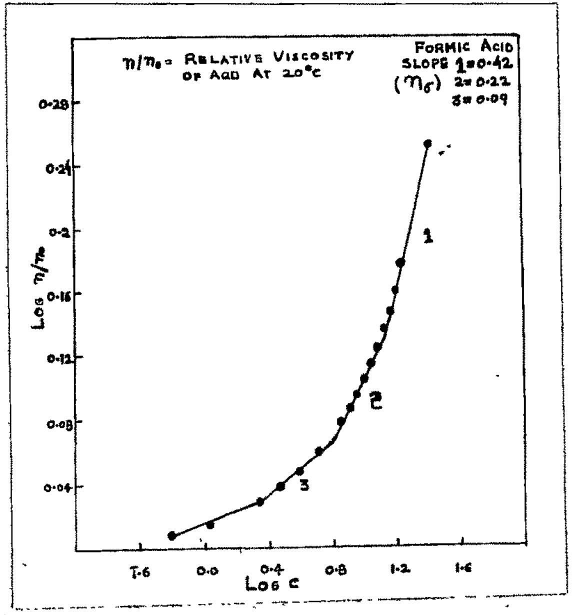


Fig. 4.33 Plot of log σ versus log C for formic acid.

(CRC handbook, 1976). The values of η_δ for different concentration regions of formic acid are listed in table 4.10 (fig. 4.33). Unlike comparable values of n_t, n_s and n_δ for lactic acid, the values of n_t, n_s, for formic aicd are higher than those of n_δ . This indicates that viscosity of formic acid does not affect the etch rates significantly, where as the decrease in ionic mobility of lactic acid is likely to be due to its increase in the viscosity. However decrease in the ionic mobility with increasing concentration of formic acid cannot be understood by considering viscosity data. It is therefore reasonable to conclude that viscosity of etchant is not the only factor which governs ionic mobility and rate of reaction but there are some other unknown factors, likely to be of chemical nature, associated with it.

(d) Inhibition by reaction products :

The dependence of reaction on time for weak and strong adsorption of reaction products (Laidler, 1950) is given by

$$D = K_1 t \qquad \text{.........} \; (4.9)$$

$$D^2 = K_2 t \qquad \text{.........} \; (4.10)$$

If the adsorption of reaction product is weak, the plot of reaction versus time, according to equation 4.9, should be a straight line and the rate of reaction should be independent of time. The plots of length of an etch pit along [110] and weight less per cm^2 versus time (fig. 4.15, 4.16, 4.17 and 4.18) are straight lines. Hence the adsorption of reaction product is weak in dissolution of calcite in lactic and formic acids. If the adsorption of reaction product is strong, the plot of reaction versus etching time should be a parabola. Since the adsorption of reaction product is weak, the rate of chemical reaction is not inhibited by reaction products.

4.5 CONCLUSIONS :

(1) Shape of an etch pit depends upon the concentration (range) of an etchant.

(2) Both lactic and formic acids are dislocation etchants and reveal equal number of dislocations terminating on the cleavage face of calcite irrespective of the concentration of the acid.

(3) Etch rate is independent of etching time.

(4) Graph of etch rate versus etchant concentration is quite complex, showing a maximum at a particular acid concentration.

(5) Appearance of maximum in V-C plots is the property of an etchant and not of a crystal surface.

(6) Rate of chemical reaction depends jointly on availability of ions, ionic mobility and viscosity of the etchant.

(7) Order of the reaction is independent of the temperature of etching.

(8) Chemical reaction of organic acids on a calcite cleavage surface provides poor adsorption of reaction products.