CHAPTER 3

KINETICS OF ION EXCHANGE

IN

AQUEOUS ACETONE-SUCCINIC ACID MEDIUM

INTRODUCTION

The speed of ion-exchange is an important practical consideration. Many ionic reactions in solution are very rapid, and are limited by the speed with which the reacting ions can approach each other. Ion-exchange reactions are generally much slower-some are very slow indeed because they are heterogeneous reactions involving diffusion processes which are slower than those occuring in solution.

The overall mechanism of the exchange reaction.

$$RA + B^{+} \rightleftharpoons RB + A^{+}$$

can be studied in the following stages :

1. Diffusion of B^{+} from the bulk of the solution to the surface of the exchanger, replacing ions which have diffused from the surface layer of solution into the solid.
2. Diffusion of B^{+} within the solid to sites where A^{+} is located. Exchange of A^{+} and B^{+} at these sites.
3. Diffusion of A^{+} through the solid to the surface.
4. Diffusion of A^{+} through the surface layer of solution into the bulk solution.

In all but a few special cases third step is very fast, and rates of exchange can usually be interpreted as two types of ionic diffusion process, that in the solid and that in a surface layer of solution surrounding the particle, where the ionic concentration differs from that in the bulk solution. The presence of this surface layer or film can not be demonstrated directly, but its thickness can be estimated to be of the order of 10^{-6} to 10^{-7} m, its presence arises from the fact that it is impossible to achieve complete mixing of the solution, however, efficiently stirred, although the thickness can be reduced by improved stirring. The ionic diffusion coefficients involved are the net coefficients for the two exchanging ions, since it is difficult to separate the contributions of the individual species.

The kinetic equations involving two types of diffusion processes are extremely complex, but it is possible to select conditions where either solid diffusion or liquid film diffusion becomes the controlling factor. The factors which favour solid diffusions as the controlling process are those which minimize surface effects, either by reducing the thickness of the film, swamping the exchanger with ions, or reducing the importance of surface relative to volume. These can be listed as (a) large particle size of exchanger, (b) efficient stirring, (c) concentrated solutions, (d) large ions and (e) a high degree of crosslinking. Conditions which make film diffusion the controlling factor include (a) small exchange particles, (b) in-efficient stirring, (c) dilute solutions, (d) small ions and (e) a low degree of cross-linking.

When the process of solid diffusion is rate determining the diffusion coefficients of ions in the exchanger are lower than diffusion coefficients of the same ions in solutions. The activation energy for diffusion is about the same in a strongly acid cation exchange resin as in aqueous solution. This suggests that the processes are similar, but that the absolute rate in the exchange is reduced compared to that in aqueous solution because of steric factors. The kinetics[1] of the ion exchange process are abviously important in the efficient operation of columns for separation processes where one aims to approach as near as possible to equilibrium at each contacting of the solution with the exchanger particle. The equilibrium is attained by (1) Variation in solution concentration in the spaces between the particles, (2) Variation within the exchange particles, (3) Irregular flow of solution down the column which tends to spread out the bands and decrease separation factors by causing them to overlap. The highest possible efficiency can be achieved by (1) Use of resins of small particle size, (2) Use of a low rate of flow, (3) Use of elevated temperature to increase diffusion rates, (4) Great care in packing columns.

Non-electrolyte sorption can be accurately described in terms of a constant diffusion coefficient. The kinetics thus essentially obeys the same simple rate laws as isotopic exchange. Electrolyte sorption involves coupled diffusion of the counter ion and the co-ion; electroneutrality requires that the fluxes of these species be equal. The co-ion, because of the Donnan effect, is in the minority and hence determines the rate. The same simple rate laws as in isotopic exchange apply, provided that the Donnan exclusion is strong.

The rate of laws of ion exchange and sorption involve the "effective" diffusion coefficients of the mobile species in the ion exchanger.

EARLIEAR WORK

Kinetics of exchange reactions in water as a solvent has been studied by many workers[2]. Bodamer and Kunin[3] studied the behaviour of ion-exchange in solvents other than water. Shukla and Bhatnagar[4] studied the kinetics of the exchange reaction of copper ion in non-aqueous solvents. The exchange reactions of copper ion in ethyl alcohol and acetone at 30.5° and 40.1° in Amberlite IRC-50 and IR-120 as cation exchange resins were carried out. The rate constants k were calculated for all systems and it was reported that the reaction did not obey first or second order.

The kinetics of exchange of Ca^{2+}/H^{+} was reported[5] in absolute and aqueous ethanol. Kinetics of exchange of Li^{+}/H^{+} has been studied in absolute and aqueous ethanol solution. The formal overall reversible second order rate constant was reported[6]. The rates in general are slower in perfectly non-aqueous systems and slightly faster in such systems containing air dried or dehydrated resin. Then the process is considered as an adsorption phenomenon; the rate increases with water content of the mixed solvent systems. The exchange under investigation has been studied as a diffusion phenomenon. This is because of the fact that empirical rate laws have their own limitations. The rate determining step is found to be governed equally by particle and film diffusion steps.

PRESENT WORK

Kinetics of exchange reactions Cu^{2+}/H^{+}, Co^{2+}/H^{+},

Ca^{2+}/H^+, Th^{4+}/H^+, Cd^{2+}/H^+, Mn^{2+}/H^+, Pb^{2+}/H^+, Mg^{2+}/H^+ and Zn^{2+}/H^+ in water-acetone and water acetone-succinic acid media have been studied. The rate constants k were calculated for these systems at various concentrations of acetone (0, 20, 30 and 50%) and at 0.05 M molarity of metal ions. The experimental results have been utilized to know the probable time required for attaining equilibrium and to explore the mechanism of ion-exchange process.

EXPERIMENTAL

Solutions

(1) Chlorides of Cu, Cd, Ni, Mg, Ca, Co, Zn, Al, Mn, and nitrates of Pb, Th (IV), Hg - 0.05M.

(2) Acetone % - 0, 20, 30, 50.

(3) Succinic acid - 0.5 M.

PROCEDURE

2 g of air dried Dowex 50W-X8 in H^+ form was taken in a 250 ml iodine flask. 100 ml of a mixture containing acetone-water-succinic acid was added. 8 ml of the metal ion solution was poured, the solution was stirred. The change in metal ion concentration was noted at different time intervals titrimetrically.

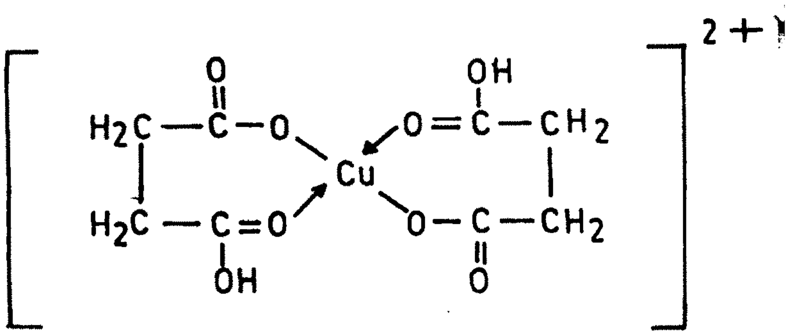
DISCUSSIONS:-

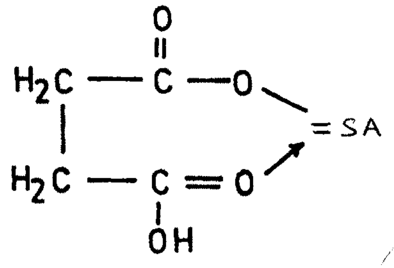
The kinetics of exchange of Cu(II), Zn(II), Ca(II), Pb(II) Th(IV), Al(III), Hg(II), Ni(II), Cd(II), Co(II), Mn(II) and Mg(II) in 0, 20, 30, 50, percentages acetone in absence and presence of succinic acid (SA) (0.5M) was studied. The Kinetics of exchange of the metal ions under study in aqueous acetone system represents the mechanism of M^{n+}/H^{+} exchange reactions.

$$2(R\,SO_3^-)_H^+ + M^{+2}(Soln) \rightleftharpoons (RSO_3)_2^- \; M^{2+} + 2H^+(soln.)$$

The reaction involves in addition to the electrostatic hydrogen-metal exchange, rapid chemical change[7] from the dissolved H-spescies to the nondissociated metal - species. Put in another way, the addition of a metal ion to the dissociated sulphonate group partially localizes a pair of electrons and thereby converts a functional group from a dissociated to a nondissociated species.

The rates of exchange of metal ions in aqueous acetone-succinic acid represent the studies of exchange of $M^n(n\ SA)^{n+}/H^+$ where n is the valency of metal ion. Let us consider the example of exchange of Cu^{2+} ions in aqueous acetone succinic acid on Dowex 50 W X 8. The following complex is formed.





The extent of reaction, F, Fractional attainment of equilibrium is expressed as,

$$F = \frac{\text{The amount of exchange at time } t}{\text{The amount of exchange at infinite time}}$$

Now, in the present case $CV \gg \bar{C}\bar{V}$ where C is the concentration of metal ion in the solution phase, V is the volume of the solution, $\bar{C}$ is the concentration of the metal ion in the exchanger phase, and $\bar{V}$ is the volume of the exchanger. Thus, although the system is, in principle, a limited bath, the equation applicable to the infinite bath can be used in this case also as verified by Reichenberg[8], Helfferich[9] and Blickenstaff in their studies.

$$\text{Hence, } F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \cdot e^{-n^2 Bt} \quad \text{-----(1)}$$

$$\text{Where } B = \frac{\pi^2}{r^2} D$$

r = radius of fully swollen resin bed and D = the effective diffusion coefficient of the two ions undergoing exchange within the exchanger, and n = an integer having any value from 1 to ∞.

The values 'F' are presented in tables $3C_1$ to $3C_{21}$ are presented by Figs. 3.1 to 3.12. and 3.23 to 3.30. Values of Bt as a function of F are calculated as given by Reichenberg [12]. The Bt versus t plots are shown by Figs. 3.41 to 3.48 and values of B are obtained from the slopes of these plots. The values of B are given in tables $3C_{25}$.

From the second Flick's law Barrer developed an expression for the mathematical description of particle mechanism.

RESULTS

TABLE - 3 B_1

REICHENBERG TABLE FOR INTERPRETING 'F' IN TERMS OF Bt.

F	Bt	F	Bt	F	Bt	F	Bt
0.01	0.00009	0.26	0.0678	0.51	0.3160	0.76	0.9440
0.02	0.00036	0.27	0.0736	0.52	0.3320	0.77	0.9850
0.03	0.00076	0.28	0.0797	0.53	0.3480	0.78	1.028
0.04	0.00141	0.29	0.0861	0.54	0.3650	0.79	1.073
0.05	0.00219	0.30	0.0928	0.55	0.3800	0.80	1.12
0.06	0.0032	0.31	0.0998	0.56	0.4000	0.81	1.171
0.07	0.0044	0.32	0.107	0.57	0.4190	0.82	1.224
0.08	0.0057	0.33	0.1147	0.58	0.4380	0.83	1.28
0.09	0.0073	0.34	0.1226	0.59	0.4580	0.84	1.34
0.10	0.0091	0.35	0.1308	0.60	0.4790	0.85	1.404
0.11	0.0111	0.36	0.1391	0.61	0.5000	0.86	1.468
0.12	0.0132	0.37	0.1485	0.62	0.5220	0.87	1.543
0.13	0.0156	0.38	0.1577	0.63	0.5450	0.88	1.623
0.14	0.0183	0.39	0.1670	0.64	0.5690	0.89	1.710
0.15	0.021	0.40	0.1770	0.65	0.5940	0.90	1.8
0.16	0.0241	0.41	0.1880	0.66	0.6200	0.91	1.91
0.17	0.0274	0.42	0.1990	0.67	0.6470	0.92	2.03
0.18	0.0309	0.43	0.2100	0.68	0.6750	0.93	2.16
0.19	0.0346	0.44	0.2220	0.69	0.7030	0.94	2.32
0.20	0.0386	0.45	0.2340	0.70	0.7340	0.95	2.5
0.21	0.0428	0.46	0.2460	0.71	0.7650	0.96	2.7
0.22	0.0473	0.47	0.2590	0.72	0.7980	0.97	3.01
0.23	0.052	0.48	0.2730	0.73	0.8320	0.98	3.41
0.24	0.057	0.49	0.2870	0.74	0.8680	0.99	4.11
0.25	0.0623	0.50	0.3010	0.75	0.9050	1.0	-

FRACTIONAL EXCHANGE

TABLE - 3C1

DEPENDENCE OF F VALUES ON THE PERCENTAGE OF ACETONE

Metal Ion - Cu(II) (0.004 M)

Time in minute	Fractional attainment of equilibrium (F)							
	ACETONE PERCENTAGE							
	0		20		30		50	
	a	b	a	b	a	b	a	b
1	2	3	4	5	6	7	8	9
0	0	0	0	0	0	0	0	0
5	0.246	0.072	0.05	0.173	0.145	0.097	0.378	0.174
10	0.333	0.101	0.130	0.304	-	-	-	-
15	0.376	0.159	0.304	0.304	-	-	-	-
20	0.434	0.173	0.318	0.391	0.291	0.383	0.504	0.291
25	0.449	0.376	0.318	0.391	-	-	-	-
30	0.449	0.391	0.333	0.478	-	-	-	-
40	0.449	0.521	0.347	0.492	-	-	-	-
50	0.579	0.536	0.347	0.536	-	-	-	-
60	0.579	0.666	0.347	0.608	0.485	0.533	0.679	0.543
90	0.710	0.739	0.579	0.637	0.0	-	-	-
120	0.797	0.804	-	0.797	0.689	0.844	0.864	0.786
170	-	-	-	-	0.854	-	-	0.902
180	0.884	-	0.695	-	-	1.0	1.0	-
240	1.0	0.811	-	0.897	1.0	-	-	0.932
245	-	-	1.0	-	-	-	-	-
300	-	0.869	-	0.927	-	-	-	-
360		1.0		1.0				1.0

a = Aqueous acetone

b = Aqueous acetone + 0.5 M SA .

TABLE- $3C_2$ Metal Ion- Ca (II) (0.004 M)

1	2	3	4	5	6	7	8	9
0	0	0	0	0	0	0	0	0
5	0.252	0.068	0.160	0.149	0.131	0.166	0.298	0.24
10	0.264	0.080	0.333	0.183	-	-	-	-
15	-	0.195	0.333	0.206	0.0	-	-	-
20	0.287	0.298	0.333	0.287	-	-	-	-
25	0.321	0.298	0.356	0.298	-	-	-	-
30	0.367	0.298	0.425	0.310	0.278	0.216	0.385	0.448
40	0.413	0.344	0.494	0.367	0.0	-	-	-
50	0.594	0.528	0.597	0.402	-	-	-	-
60	0.517	0.0	0.655	0.0	0.557	0.5	0.562	0.586
90	0.666	0.540	0.781	-	-	-	-	-
120	0.666	0.551	0.781	0.551	0.803	0.766	0.614	0.603
180	0.666	0.804	0.839	0.678	0.868	0.833	0.736	0.75
240	0.793	0.827	0.862	0.793	0.0	-	-	-
300	0.793	0.827	0.862	0.850	0.885	0.0	0.754	0.844
360	0.896	0.827	0.862	0.850	-	-	-	-
420	1.0	-	1.0	-	1.0	1.0	0.877	0.86
480	-	0.862		0.885			-	-
520	-	1.0	-	1.0			-	-
∞							1.0	1.0

TABLE- $3C_3$ Metal Ion - Zn (II) (0.004M)

1	2	3	4	5	6	7	8	9
0	0	0	0	0	0	0	0	0
5	0.565	0.173	0.450	0.202	0.316	0.66	0.448	0.586
10	0.623	0.253	0.442	0.333	0.436	0.678	0.0	0.609
15	0.666	0.289	0.579	0.376	-	-	-	-
20	0.666	0.311	0.594	0.384	0.528	0.0	0.517	0.632
25	0.753	0.478	0.608	0.521	-	-	-	-
30	0.768	0.550	0.623	0.521	0.609	-	-	0.637
40	0.826	0.565	0.623	0.608	-	-	- 5	-
50	0.855	0.673	0.637	0.724	-	-	-	-
60	0.855	0.768	0.753	0.724	-	0.77	0.609	-
65	-	-	-	-	0.678	-	-	0.816
90	0.927	0.869	0.846	0.724	-	-	-	-
120	0.977	0.985	0.869	0.884	0.758	0.85	0.655	0.856
180	1.0	-	1.0	-	0.902	0.908	0.77	0.954
240		1.0		1.0	0.908	1.0	0.839	1.0
300					0.913		0.919	
360					1.0		0.925	
480							0.988	
540							1.0	

TABLE- $3C_4$ Metal Ion - Mg (II) (0.004 M)

1	2	3	4	5	6	7	8	9
0	0	0	0	0	0	0	0	0
5	0.067	0.109	0.012	0.240	0.292	0.256	0.195	0.174
10	0.146	0.146	0.048	0.146	-	-	-	-
15	0.164	0.219	0.073	0.170	-	-	-	-
20	0.207	0.243	0.121	0.182	0.365	0.280	0.353	0.291
25	0.243	0.256	0.134	0.219	-	-	-	-
30	0.292	0.262	0.134	0.219	-	-	-	-
40	0.365	-	0.195	-	-	-	-	-
50	0.414	-	-	-	-	-	-	-
60	0.50	0.439	0.0	0.268	0.390	0.62	0.512	0.543
80	-	-	0.378	-	-	-	-	-
90	0.536	0.439	-	-	-	-	-	-
100	-	-	-	0.414	-	-	-	-
120	0.597	0.536	0.536	0.487	0.573	0.0	-	0.786
130	-	-	-	-	-	0.792	0.634	-
170	-	-	-	-	-	0.841	0.719	0.902
180	0.707	0.585	0.682	0.646	0.658	-	-	-
240	-	-	-	-	0.707	0.878	0.829	0.932
300	0.853	0.804	0.817	0.792	0.817	-	-	-
360	0.890	-	0.902	-	0.865	0.963	0.975	1.0
420	-	0.902	- -	0.878	-	1.0	1.0	
480	1.0	1.0	1.0	-	0.975			
540					1.0			
680				1.0				

TABLE- $3C_5$ Metal Ion - Ni (II) (0.004 M)

1	2	3	4	5	6	7	8	9
0	0	0	0	0	0	0	0	0
5	0.126	0.242	-	0.231	0.092	0.271	0.016	0.015
8	-	-	0.028	-	-	-	-	-
10	0.174	0.257	0.166	0.231	-	-	-	-
15	0.206	0.287	0.289	0.0	-	-	-	-
20	0.246	0.409	0.289	0.333	-	-	-	-
25	0.301	0.439	0.304	0.333	-	-	-	-
30	0.349	0.454	0.405	0.391	0.11	0.406	0.084	0.031
40	-	-	-	-	-	-	-	-
60	0.539	0.0	0.637	0.0	0.185	0.423	0.288	0.14
70	-	0.507	-	-	-	-	-	-
90	-	0.621	-	0.594	-	-	-	-
120	0.714	0.636	0.811	0.898	0.777	0.542	0.644	0.453
240	-	0.803	-	0.898	0.833	0.644	0.830	0.765
320	0.904	-	0.913	-	-	-	-	-
330	-	-	-	-	0.87	0.711	0.864	0.796
390	-	-	-	- -	0.88	0.0	-	-
400	0.904	-	0.971	-	-	-	-	-
420	-	0.984	-	0.971	-	0.779	0.915	0.921
480	-	-	-	-	0.944	-	-	-
510	-	-	-	-	-	0.847	0.983	1.0
570	-	-	-	-	1.0	-	-	
690	-	-	-	-		0.983	-	
∞	1.0	1.0	1.0	1.0		1.0	1.0	

TABLE- 3C$_6$ Metal Ion - Cd (II) (0.004M)

1	2	3	4	5	6	7	8	9
0	0	0	0	0	0	0	0	0
5	0.025	0.237	0.037	0.212	0.53	0.562	0.237	0.337
10	0.087	0.262	0.162	0.275	-	-	-	-
15	0.187	0.400	0.212	0.487	-	-	-	-
20	0.187	0.475	0.212	0.737	-	-	-	-
25	0.275	-	0.312	-	-	-	-	-
30	0.312	0.587	0.337	0.837	0.55	0.787	0.400	0.625
35	-	0.65	-	0.662	-	-	-	-
40	-	0.712	-	0.825	-	-	-	-
45	-	0.9	-	-	-	-	-	--
50	-	-	-	0.875	-	-	-	-
55	-	0.9	-	-	-	-	-	-
60	0.575	-	0.512	0.9	0.625	0.793	0.493	0.762
70	-	0.9	-	0.962	-	-	-	-
75	-	0.937	0.0	0.975	-	-	-	-
90	-	0.975	-	0.987	-	-	-	-
120	0.762	0.0	0.687	0.0	0.631	0.8	0.625	0.775
150	-	1.0	-	1.0	-	-	-	-
180	0.862		0.787		0.737	0.962	0.712	1.0
240	0.9		0.862		0.887	1.0	0.912	
300	0.925		0.925		0.962		0.962	
330	0.95		0.937		-		-	
360					1.0		0.987	
∞	1.0		1.0				1.0	

TABLE- $3C_7$ Metal Ion- Co(II) (0.004 M)

1	2	3	4	5	6	7	8	9
0	0	0	0	0	0	0	0	0
5	0,024	0.256	0.012	0.134	0.308	0.35	0.382	0.512
10	0.109	0.317	0.195	0.219	-	-	-	-
15	0.158	0.317	0.207	0.256	-	-	-	-
20	0.170	0.353	0.243	0.292	0.345	-	-	0.524
25	0.170	0.353	0.256	0.292	-	-	-	-
30	0.176	0.378	0.292	0.317	-	-	-	-
35	-	-	0.365	-	-	-	-	-
40	0.182	0.411	0.378	0.353	-	-	-	-
45	0.268	-	0.378	-	-	-	-	-
50	0.353	0.432	0.5	0.365	-	-	-	-
60	0.365	0.469	0.560	0.426	0.382	0.634	0.506	0.652
90	0.50	0.542	0.670	0.560	-	-	-	-
120	0.536	0.609	0.719	0.615	0.530	0.768	0.6	0.756
180	0.646	0.658	0.804	0.719	0.641	-	-	0.804
190	-	-	-	-	-	0.853	0.66	-
240	0.853	0.719	0.817	0.780	-	-	-	-
250	-	-	-	-	0.753	0.9	0.740	0.853
300	0.853	0.804	0.865	0.853	-	-	-	-
310	-	-	-	-	-	0.95	0.765	-
360	0.859	0.817	0.926	0.878	-	-	-	-
370	-	-	-	-	0.925	-	-	0.951
420	0.878	0.878	-	0.926	-	-	-	-
430	-	-	-	-	0.932	0.975	0.925	0.987
480	-	0.890	-	0.963	-	-	-	-
490	-	-	-	-	0.951	-	-	1.0
610	-	-	-	-	1.0	-	0.987	
660	-	0.987	-	1.0				
745	-	-	1.0					
865	1.0							
∞		1.0				1.0	1.0	

TABLE- $3C_8$ Metal Ion- Mn (II) (0.004 M)

1	2	3	4	5	6	7	8	9
0	0	0	0	0	0	0	0	0
5	0.077	0.051	0.038	0.129	0.038	0.305	0.20	0.178
10	0.077	0.051	0.064	0.142	-	-	-	-
15	0.168	0.168	0.116	0.142	-	-	-	-
20	0.220	0.168	0.116	0.168	-	-	-	-
25	0.246	0.272	0.168	0.181	-	-	-	-
30	0.272	0.363	0.194	0.207	-	-	-	-
60	0.350	0.571	0.246	0.285	0.142	0.508	0.363	0.198
120	0.506	0.571	0.337	0.402	0.155	0.508	0.381	0.653
180	-	-	-	-	0.714	0.644	0.690	0.851
240	0.623	-	0.584	-	-	-	-	-
247	-	0.636	-	0.584	-	-	-	-
300	-	-	-	-	0.720	0.813	0.709	0.990
367	-	0.766	-	0.649	-	-	-	-
420	0.753	-	0.675	-	-	-	-	-
427	-	0.766	-	0.688	-	-	-	-
487	-	0.766	-	0.701	-	-	-	-
440	-	-	-	-	0.727	0.932	0.963	0.99
547	-	0.844	-	0.727	-	-	-5	-
720	-	-	-	-	0.766	0.966	0.981	0.99
∞	0.870	0.870	0.779	0.766	1.0	1.0	1.0	1.0

TABLE- $3C_9$ Metal Ion- Pb (II) (0,004 M)

1	2	3	4	5	6	7	8	9
0	0	0	0	0	0	0	0	0
5	0.258	0.294	0.305	-	0.411	0.352	0.282	0.305
7	-	-	-	0.261	-	-	-	-
10	0.388	0.323	0.329	0.369	-	-	-	-
15	0.41	0.352	0.376	0.44	-	-	-	-
20	0.423	0.4	0.423	0.471	-	-	-	-
25	0.429	0.411	0.435	-	-	-	-	-
30	-	0.477	0.488	0.488	0.588	0.576	0.317	0.494
35	0.447	-	-	-	-	-	-	-
40	-	0.541	0.547	0.5	-	-	-	-
45	0.552	-	-	-	-	-	-	-
50	-	0.611	0.627	0.547	-	-	-	-
60	-	0.67	0.682	0.642	0.741	0.741	0.4	0.705
90	-	0.776	0.729	0.76	-	-	-	-
120	-	0.847	0.8	0.82	0.823	0.823	0.552	0.8
180	-	0.882	0.894	0.857	0.87	0.894	0.6	0.882
300	-	-	0.952	-	0.982	0.982	0.917	0.976
390	-	---	-	-	0.988	0.988	0.952	0.988
480	-	-	0.988	-	0.994	1.0	0.976	1.0
570	-	-	-	-	-	-	1.0	
900	-	1.0	1.0	-	-			
∞	-	-	-	1.0	1.0			

TABLE- 3C$_{10}$ Metal Ion - Th(IV) (0.004 M)

1	2	3	4	5	6	7	8	9
0	0	0	0	0	0	0	0	0
5	0.297	0.214	0.226	0.238	0.32	0.202	0.202	0.142
10	0.309	0.357	0.285	0.285	-	-	-	-
15	0.345	0.38	0.345	0.297	-	-	-	-
20	0.416	0.428	0.369	0.345	-	-	-	-
25	0.428	0.476	0.440	0.392	-	-	-	-
30	0.440	0.5	0.440	0.416	0.51	0.32	-	0.333
35	0.464	0.523	-	0.440	-	-	-	-
40	0.511	0.547	0.464	0.464	-	-	-	-
45	-	0.619	0.5	0.571	-	-	-	-
50	0.654	0.714	0.547	0.619	-	-	-	-
60	0.654	0.733	0.595	0.666	0.669	0.595	0.583	0.559
90	0.797	0.809	0.690	0.738	-	-	-	-
120	0.809	-	0.75	-	0.838	0.761	0.773	0.761
150	-	0.869	-	0.809	-	-	-	-
180	0.845	-	0.845	-	-	-	-	-
210	-	0.916	-	0.892	-	-	-	-
240	0.880	-	0.892	-	-	-	-	-
270	-	0.952	-	0.928	-	-	-	-
300	0.940	-	0.940	-	-	-	-	-
330	-	0.964	-	0.952	-	-	-	-
360	-	-	-	-	0.958	0.976	0.916	0.940
390	-	0.964	-	0.952	0.982	0.988	0.922	0.946
450	-	0.976	-	0.976	-	-	-	-
480	-	-	-	-	0.994	1.0	0.940	-
510	-	-	-	1.0	1.0	-	-	-
∞	1.0	1.0	1.0				1.0	1.0

TABLE - $3C_{11}$ Metal Ion- Al(III) (0,004 M)

1	2	3	4	5	6	7	8	9
0	0	0	0	0	0	0	0	0
5	0.013	0.012	0.075	0.137	0.027	0.162	0.11	0.581
10	0.013	0.012	0.088	0.241	-	-	-	-
15	0.013	0.049	0.101	0.367	-	-	-	-
20	0.013	0.049	0.126	0.448	0.055	0.216	0.33	0.604
25	0.065	0.049	0.189	0.586	-	-	-	-
30	0.065	0.049	0.215	0.747	-	-	-	-
60	0.342	0.209	0.227	0.827	-	-	-	-
70	-	-	-	-	0.166	0.243	0.36	0.627
90	0.355	0.419	0.253	0.954	-	-	-	-
120	-	0.555	-	-	0.388	0.486	0.61	0.651
125	0.5	-	0.329	1.0	-	-	-	-
360	-	-	-	-	0.944	1.0	0.88	0.790
480	-	-	-		1.0		1.0	0.837
520	-	-	-	-				1.0
540	-	0.938	0.886	-				
660	-	0.938	0.949					
∞	1.0	1.0	1.0					

TABLE- 3C$_{12}$ Metal Ion- Hg (II) (0.004 M)

1	2	3	4	5	6	7	8	9
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5	0.068	-	-	0.589	0.770	0.775	0.766	0.807
8	-	0.078	0.773	-	-	-	-	-
10	0.103	0.176	0.773	-	-	-	-	-
15	0.137	0.313	0.773	0.803	-	-	-	-
20	0.241	0.372	0.981	0.857	-	-	-	-
25	0.31	0.382	0.981	-	-	-	-	-
30	0.344	-	1.0	0.892	0.783	0.787	0.779	0.820
60	0.396	-	-	-	0.797	0.812	0.818	0.871
90	0.431	0.647	-	0.910	-	-	-	-
120	0.534	0.725	-	-	0.837	0.825	0.831	0.910
240	-	0.725	-	0.91	0.851	0.837	0.883	0.923
300	1.0	-		-	-	-	-	-
360		-		-	0.918	1.0	1.0	1.0
∞		1.0		1.0	1.0			

FRACTIONAL EXCHANGE

TABLE - $3C_{13}$

DEPENDENCE OF F VALUES ON THE TEMPERATURE METAL ION - Th (IV)(0.004M)

Time in min.	Fractional Attainment of Equilibrium (F)							
	TEMPERATURE IN °C							
	30		35		40		45	
	a	b	a	b	a	b	a	b
1	2	3	4	5	6	7	8	9
0	0	0	0	0	0	0	0	0
5	0.634	0.509	0.27	0.397	0.595	0.404	0.361	0.562
30	0.646	0.533	0.387	0.65	0.-	-	0.385	0.610
60	0.694	0.593	0.424	0.698	0.636	0.678	0.626	0.754
90	-	-	-	-	0.726	0.735	-	-
120	0.706	0.739	0.581	0.831	0.779	0.821	0.674	0.79
180	-	-	0.678	0.879	-	-	0.777	0.844
240	0.874	0.896	-	-	0.926	0.892	0.807	0.91
300	-	-	0.787	0.927	0.928	0.912	0.855	0.934
360	0.946	0.933	-	-	0.952	0.964	0.903	0.940
420	-	-	0.921	0.939	1.0	0.988	-	-
455	-	-	-	-		-	0.927	0.952
480	0.970	0.957	-	-		-	-	-
525	0.988	0.975	-	-		-	-	-
540	-	-	0.933	0.975		-	-	-
695	-	-	-	-		-	0.975	0.994
∞	1.0	1.0	1.0	1.0		1.0	1.0	1.0

a = 20 % Acetone

b = 20 % Acetone + 0.5 M SA

FRACTIONAL EXCHANGE

TABLE - $3C_{14}$

Dependence of F values on the temperature, Metal Ion -Mg(II) 0.004 M

1	2	3	4	5	6	7	8	9
0	0	0	0	0	0	0	0	0
5	0.17	0.192	0.182	0.048	-	-	0.39	0.26
10	0.205	0.39	0.256	0.231	0.658	0.35	0.50	0.27
20	0.247	0.396	0.365	0.292	0.67	0.36	0.52	0.31
30	0.268	0.487	0.378	0.371	0.682	0.41	0.53	0.41
60	0.317	0.585	0.451	0.378	0.71	0.46	0.56	0.52
90	0.378	0.682	0.463	0.524	0.73	0.47	0.67	0.57
110	0.39	0.689	-	-	-	-	-	-
120	-	-	0.524	0.634	0.75	0.49	0.76	0.60
170	0.56	0.743	-	-	-	-	-	-
180	-	-	0.731	0.731	0.79	0.64	0.76	0.76
300	-	-	0.89	0.939	0.85	0.80	-	-
410	0.87	1.0	-	-		- -	-	-
420	-		0.987	1.0	-	--	-	-
480	-		1.0		-	-	-	-
00	1.0				1.0	1.0	1.0	1.0

a= 20% acetone and b=20% acetone + 0.5_M SA

TABLE-3C$_{15}$ Metal Ion-Cu(II) (0.004 M)

1	2	3	4	5	6	7	8	9
0	0	0	0	0	0	0	0	0
5	0.188	0.086	0.10	0.31	0.07	0.05	0.01	0.159
10	0.246	0.115	0.21	0.44	0.15	0.07	0.05	0.24
20	0.30	0.13	0.33	0.45	0.33	0.40	0.07	0.39
30	0.347	0.144	0.36	0.46	0.347	0.49	0.08	0.40
60	0.362	0.318	0.40	0.47	00.507	0.50	0.101	0.42
90	0.37	0.391	0.56	0.73	0.52	0.52	0.33	0.46
120	0.39	0.405	0.57	0.76	0.528	0.61	0.46	0.478
180	0.40	0.594	0.66	0.77	0.608	0.659	0.53	0.485
300	0.71	0.826	0.82	0.85	0.71	0.81	0.62	0.753
360	-	-	0.86	1.0	-	-	-	-
420	0.86	1.0	0.88		1.0	0.898	0.985	1.0
480	0.986		-				1.0	
540	1.0		0.92			1.0		
660			0.98					
720			1.0					

TABLE- 3C$_{16}$ Metal Ion-Zn(II) (0.004 M)

1	2	3	4	5	6	7	8	9
0	0	0	0	0	0	0	0	0
5	0.33	0.41	0.14	0.63	0.356	0.597	0.436	0.5
10	0.37	0.45	0.32	0.65	0.39	0.60	0.50	0.505
20	0.52	0.57	0.53	0.67	0.66	0.64	0.51	0.528
30	0.54	0.71	0.66	0.78	0.67	0.70	0.528	0.540
60	0.64	0.75	0.67	0.79	0.74	0.71	0.56	0.643
90	0.65	0.79	0.68	0.84	0.81	0.81	0.58	0.724
120	0.8	-	0.69	0.85	0.85	0.85	0.655	0.729
180	0.81	0.-	0.80	1.0	0.91	0.90	0.73	0.77
290	-	1.0	-		-	-	-	-
300	0.88		0.86		1.0	0.98	0.90	0.988
360	0.9	-	0.9			0.-	-	-
420	1.0		0.95			1.0	0.988	1.0
480	-	-	-				1.0	
540			1.0					

TABLE- $3C_{17}$ Metal Ion- Co (II) (0.004 M)

1	2	3	4	5	6	7	8	9
0	0	0	0	0	0	0	0	0
5	0.025	0.025	0.134	0.109	0.32	0.317	0.07	0.048
10	0.162	0.037	0.146	0.134	0.-	-	-	-
20	0.275	0.312	0.158	0.329	0.345	0.451	0.256	0.280
30	0.312	0.393	0.243	0.390	-	-	-	-
60	0.325	0.575	0.-	-	0.353	0.560	0.317	0.317
90	0.35	0.593	0.451	0.597	-	-	-	-
120	0.356	0.6	0.463	0.658	0.53	0.743	0.573	0.634
180	0.437	0.7	0.524	0.731	0.-	0.841	0.756	0.695
235	-	-	-	-	0.654	0.865	0.-	-
300	0.625	0.762	0.792	0.841	-	-	-	-
360	-	-	0.926	0.853	-	-	-	-
420	0.762	0.926	0.951	0.902	-	-	-	-
435	-	-	-	-	0.913	0.926	-	-
450	-	-	-	-	-	-	939	90[illegible]
480	0.837	1.0	-	-	-	-	-	-
540	0.925		0.987	1.0	-	-	-	-
600	1.0		1.0		-	-	-	-
630							0.1.0	1.0
675					0.962	1.0		
∞					1.0			

TABLE-3C18 Metal Ion- Pb (II) (0.004 M)

1	2	3	4	5	6	7	8	9
0	0	0	0	0	0	0	0	
5	0.388	0.447	0.325	0.369	0.63	0.482	0.108	0.494
10	0	0	0.325	0.369	-	-	-	-
30	0.423	0.635	0.331	0.488	0.-	0.647	0.397	0.576
60	0.552	0.670	0.445	0.619	0.-	0.67	0.542	0.694
100	-	-	-	-	0.714	0.-	-	-
120	0.635	0.741	0.-	0.75	0.-	0.87	0.662	0.764
240	0.776	0.858	0.807	0.857	0.773	0.917	0.831	0.858
360	-	-	0.891	0.892	0.-	-	0.843	0.917
420	0.905	0.917	0.927	0.940	0.-	-	-	-
0	-	-	-	-	0.904	0.941	-	-
5	0.917	0.976	-	-	-	-	-	-
540	0.988	1.0	0.951	0.988	-	-	-	-
560	-	-	-	-	0.940	0.964	-	-
600	-	-	-	-	-	-	0.987	0.952
660	-		0.987	-	-	-	-	-
680	-		-	-	0.976	0.988	-	-
780	-		0.993	-	-	-	-	-
∞	1.0		1.0	1.0	1.0	1.0	1.0	1.0

TABLE -3C$_{19}$ Metal Io-n - Ca(II) (0.004 M)

1	2	3	4	5	6	7	8	9
0	0	0	0	0	0	0	0	0
5	0.391	0.46	0.386	0.253	0.375	0.402	0.315	0.545
10	0.432	0.493	0.506	0.493	0.462	0.415	0.447	0.701
60	0.445	0.526	0.-	-	0.475	0.467	0.523	0.727
120	0.50	0.71	0.52	0.666	0.-	-	0.513	0.740
185	-	-	-	-	0.50	0.740	-	-
240	0.58	0.828	0.533	0.826	-	-	0.671	0.766
300	-	-	-	-	0.725	0.87	-	-
360	0.662	0.947	0.546	0.893	-	-	0.697	0.870
420	-	-	-	-	0.837	0.909	-	-
480	0.743	0.986	0.693	0.946	-	-	-	-
600	0.851	-	-	-	-	-	-	-
660	-	-	-	-	0.875	0.948	-	-
780	-	-	-	-	0.912	-	-	-
∞	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

TABLE- 3C$_{20}$ Metal Ion- Cd (II) (0.004 M)

1	2	3	4	5	6	7	8	9
0	0	0	0	0	0	0	0	0
5	0.375	0.662	0.289	0.5	0.289	0.525	0.282	0.462
30	0.4	0.75	0.381	0.762	0.-	-	0.461	0.5
40	-	-	-	-	0.427	0.75	-	-
60	0.412	0.8	0.486	0.875	-	-	0.615	0.775
100	-	-	-	-	0.553	0.787	-	-
120	0.512	0.9	0.602	0.925	0.-	-	0.641	0.862
160	-	-	-	-	0.654	0.925	-	-
220	-	-	-	-	[illegible]6	1.0	-	-
240	0.675	0.975	0.802	1.0			0.743	1.0
360	-	-	0.894		-		0.858	
420	0.775	1.0	0.907		-		-	
440	-	-	-		0.805		-	
485	0.937		-		-		-	
540	0.95		0.947		-		-	
560	-		-		0.968		-	
600	1.0		-		-		0.987	
660			0.986		-		-	
680			-		0.993		-	
∞			1.0		1.0		1.0	

TABLE-3C$_{21}$ Metal Ion-Mn(II) (0.004 M)

1	2	3	4	5	6	7	8	9
0	0	0	0	0	0	0	0	0
5	0.368	0.539	0.324	0.5	0.636	0.756	0.173	0.36
30	0.458	0.619	0.337	0.527	0.647	0.756	0.405	0.386
60	0.52	0.809	-	-	0.659	0.78	0.420	0.4
120	0.527	0.825	0.472	0.648	-	-	0.521	0.66
185	0.-	-	-	-	0.75	0.878	-	-
240	0.555	0.936	0.554	0.837	0.-	-	0.797	0.8
300	-	-	-	-	0.818	0.902	-	-
360	0.583	1.0	0.567	0.852	-	-	0.927	0.893
420	-	-	-	-	0.931	0.975	-	-
480	-		0.581	0.891	-	-	-	-
660	-		0.581	0.-	0.931	1.0	-	-
∞	1.0		1.0	1.0	1.0	[illegible]	1.0	1.0

Fig. 3·1

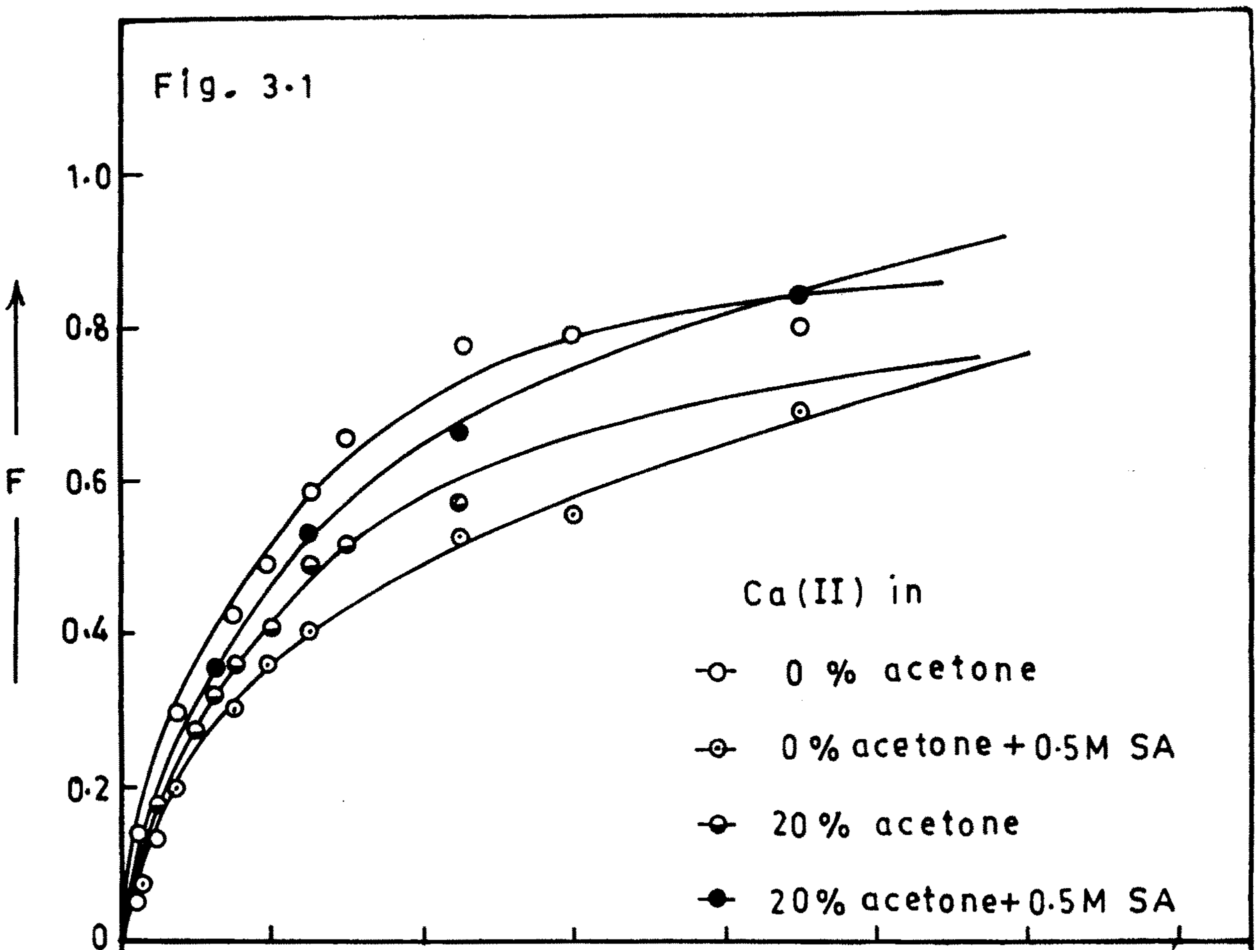
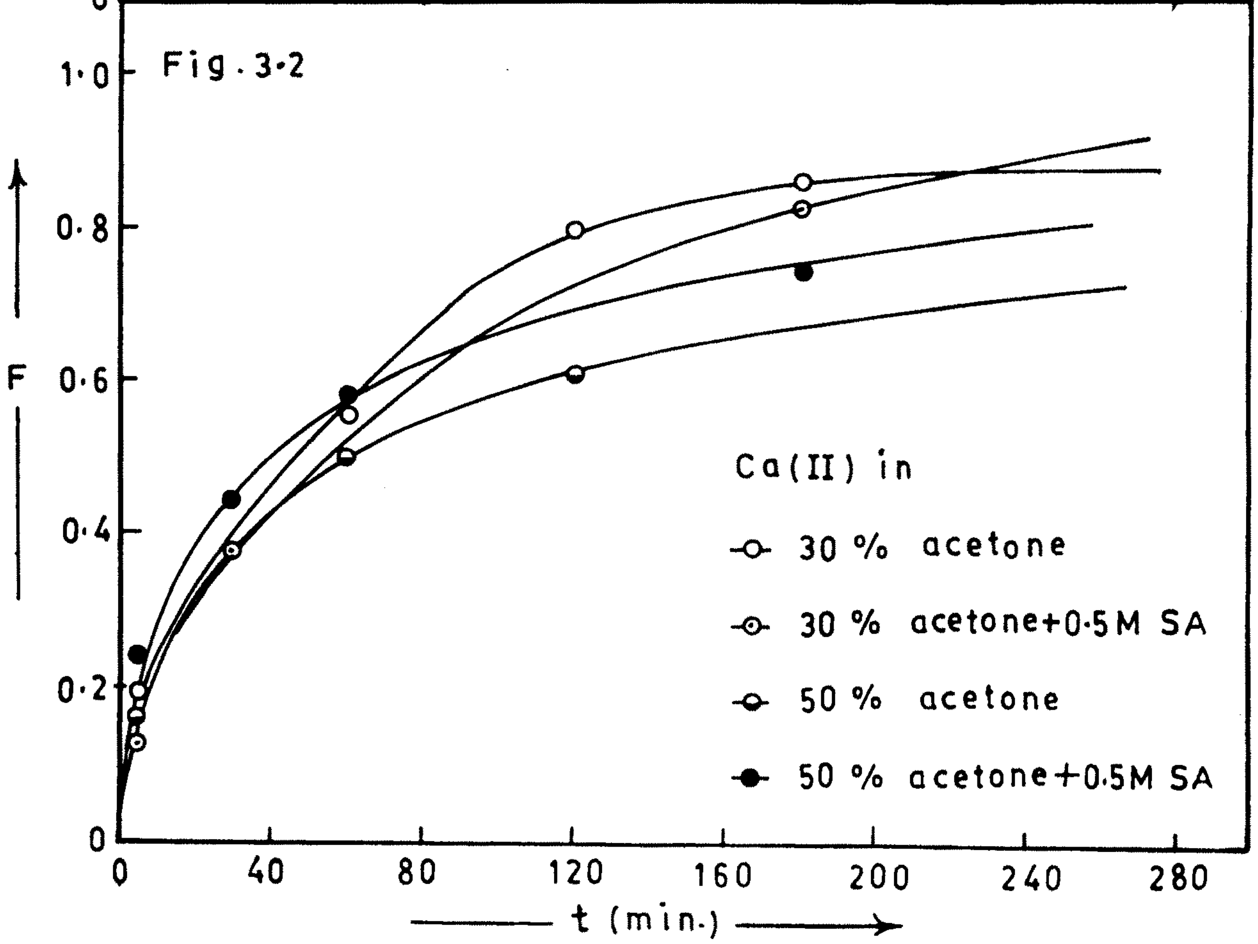

F
1·0
0·8
0·6
0·4
0·2
0
Ca(II) in
0 % acetone
0 % acetone + 0·5M SA
20 % acetone
20% acetone+0·5M SA

Fig. 3·2


F
1·0
0·8
0·6
0·4
0·2
0
0
40
80
120
160
200
240
280
t (min.)
Ca(II) in
30 % acetone
30 % acetone+0·5M SA
50 % acetone
50 % acetone+0·5M SA

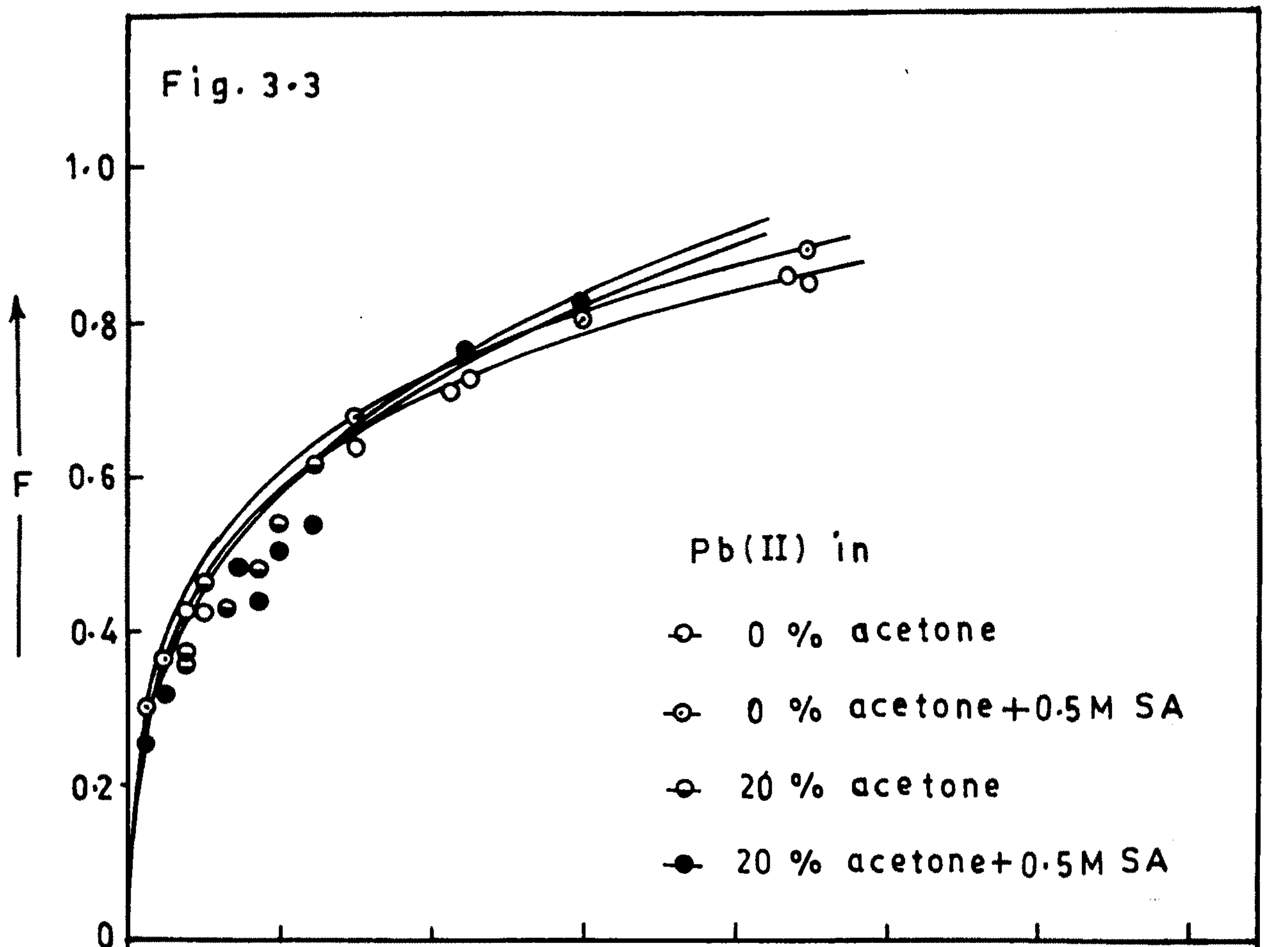


Fig. 3·3

F
1·0
0·8
0·6
0·4
0·2
0
Pb(II) in
-○- 0 % acetone
-⊙- 0 % acetone+0·5M SA
-⊖- 20 % acetone
-●- 20 % acetone+0·5M SA

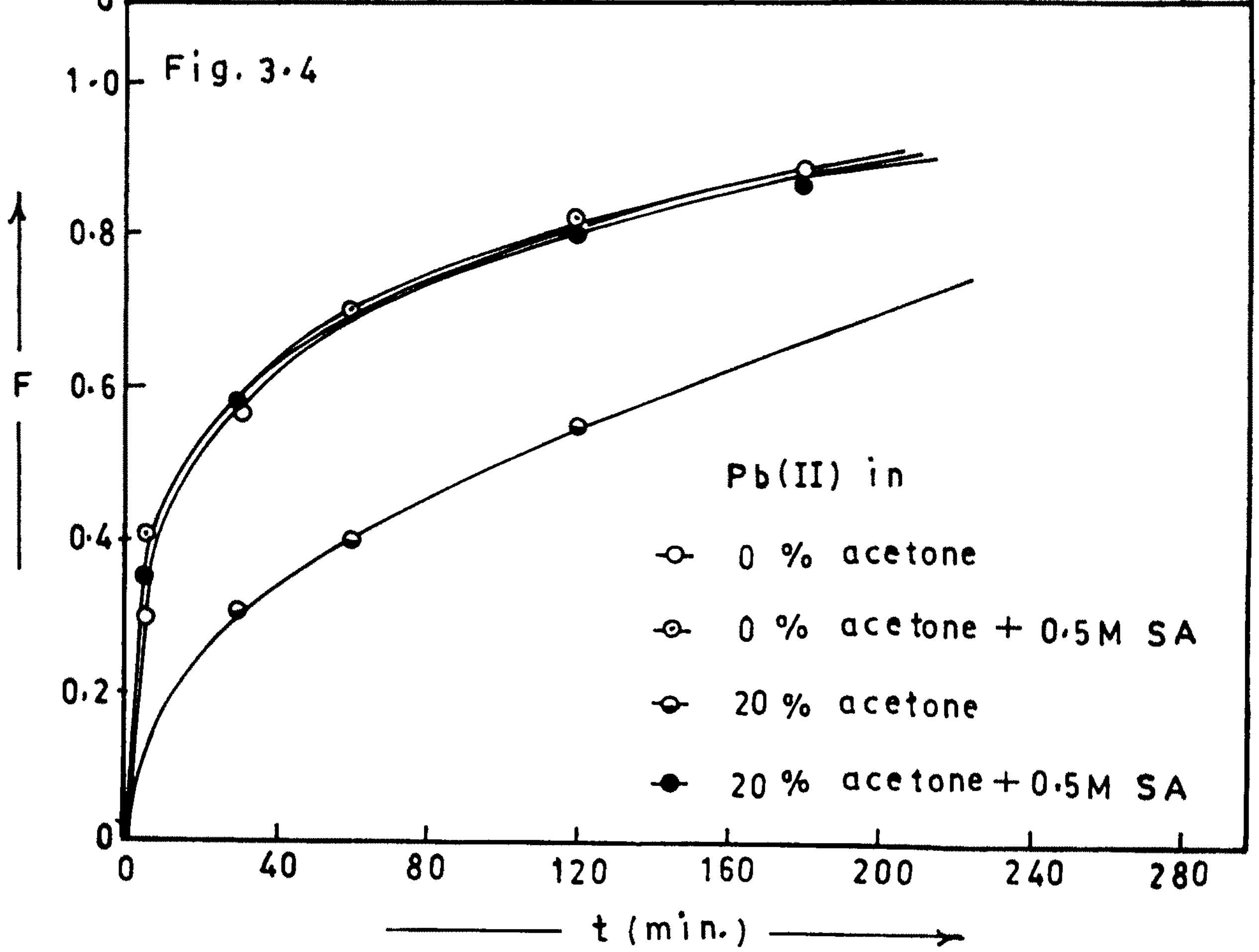


Fig. 3·4

F
1·0
0·8
0·6
0·4
0·2
0
0
40
80
120
160
200
240
280
t (min.)
Pb(II) in
-○- 0 % acetone
-⊙- 0 % acetone + 0·5M SA
-⊖- 20 % acetone
-●- 20 % acetone + 0·5M SA

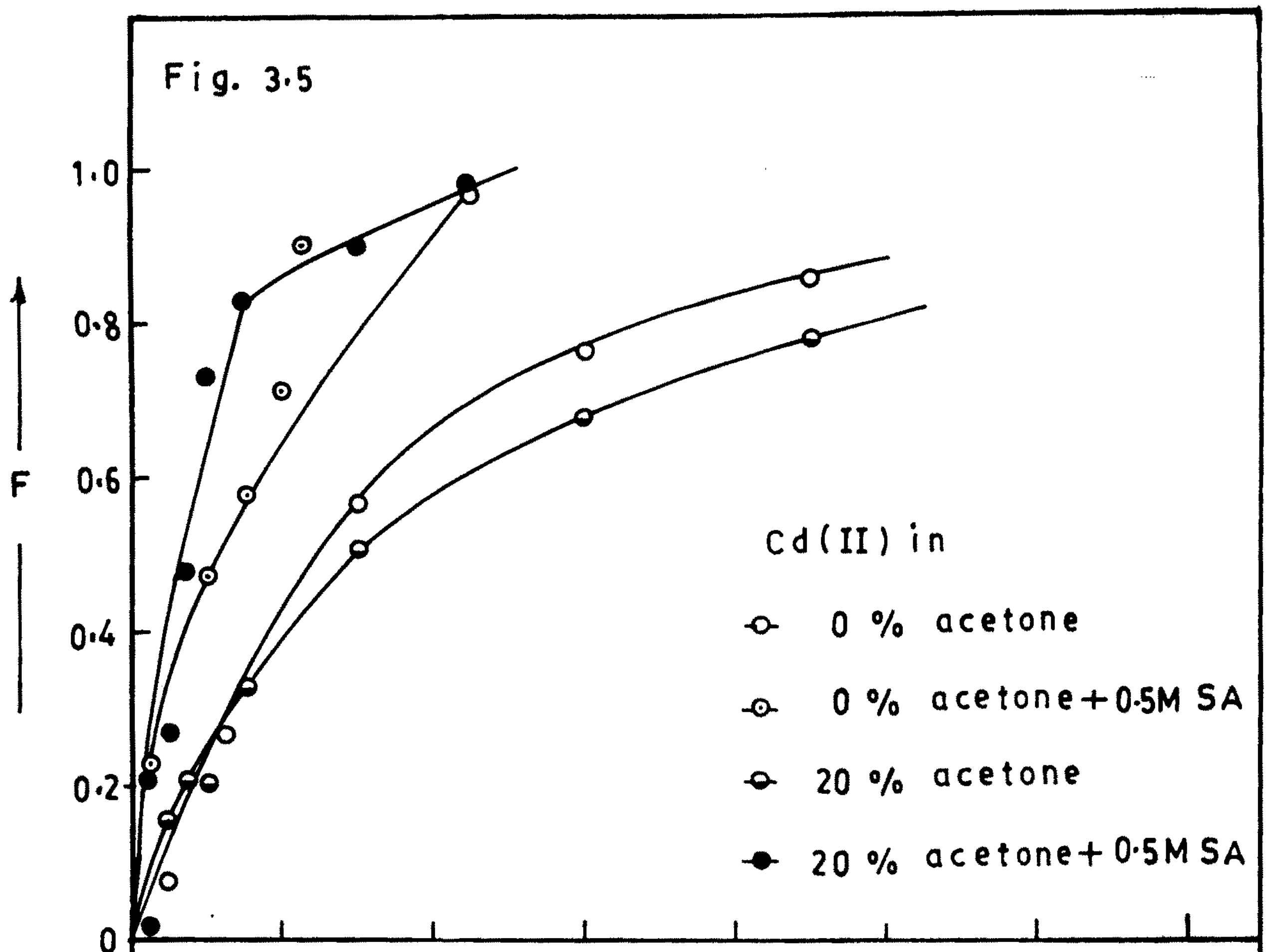


Fig. 3·5

1·0
0·8
0·6
0·4
0·2
0
F
Cd(II) in
0 % acetone
0 % acetone+0·5M SA
20 % acetone
20 % acetone+0·5M SA

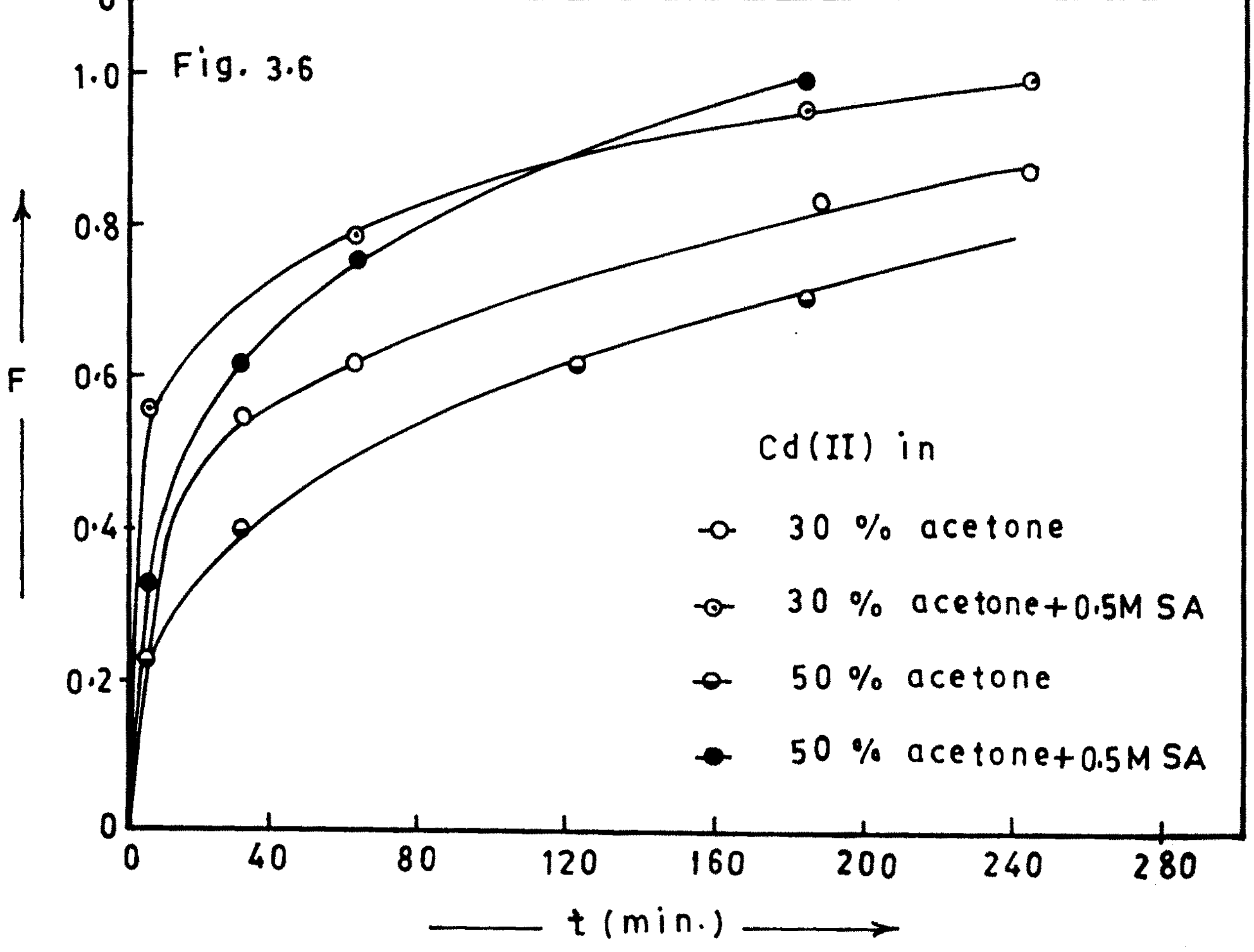


Fig. 3·6

1·0
0·8
0·6
0·4
0·2
0
F
Cd(II) in
30 % acetone
30 % acetone+0·5M SA
50 % acetone
50 % acetone+0·5M SA
0
40
80
120
160
200
240
280
t (min.)

Fig. 3·7

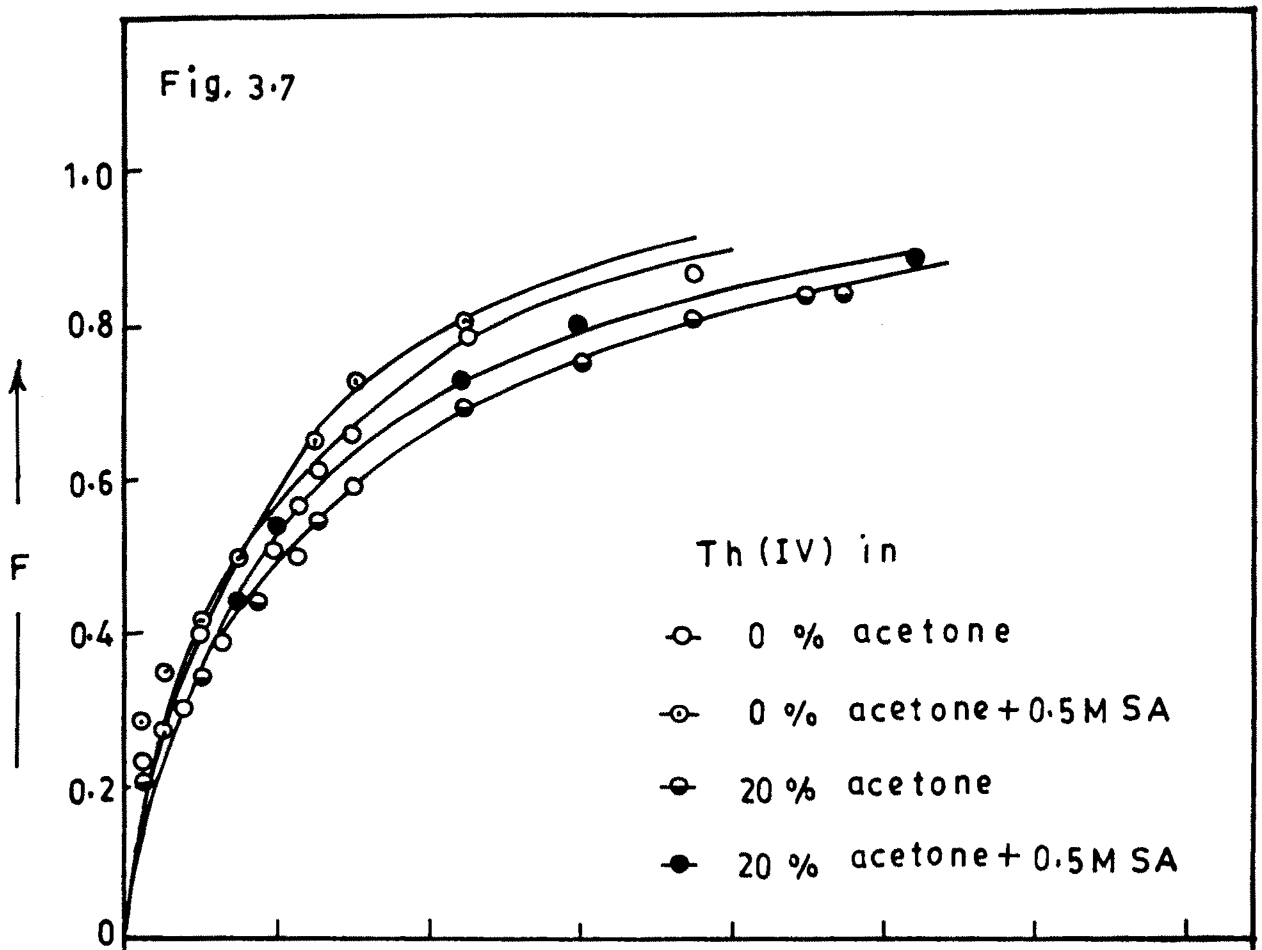
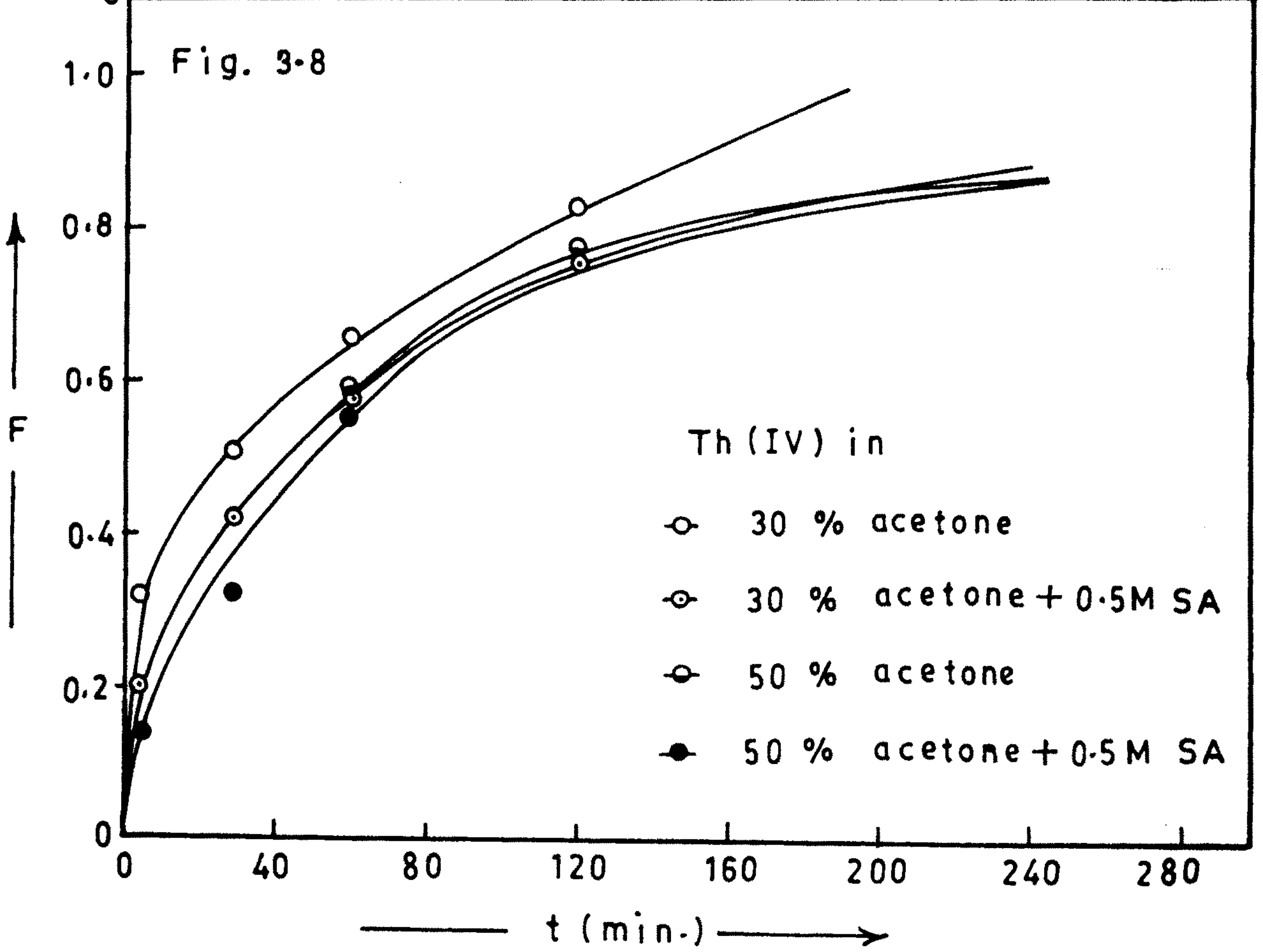

F
1·0
0·8
0·6
0·4
0·2
0
Th (IV) in
0 % acetone
0 % acetone + 0·5M SA
20 % acetone
20 % acetone + 0·5M SA

Fig. 3·8


F
1·0
0·8
0·6
0·4
0·2
0
Th (IV) in
30 % acetone
30 % acetone + 0·5M SA
50 % acetone
50 % acetone + 0·5M SA
0
40
80
120
160
200
240
280
t (min.)

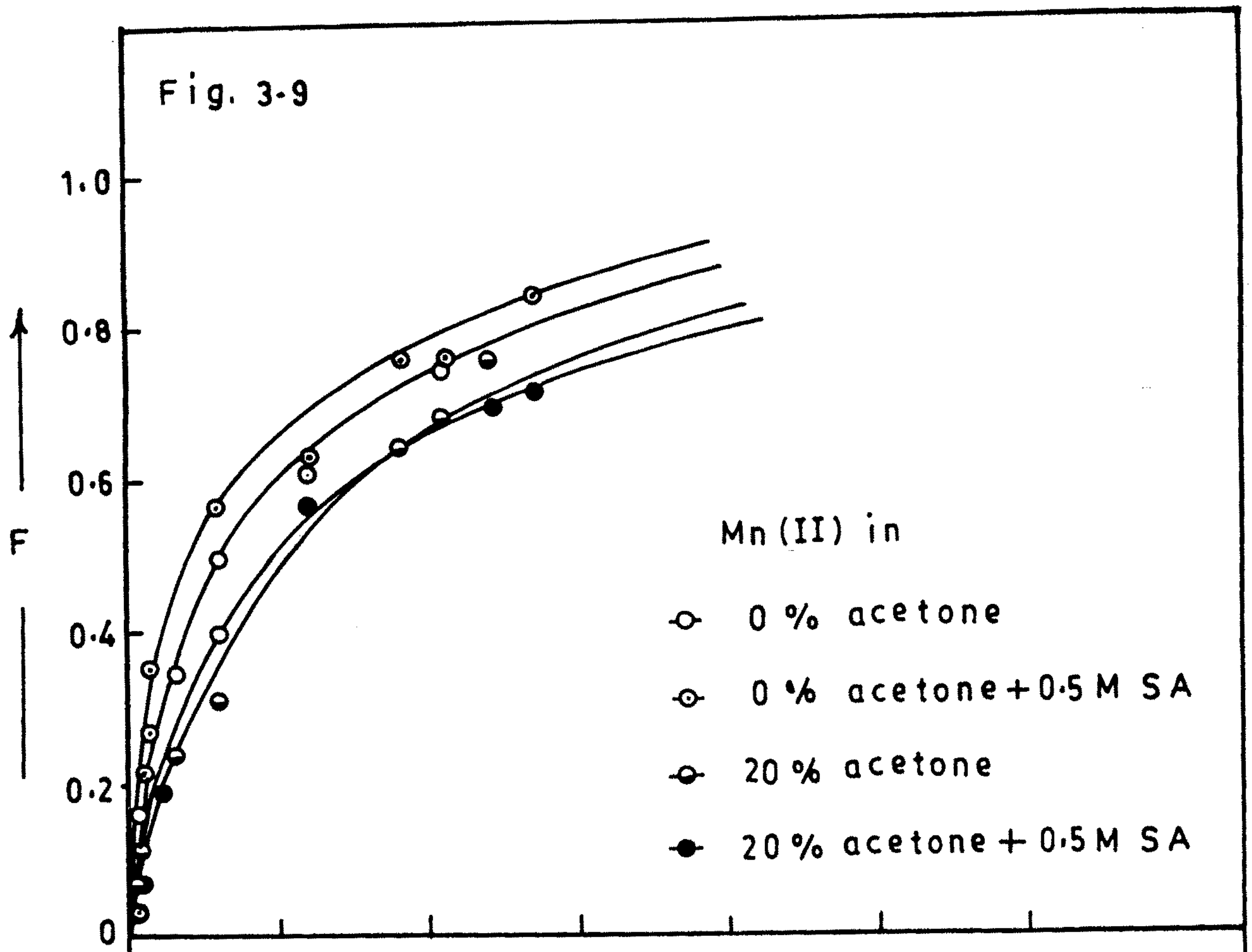


Fig. 3-9

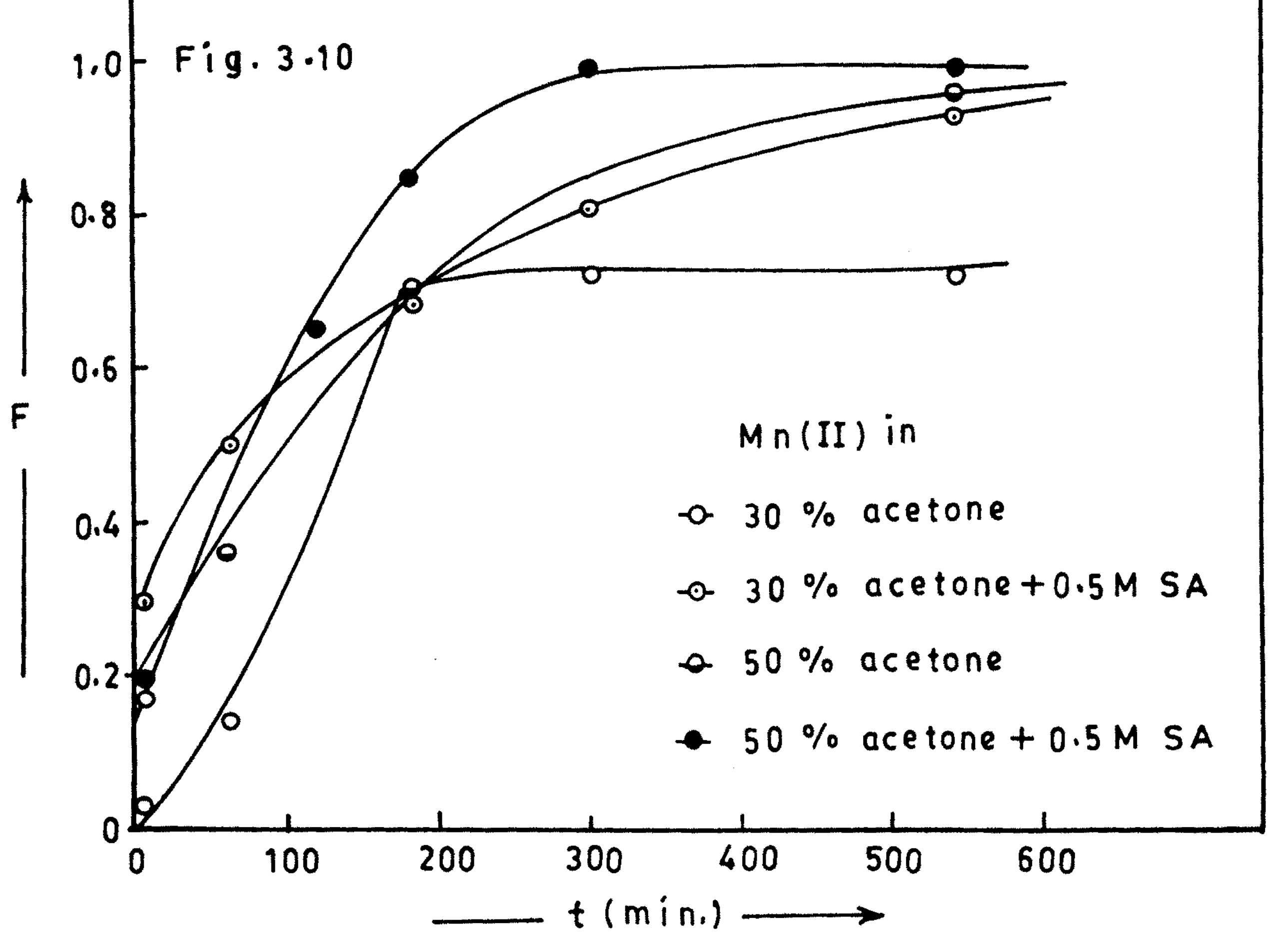
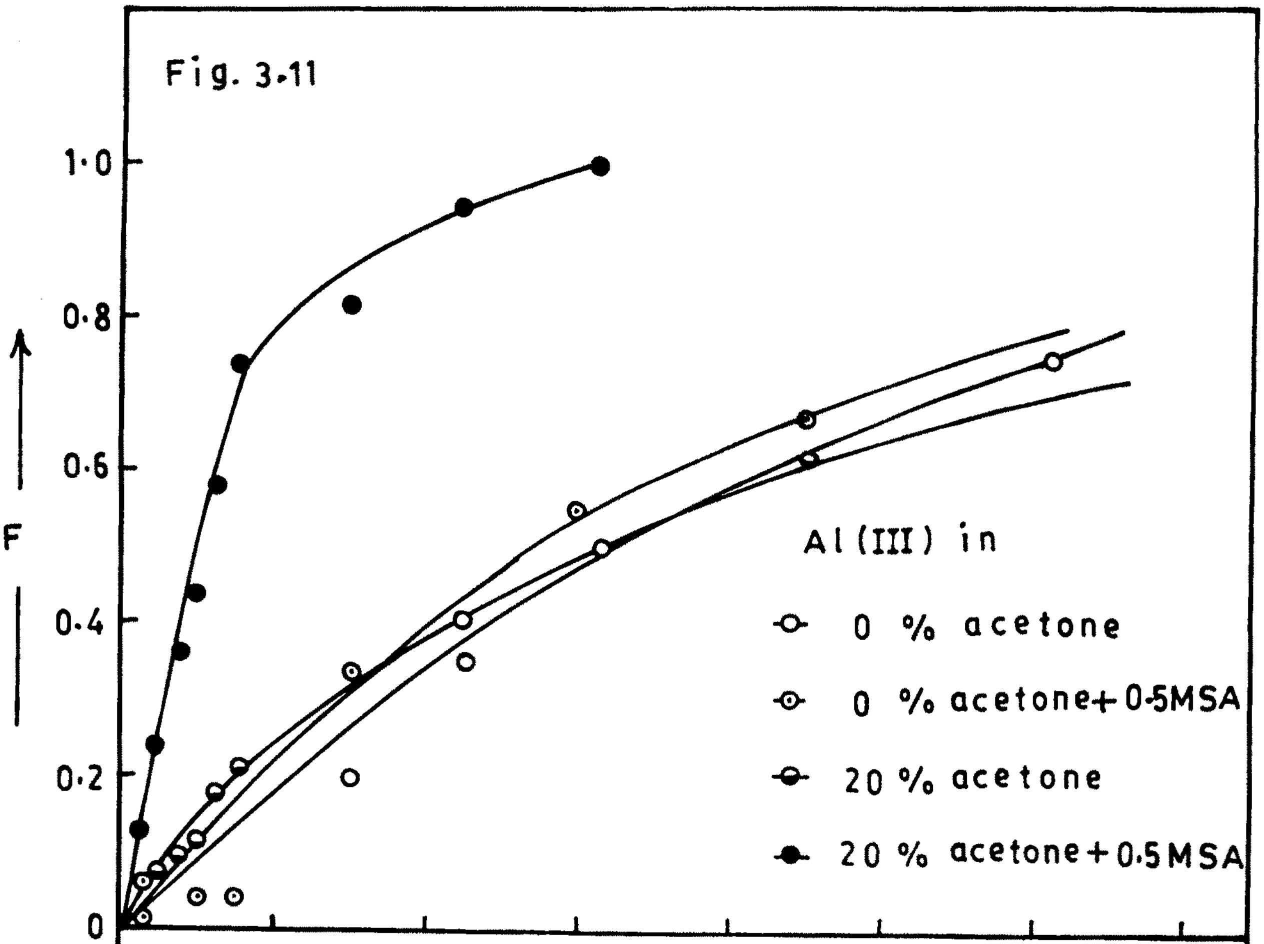


Fig. 3-10

Fig. 3.11



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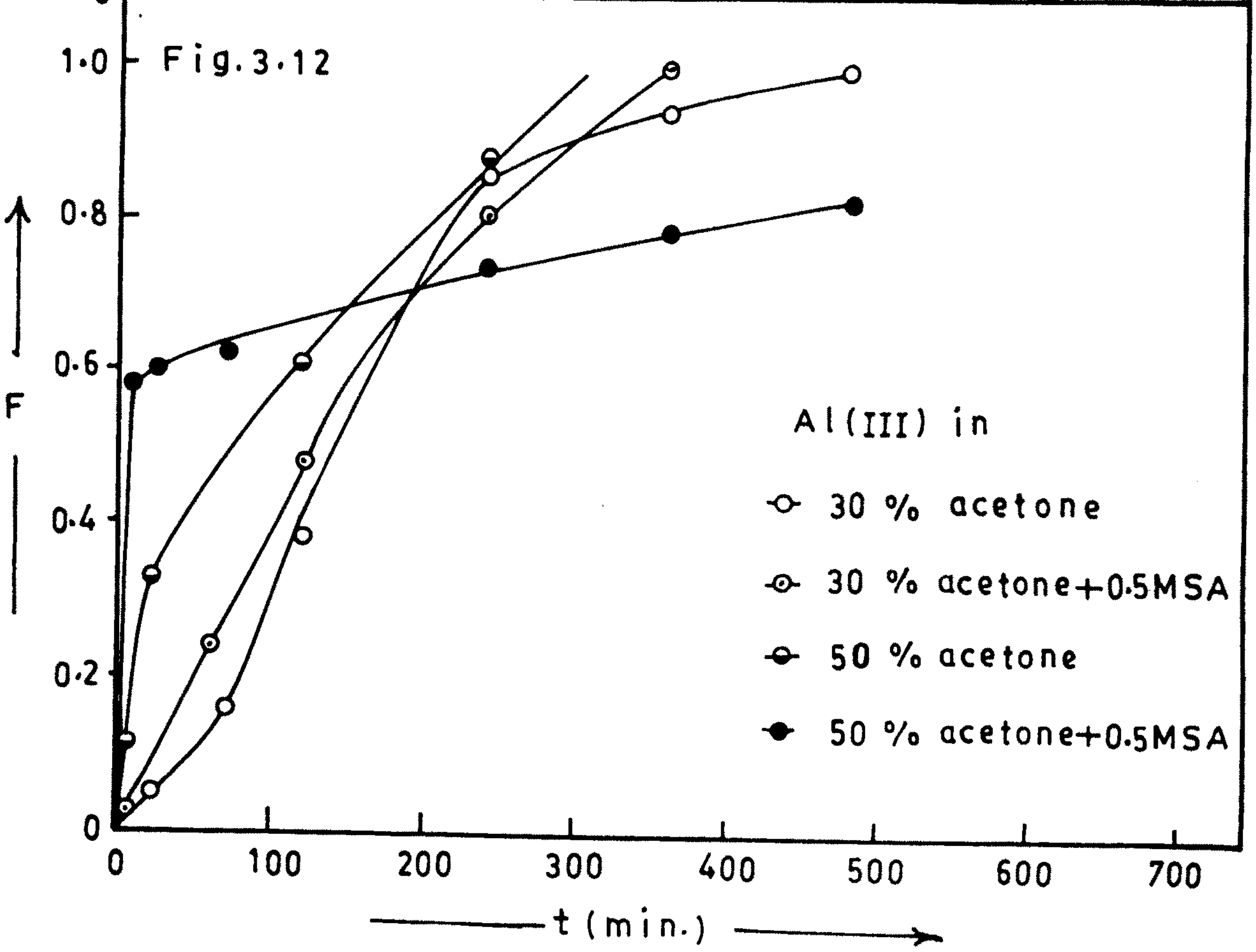


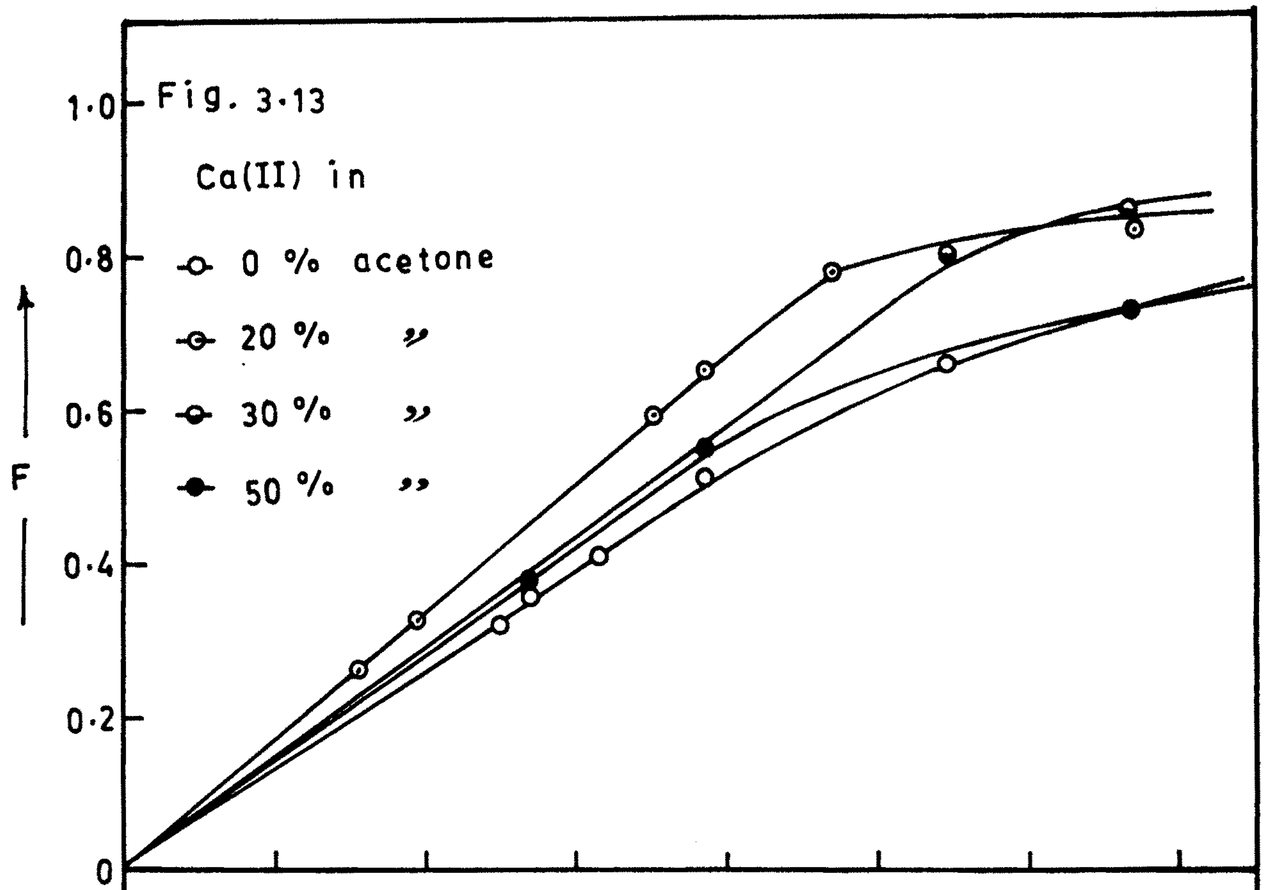


Fig. 3·13

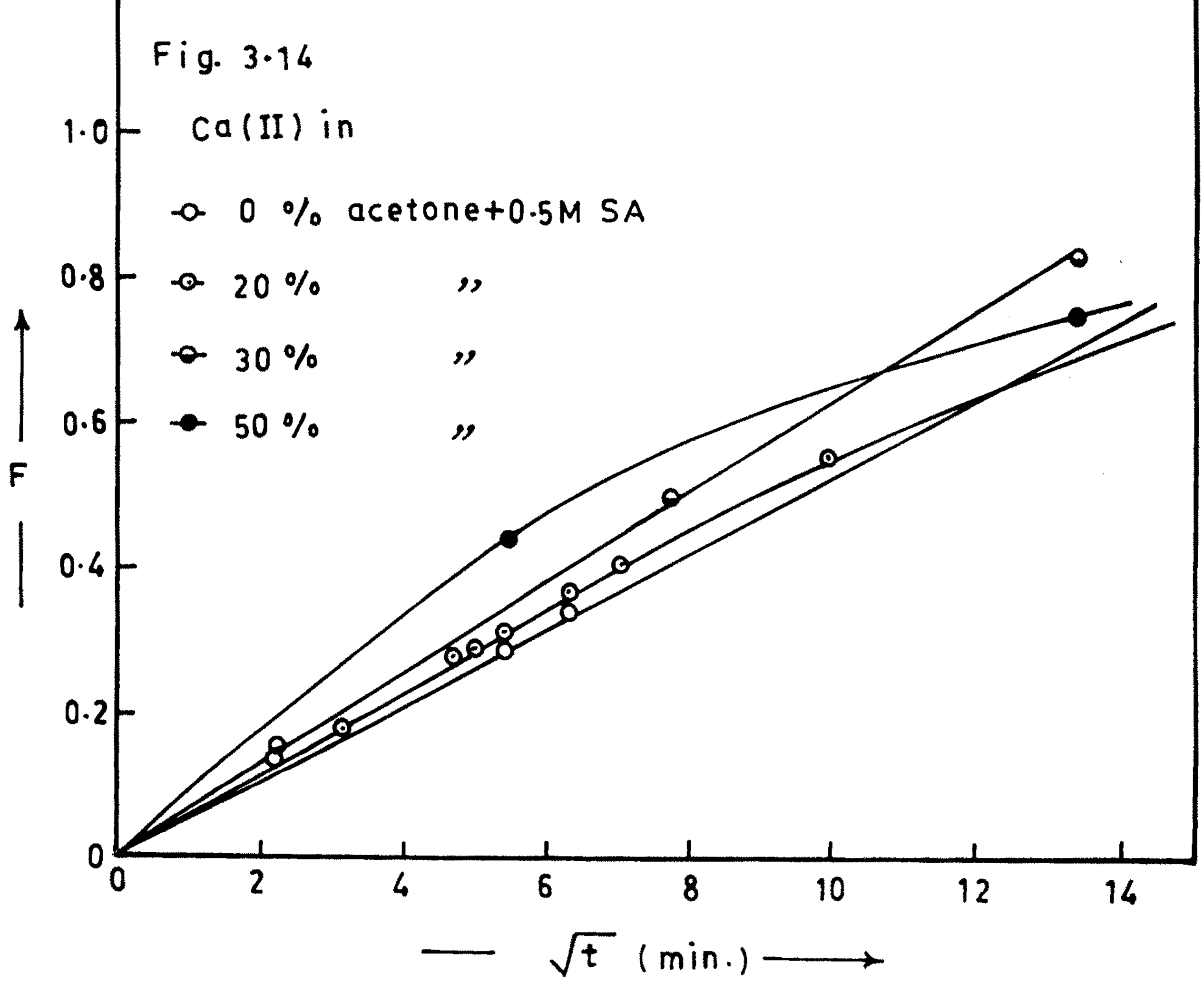


Fig. 3·14

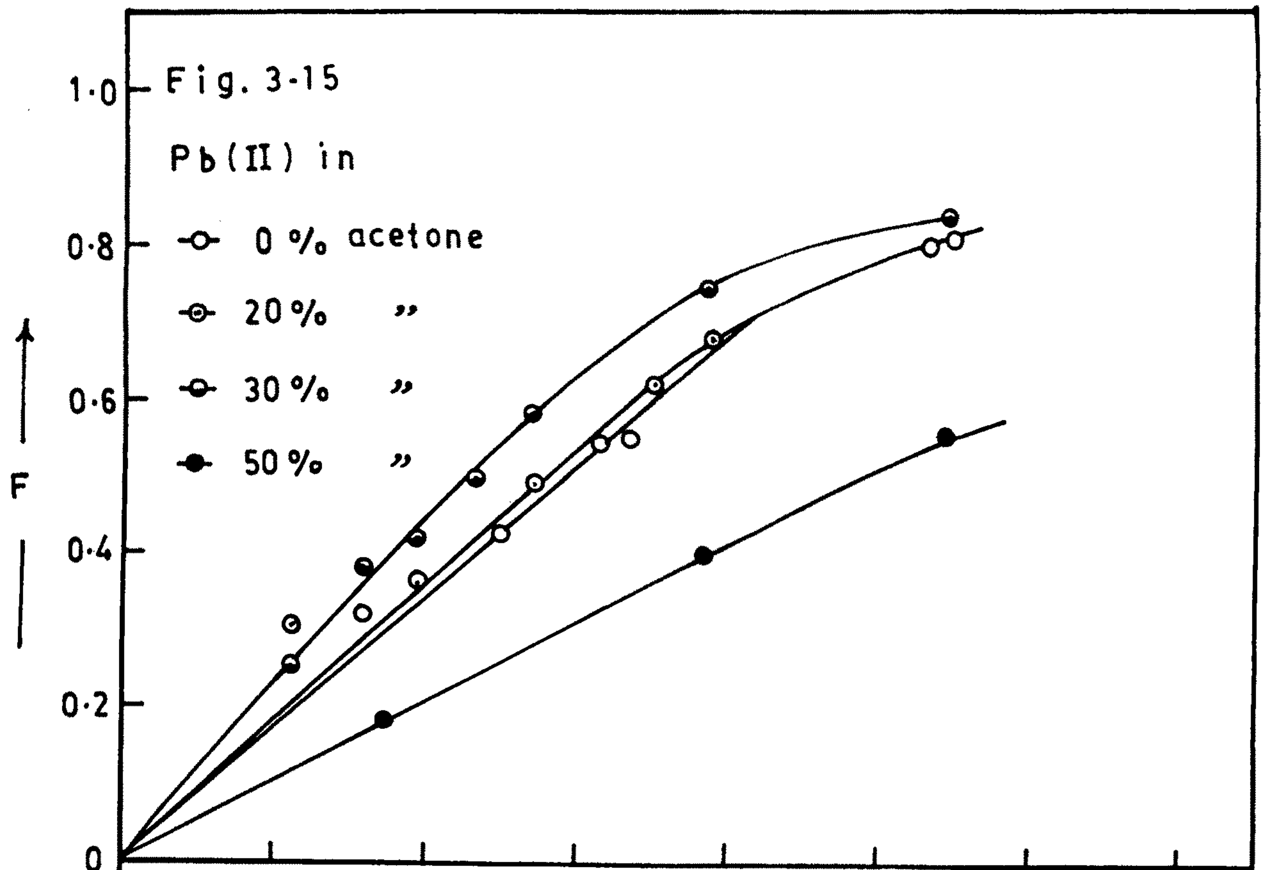


Fig. 3-15

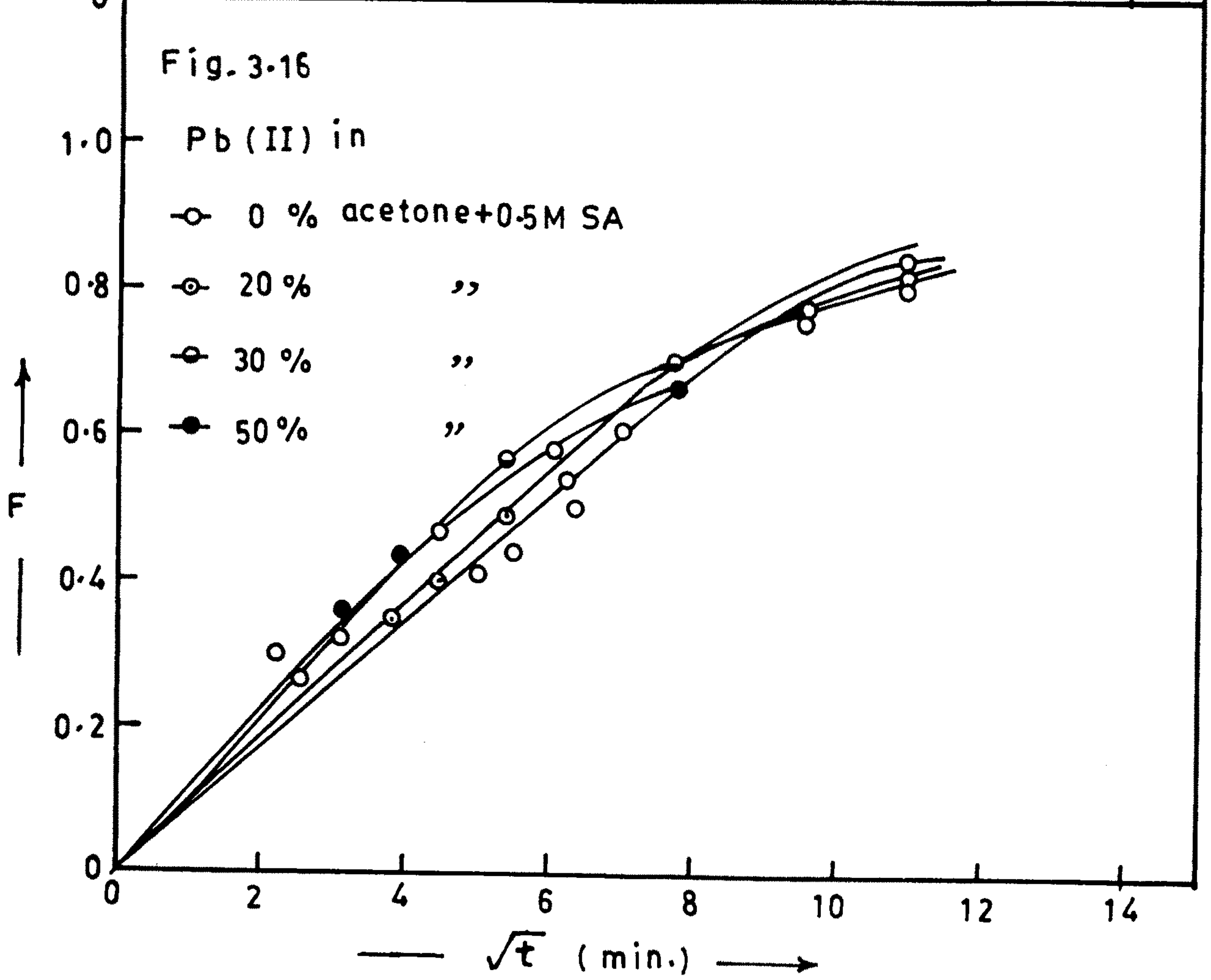


Fig. 3-16

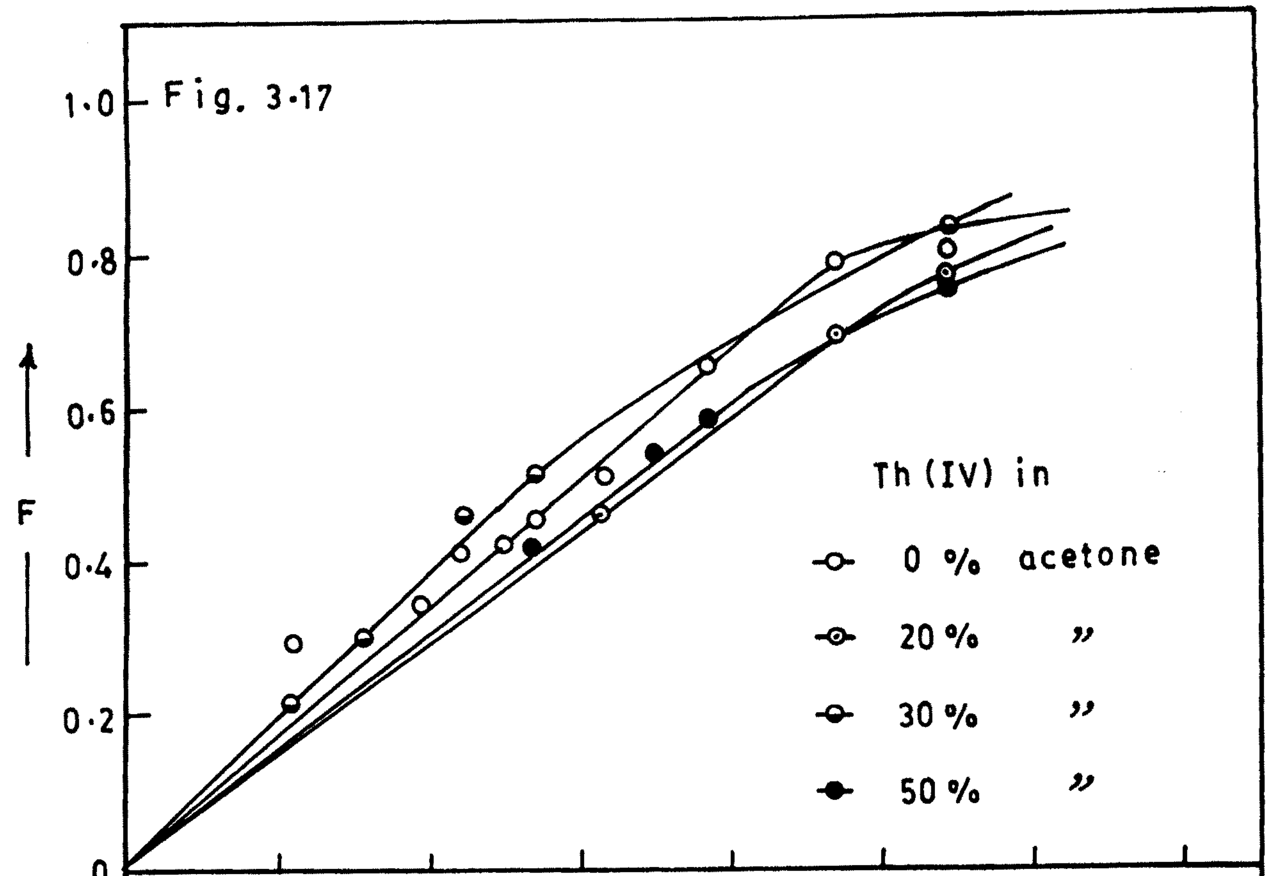


Fig. 3·17

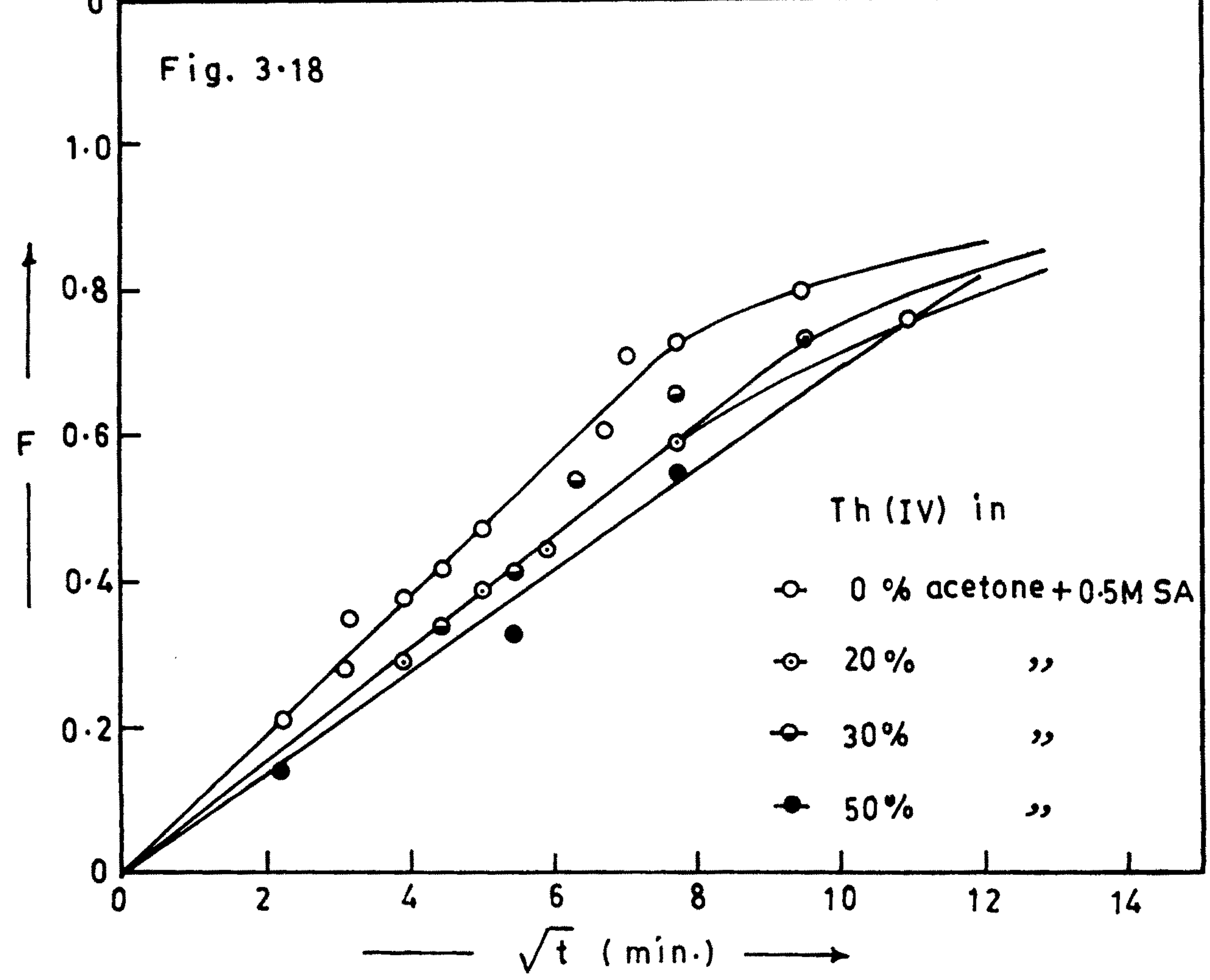


Fig. 3·18

Fig. 3·19

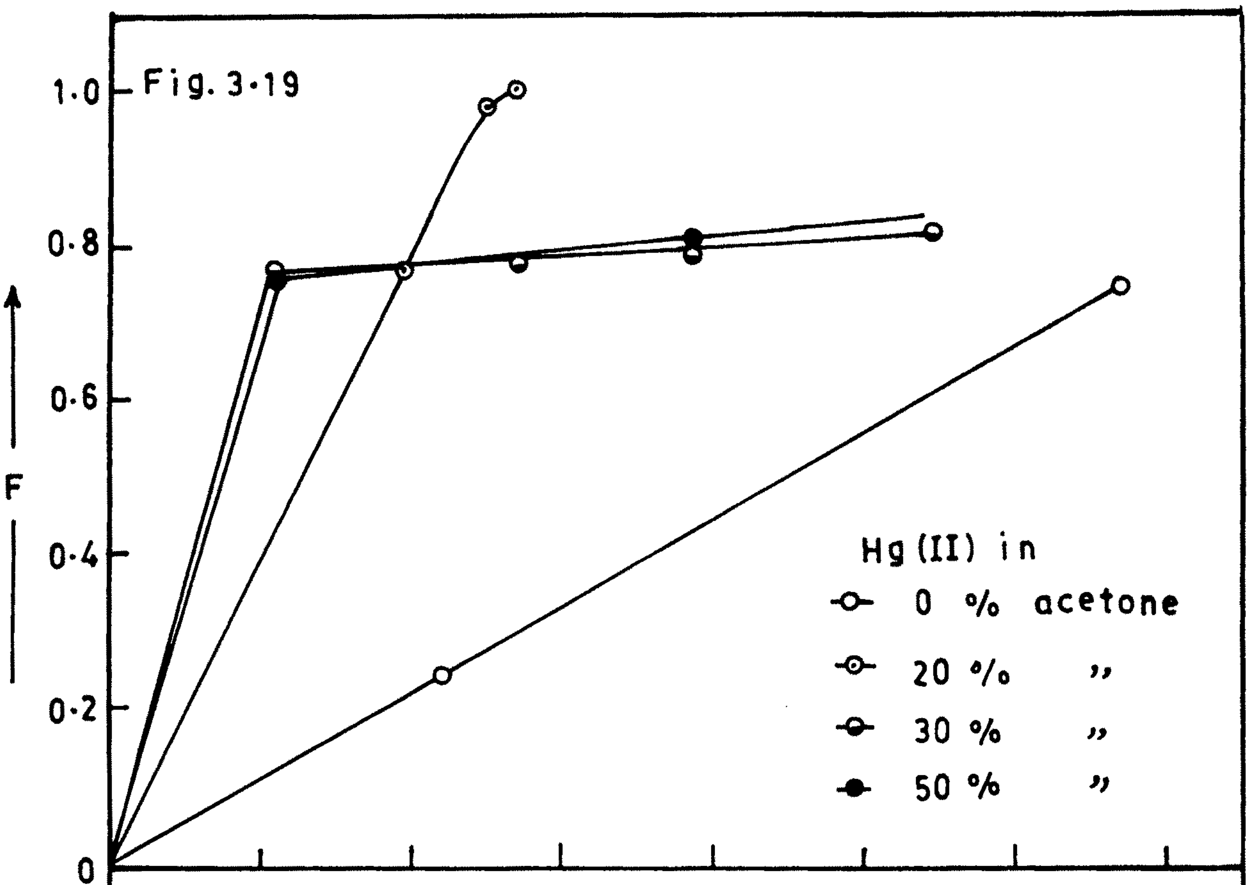
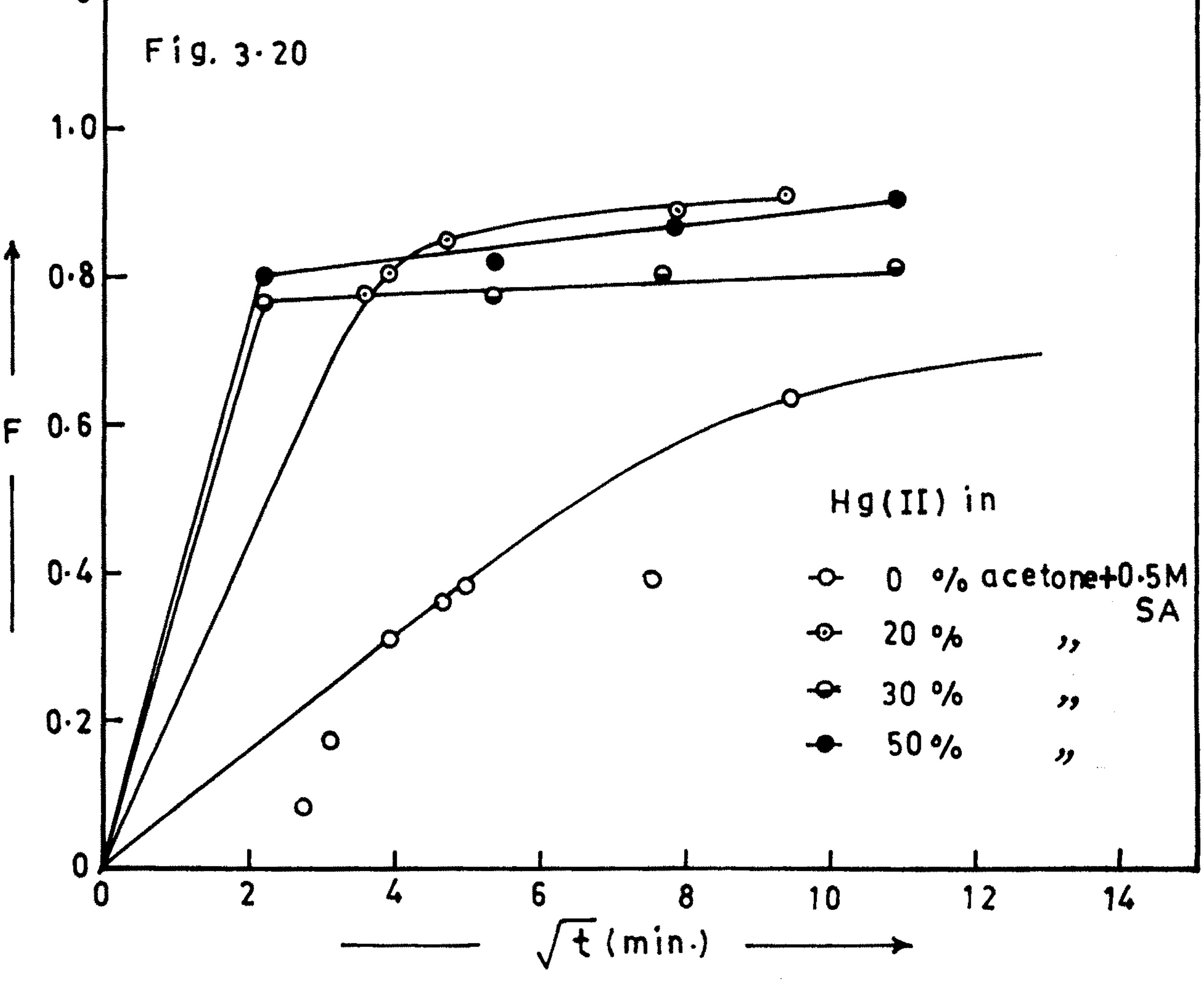


Fig. 3·20



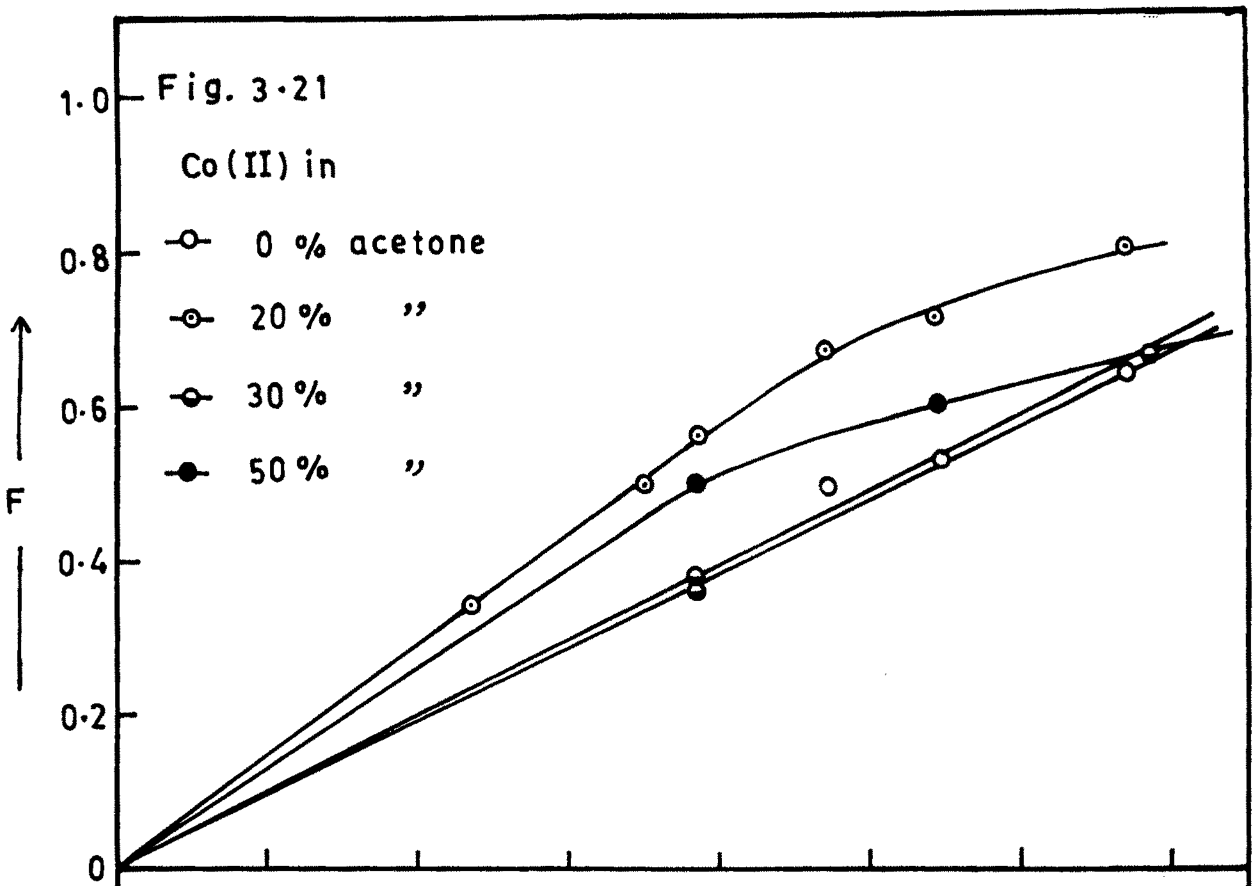


Fig. 3·21

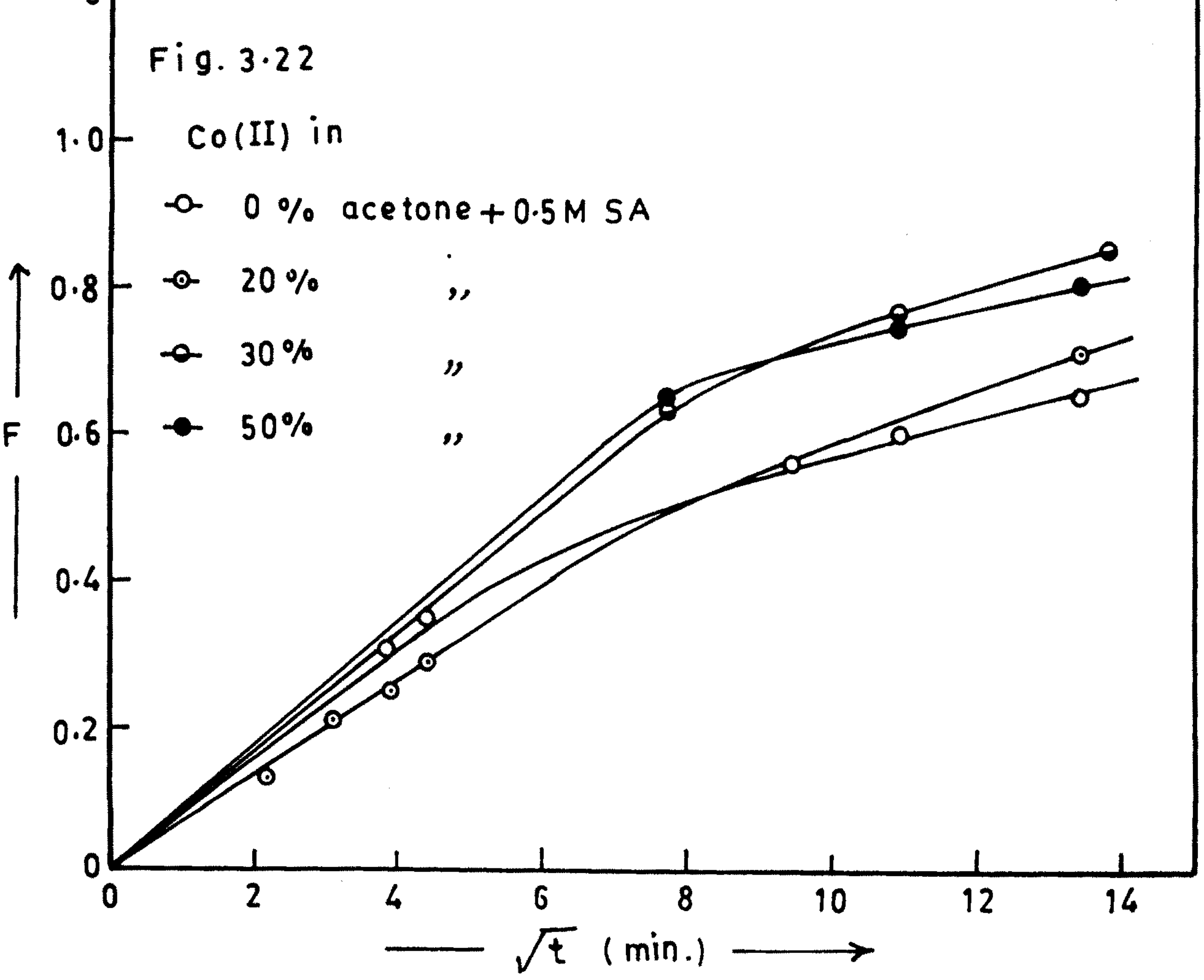


Fig. 3·22

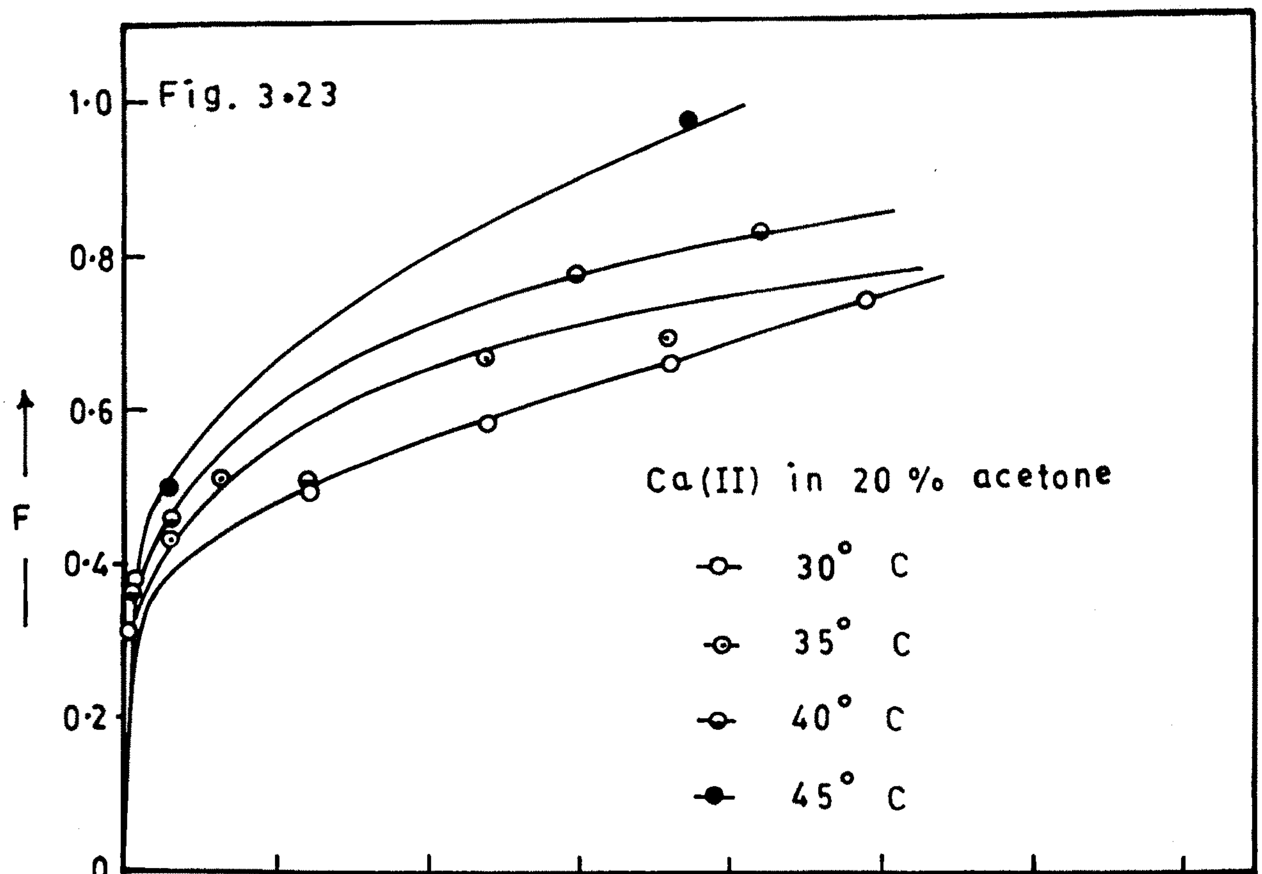
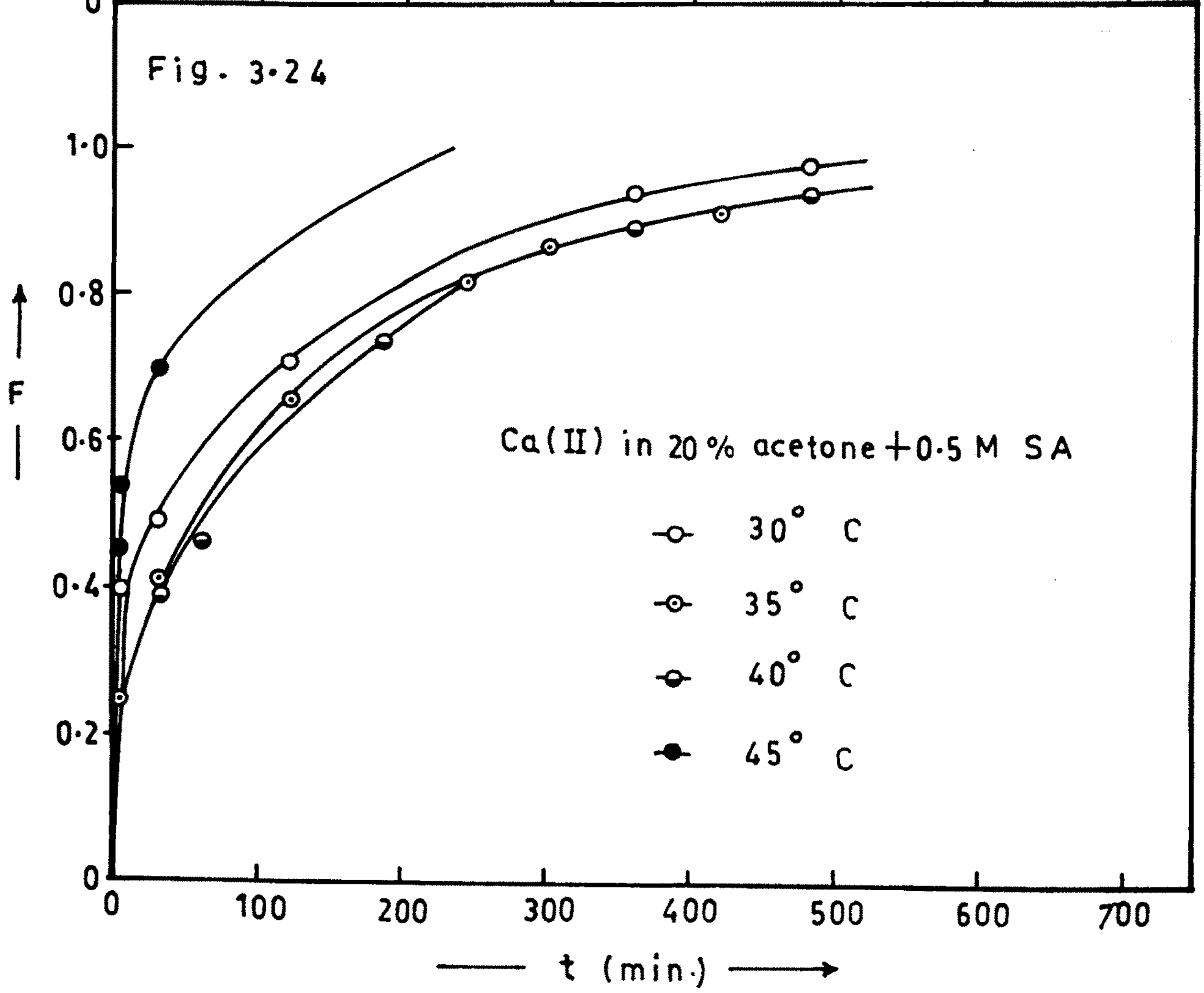


Fig. 3.23



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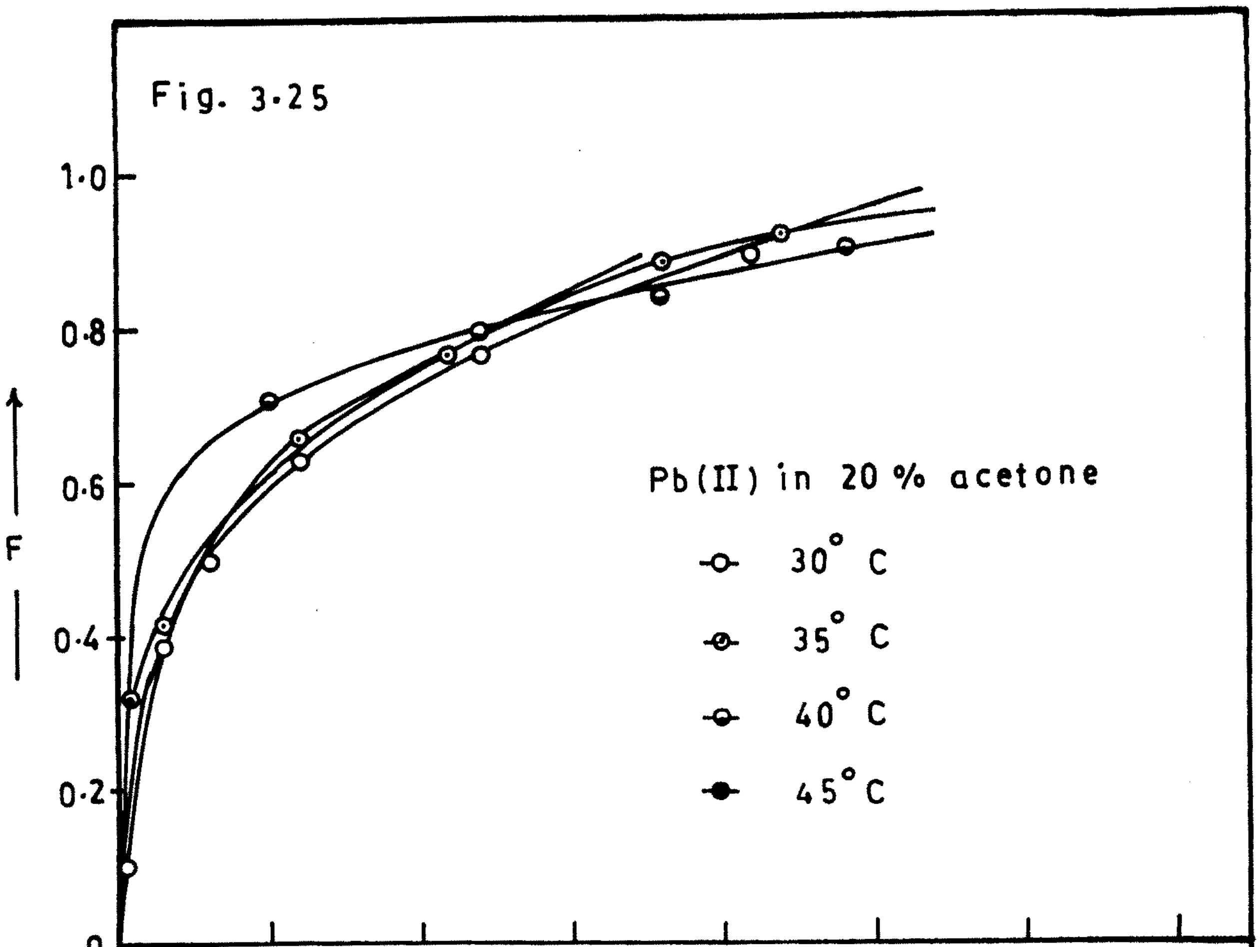


Fig. 3·25

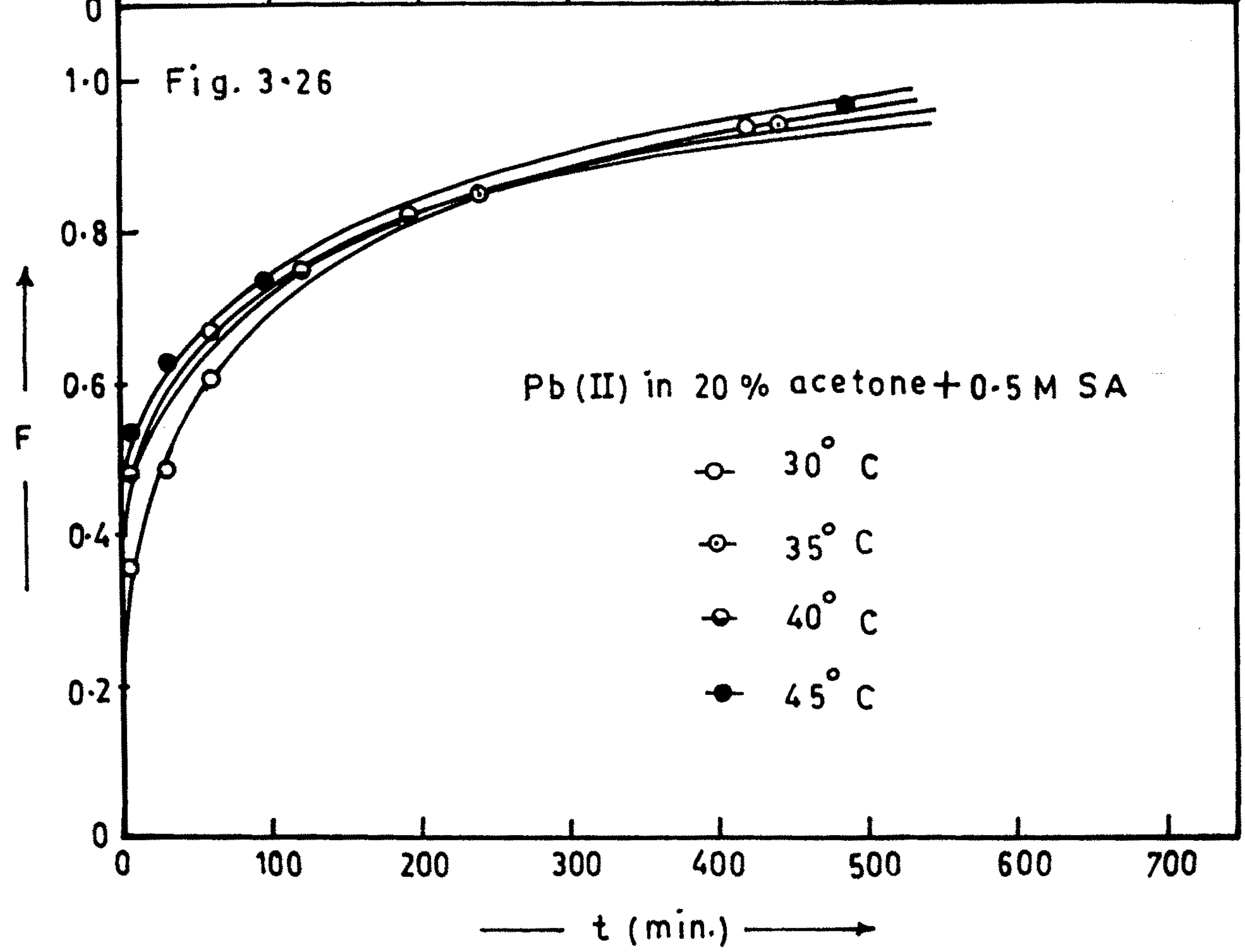


Fig. 3·26

Fig. 3·27

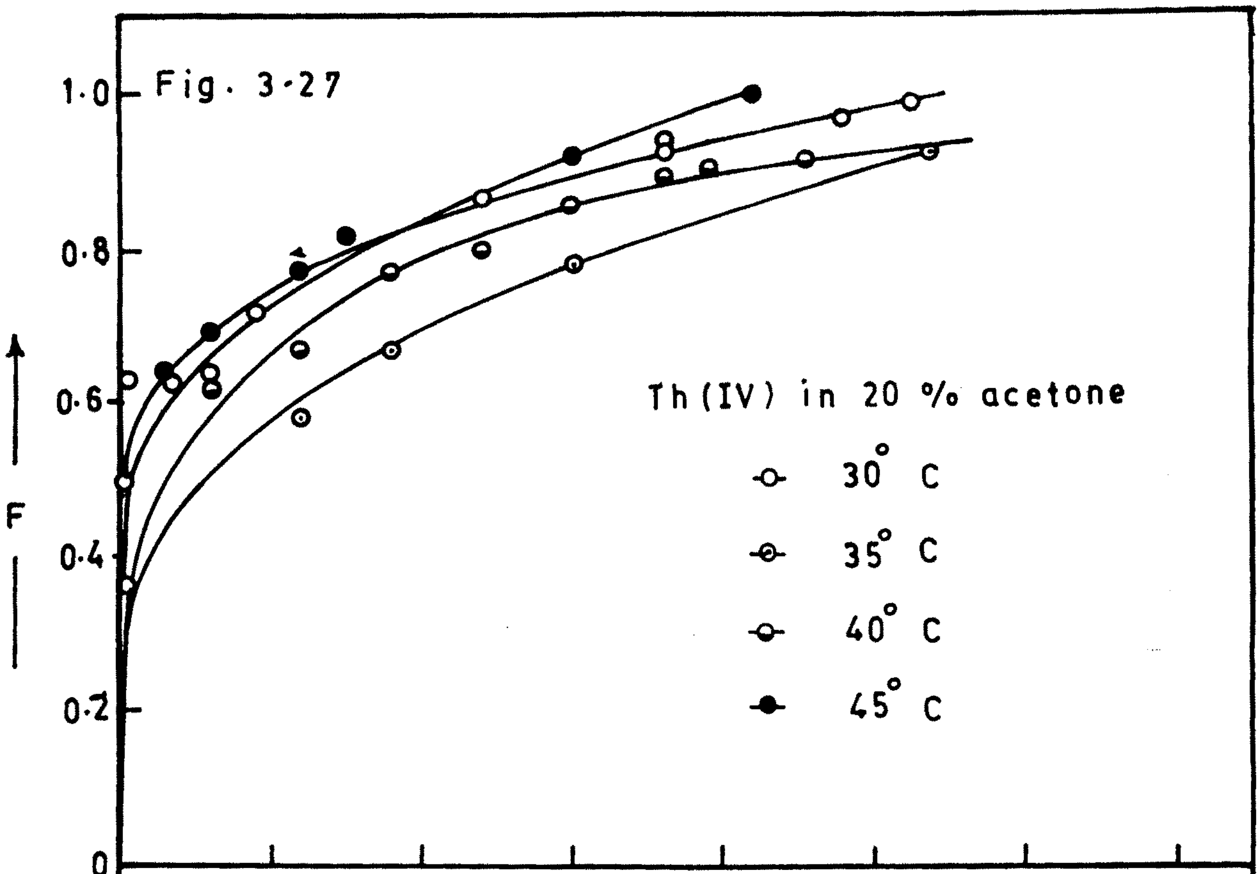


Fig. 3·28

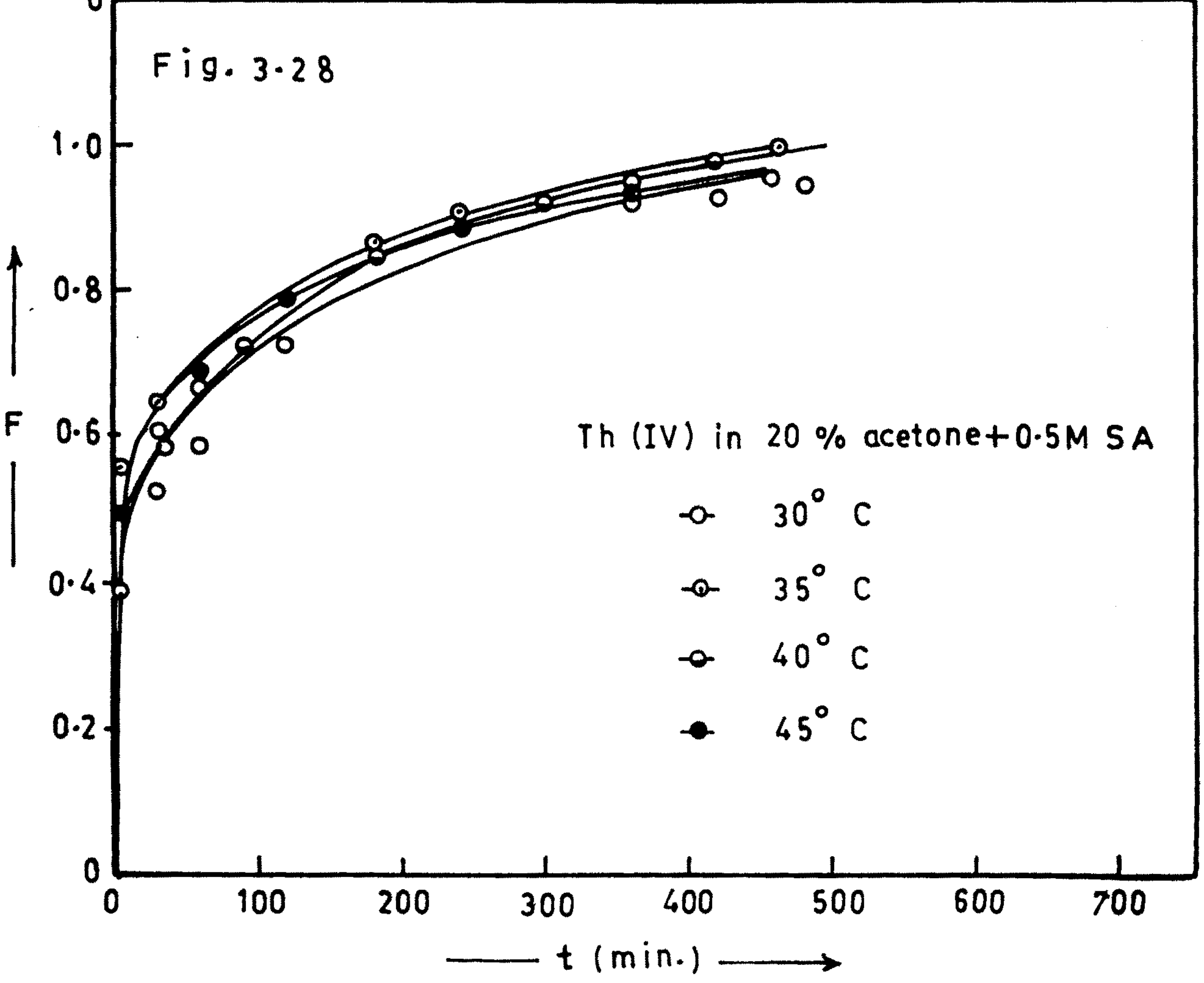


Fig. 3·29

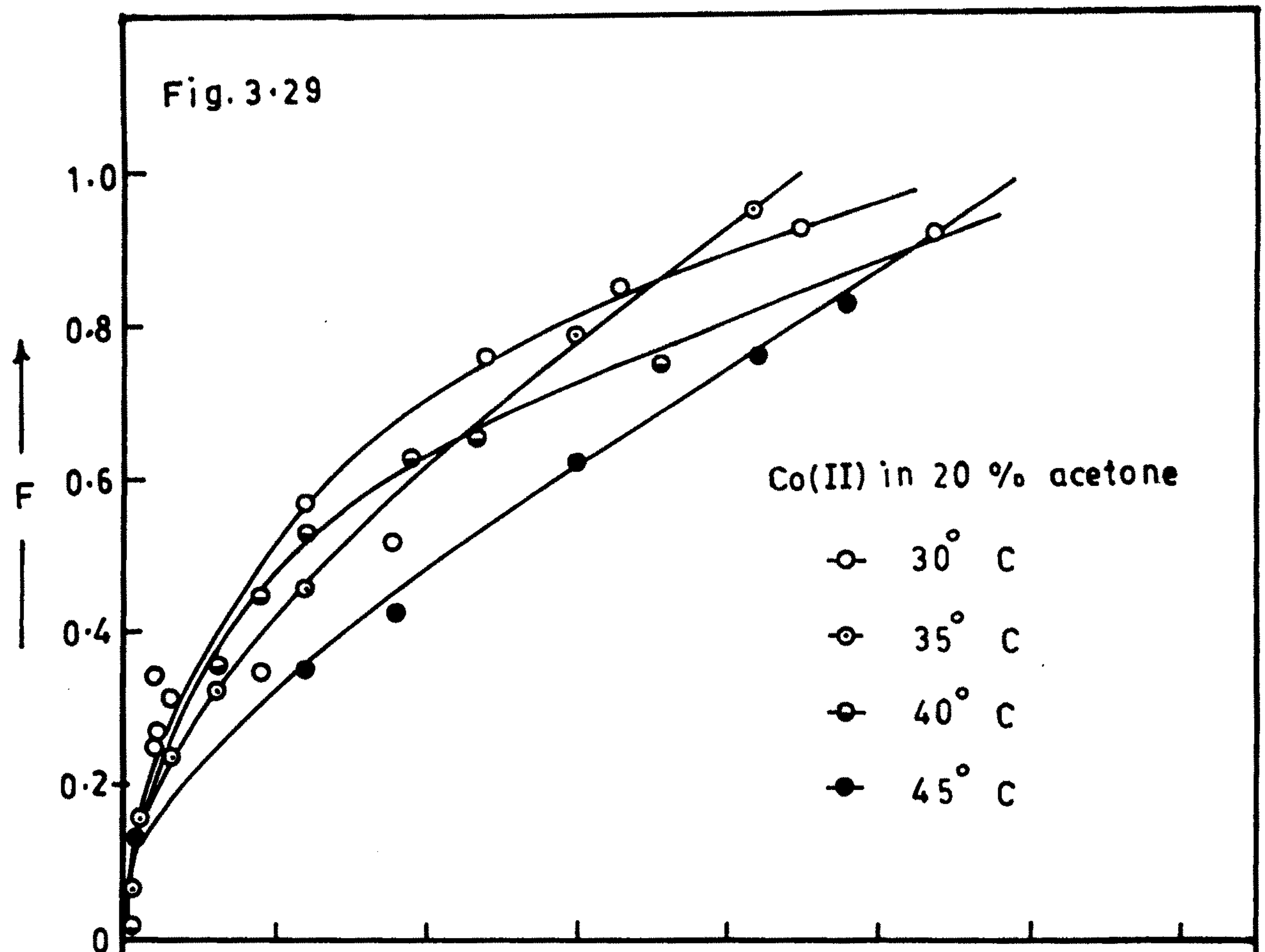
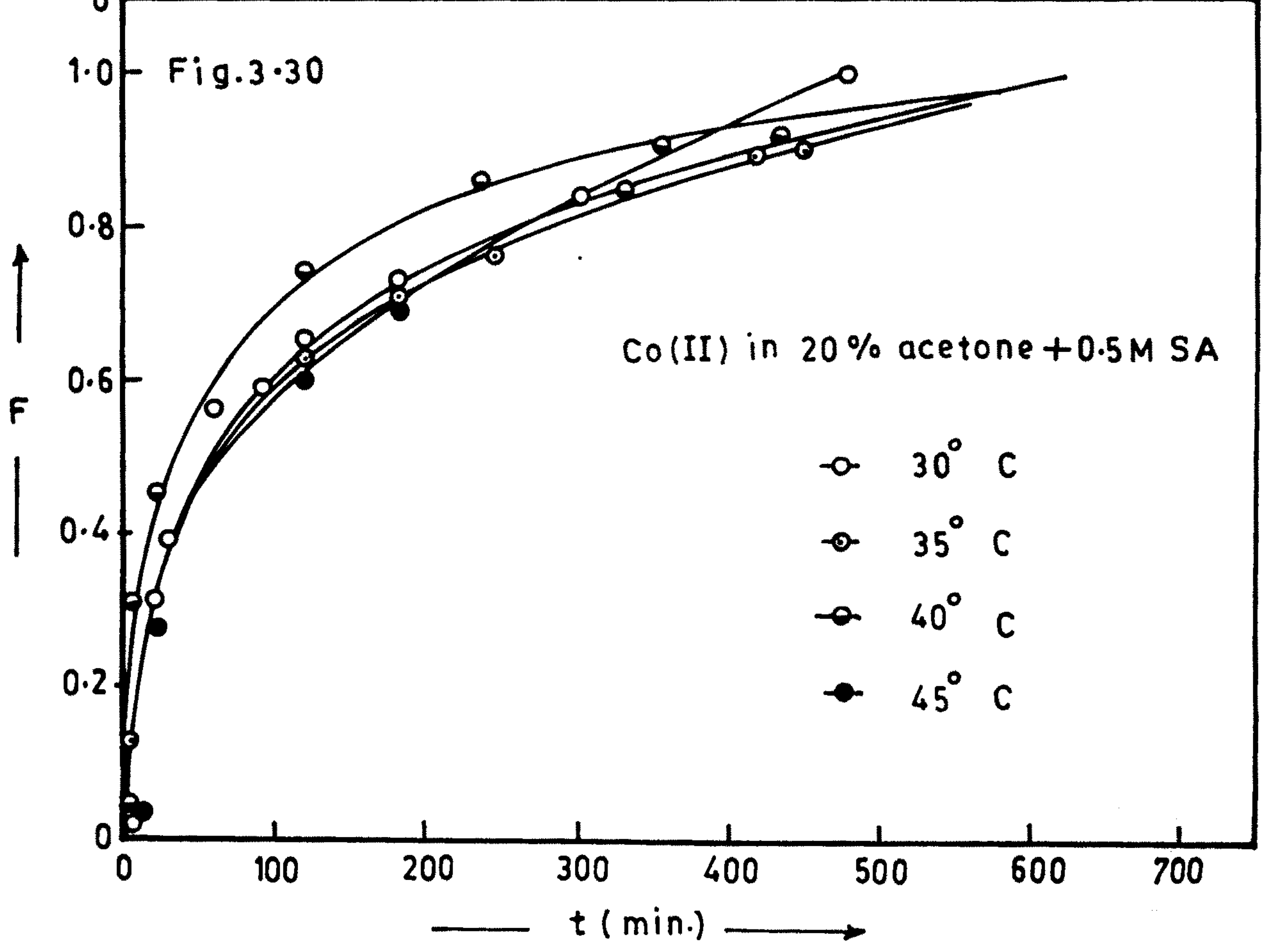


Fig. 3·30



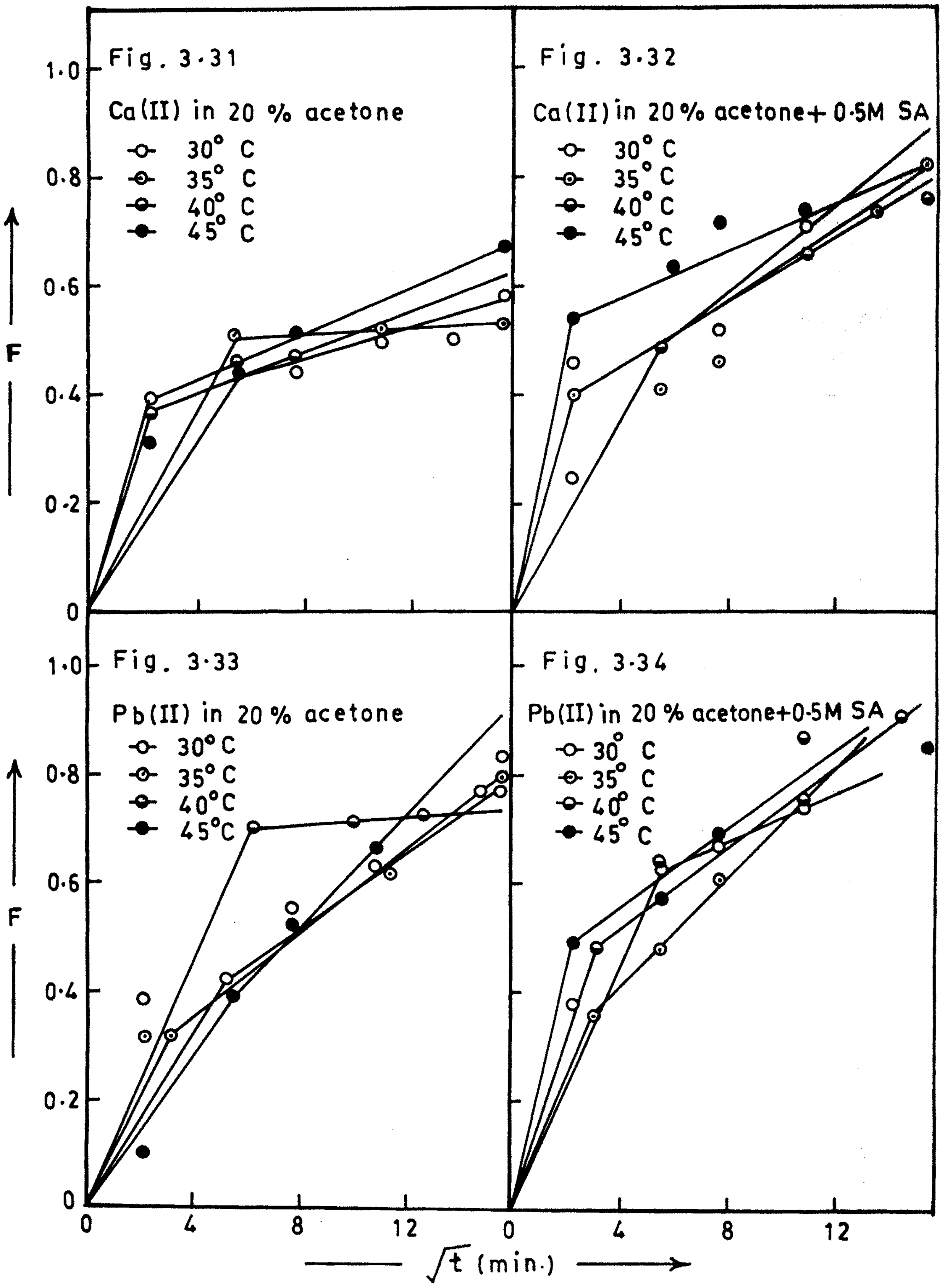


Fig. 3·31

Ca(II) in 20 % acetone

Fig. 3·32

Ca(II) in 20 % acetone + 0·5M SA

Fig. 3·33

Pb(II) in 20 % acetone

Fig. 3·34

Pb(II) in 20 % acetone+0·5M SA

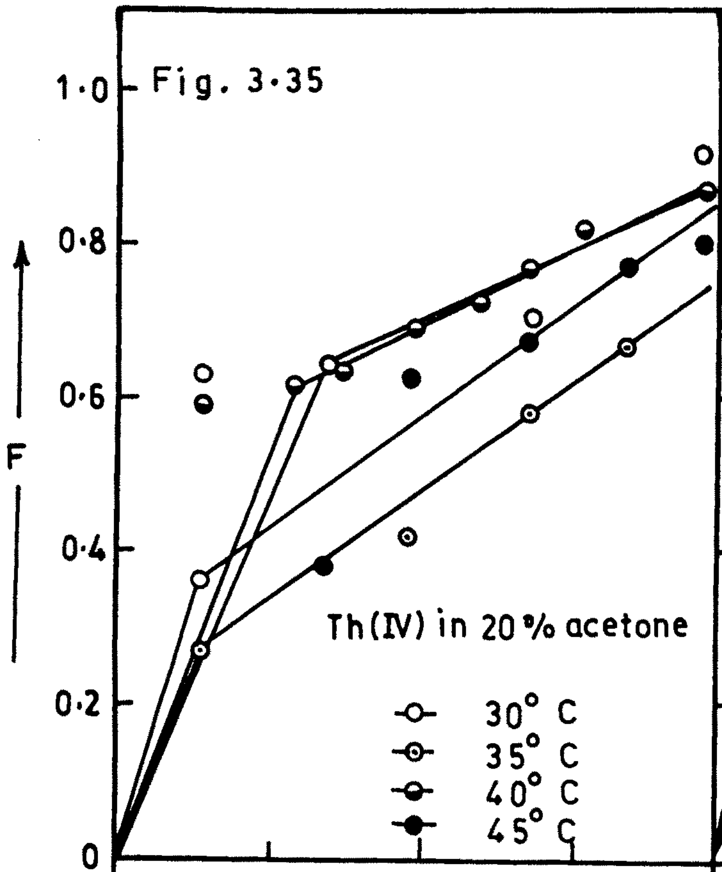


Fig. 3·35

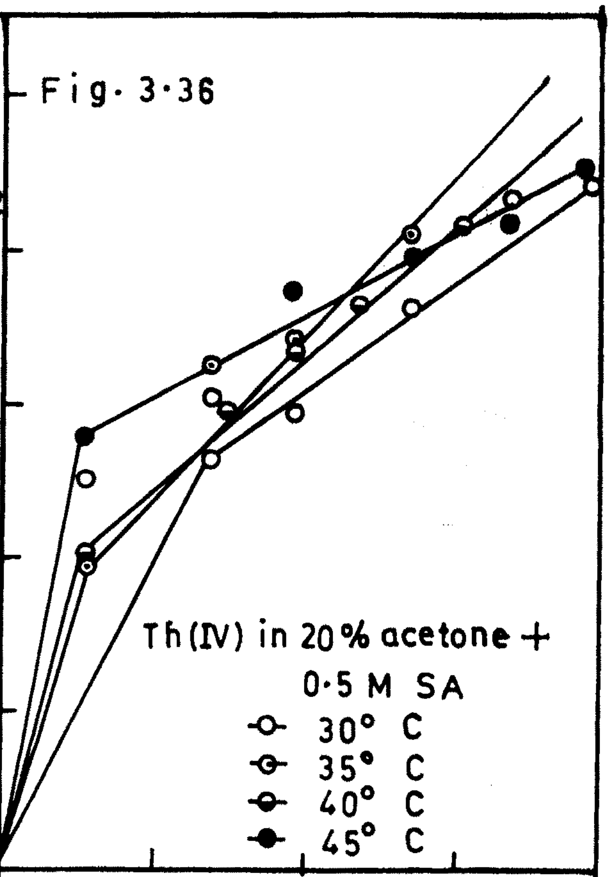


Fig. 3·36

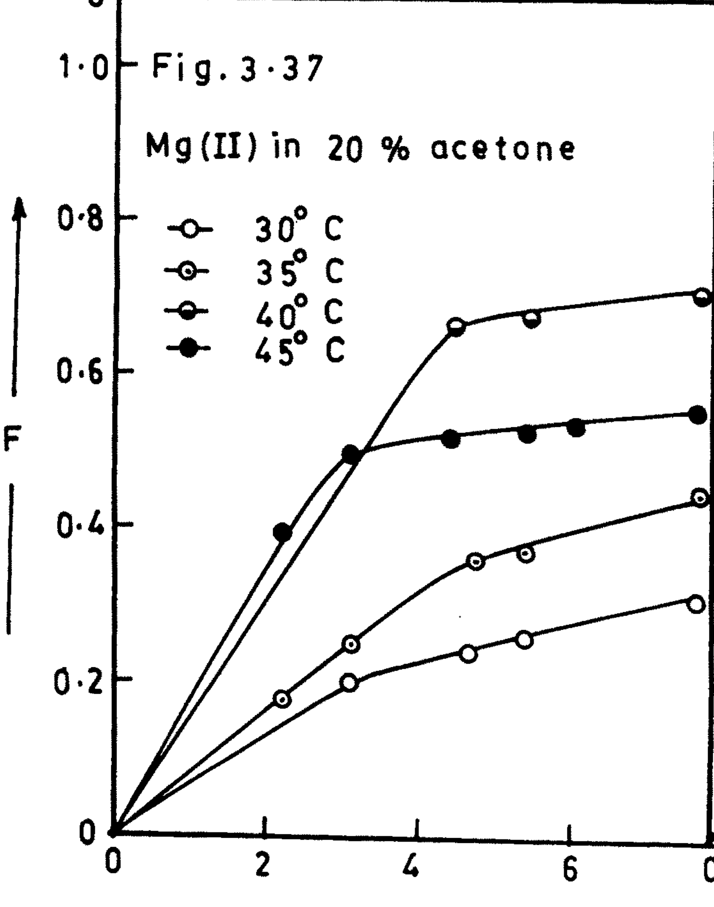


Fig. 3·37

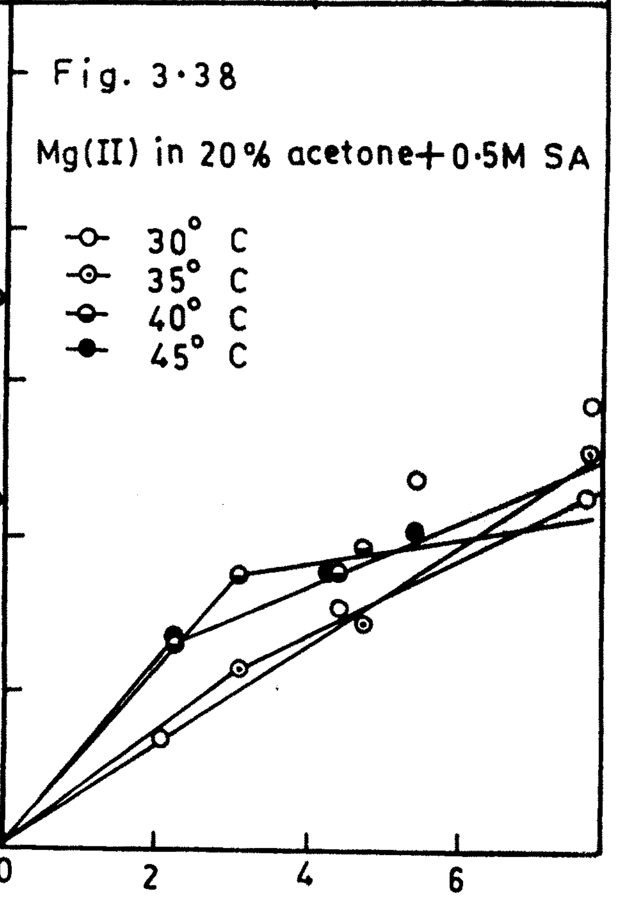


Fig. 3·38

Fig. 3·39

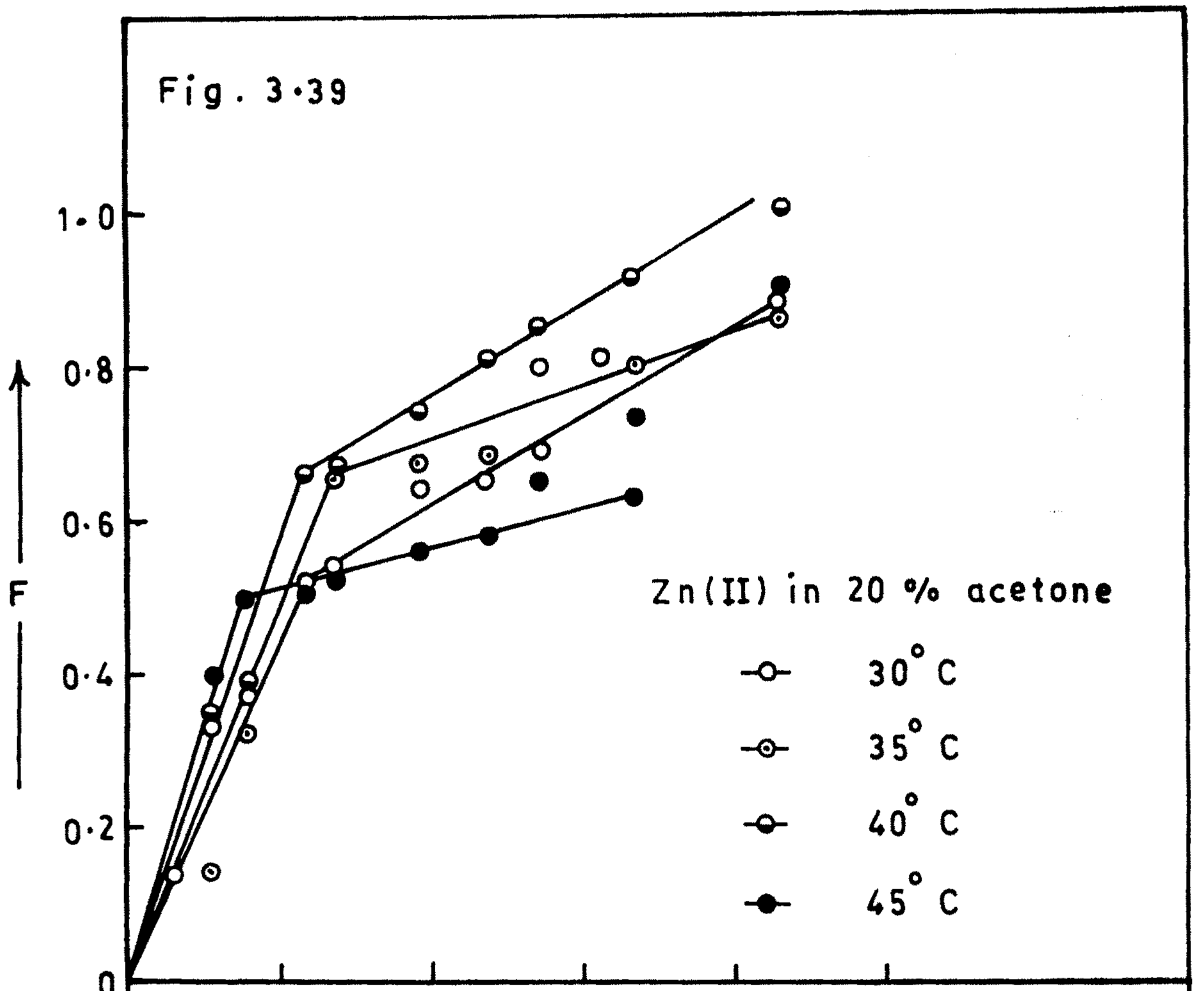
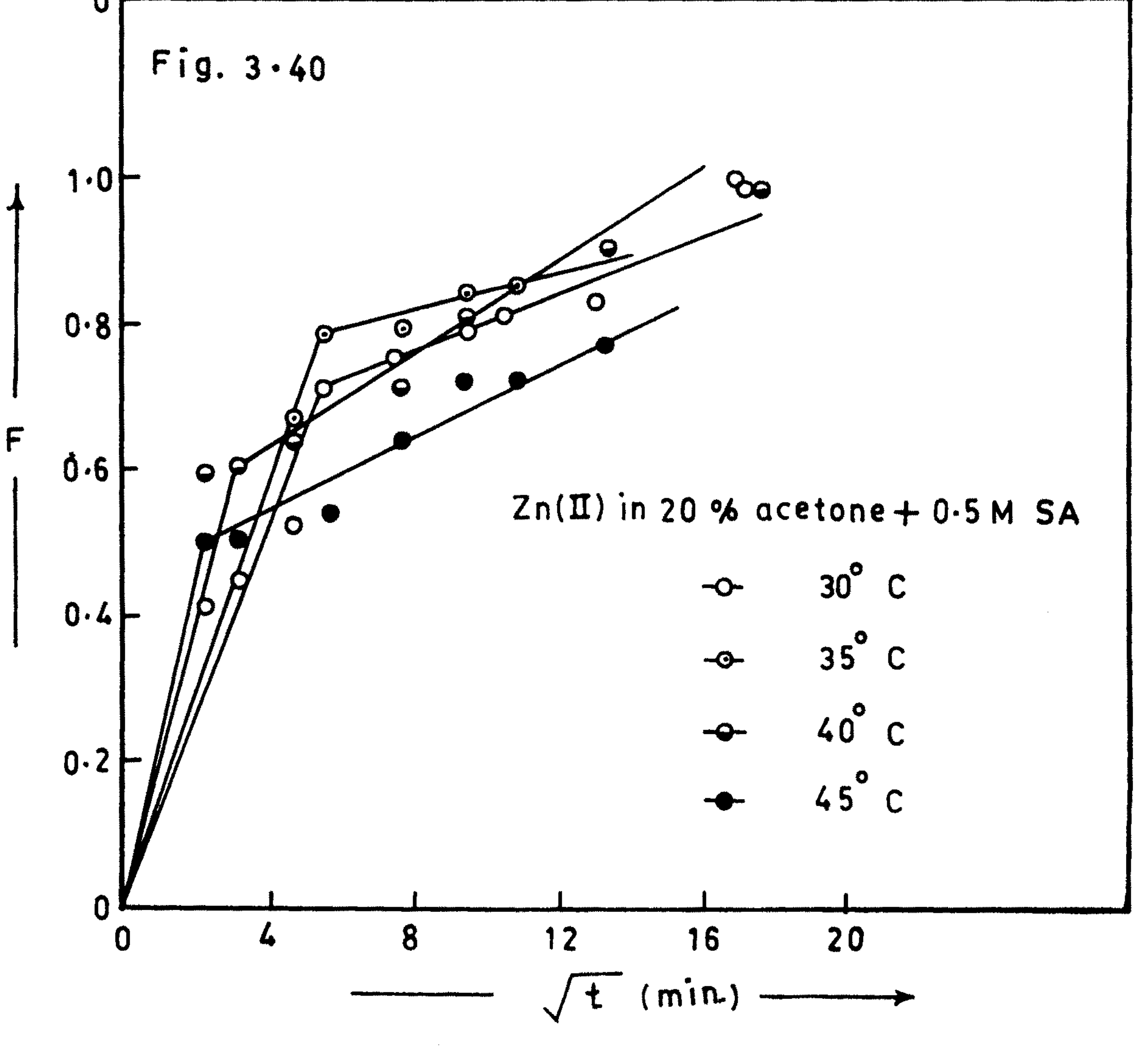


Fig. 3·40



$$F = \frac{6}{r}\sqrt{\frac{Dt}{\pi}}$$

According to this equation F against t plot gives a linear relation for small values of t and then becomes curved. The slopes of the straight lines in this figure give the values of interdiffusion coefficients of the ion exchange systems. The values of D of the various systems are given in tables $3C_{22}$ and $3C_{23}$.

The half exchange time $t_{\frac{1}{2}}$ values of interdiffusion process for the concerned ion exchange systems were calculated from equation

$$t_{\frac{1}{2}} = 0.030\,\frac{r^2}{D} \quad \text{or} \quad 0.0287\,\frac{r^2}{D}$$

(A) Effect of concentration of Acetone:

The values of F, fractional attainment of equilibrium, presented in table $3C_1$ to $3C_{21}$ and the graphs of F versus t Fig 3.1 to 3.12 and 3.23 to 3.30 give an idea about the exchange processes concerned. It was observed that managanese was least preferred by Dowex 50 W-X8 H^+ form. This can also be seen by the distribution coefficients of the managanese in aqueous acetone succinic acid solution. Very small KD values (table $4C_2$) indicate the low sorption tendency of managanese. In absence of the acids M^{n+}/H^+ exchange was shown to be slow. All other metal ions Cu, Zn, Mg, Ca. Pb, Th, Al, Hg, Ni, Cd, Co show high distribution coefficients with succinic acid. (table $4C_2$.) at each concentration of acid and acetone. So M^{n+}/H^+, $M^n({}_nSA)^{n+}/H^+$ exchanges for these metal-ions are observed to the larger extent.

TABLE-3C_{22}

KIENTIC PARAMETERS OF M^{n+} / H^{+} AT VARIOUS PERCENTAGES OF ACETONE

Metal	Acetone percentage	$t_{1/2}$ observed in min.		D $cm^2 min^{-1}$ D X 10^{-7}		k Parabolic Diffusion constant	
		a	b	a	b	a	b
1	2	3	4	5	6	7	8
Cu(II)	0	32	39	7.61	6.24	0.081	0.0766
	20	58	36	4.2	6.76	0.060	0.0766
	30	66	38	3.69	6.41	0.0621	0.0723
	50	20	52	1.21	4.68	0.0866	0.0713
Zn(II)	0	4	28	60.91	8.7	0.1391	0.0894
	20	14	26	17.4	9.37	0.1442	0.0958
	30	18	2	13.53	121.8	0.1557	0.142
	50	21	3	11.60	81.22	0.125	0.115
Mg(II)	0	80	82	3.04	2.97	0.0561	0.0484
	20	110	132	2.21	18.4	0.0512	0.0438
	30	70	32	3.48	7.6	0.0488	0.06
	50	56	80	4.35	3.04	0.0546	0.0465
Ca(II)	0	55	46	4.43	5.29	0.066	0.053
	20	38	84	6.4	2.9	0.0837	0.0625
	30	48	56	5.07	4.3	0.064	0.0638
	50	60	40	4.07	6.09	0.0714	0.0798
Pb(II)	0	30	32	8.12	7.61	0.0838	0.0862
	20	28	25	8.7	9.7	0.0728	0.0921
	30	15	18	6.2	13.5	0.0931	0.093
	50	99	16	2.46	15.5	0.091	0.0915
Th(Iv)	0	34	30	7.1	8.12	0.083	0.0956
	20	43	38	5.66	6.4	0.0703	0.0763
	30	26	45	9.3	5.53	0.0928	0.076
	50	43	50	5.66	4.87	0.0744	0.08

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1	2	3	4	5	6	7	8
Al(III)	0	124	109	1.965	2.23	0.043	0.05
	20	125	20	1.949	12.18	0.0376	0.0945
	30	137	125	1.77	1.94	0.0487	0.0528
	50	70	3	3.48	81.22	0.0561	0.072
Hg(II)	0	72	43	3.38	5.6	0.056	0.079
	20	3	5	81.2	48.7	0.2	0.208
	30	3	4	81.2	60.91	0.3575	0.347
	50	4	2	60.91	121.8	0.344	0.384
Ni(II)	0	54	66	4.5	3.69	0.06	0.0842
	20	34	56	7.16	4.35	0.0737	0.07
	30	7	115	34.81	2.11	0.0714	0.06
	50	85	135	2.86	1.8	0.0583	0.0412
Cd(II)	0	56	22	4.35	11.07	0.0702	0.108
	20	58	15	4.20	16.24	0.063	0.125
	30	20	7	12.18	34.81	0.0827	0.145
	50	60	15	4.0	16.24	0.075	0.114
Co(II)	0	111	70	2.19	3.48	0.048	0.0769
	20	52	70	4.68	3.48	0.069	0.0644
	30	104	24	2.34	10.15	0.05	0.0833
	50	60	18	4.06	13.53	0.0637	0.084
Mn(II)	0	125	70	1.942	3.48	0.0459	0.0524
	20	220	195	1.1	1.24	0.03285	0.0375
	30	140	60	1.7	4.06	0.0474	0.0467
	50	101	75	2.4	3.24	0.04125	0.06435

a= Aqueous acetone

b= Aqueous acetone + 0.5 M SA

TABLE-3C$_{23}$

KINETIC PARAMETERS OF M^{n+}/H^{+} AT VARIOUS TEMPERATURES

Metal	Temperature °C	t1/2 observed in min.		D cm^{2}min^{-1} D X 10^{-1}		Parabolic diffusion Constant k	
		a	b	a	b	a	b
1	2	3	4	5	6	7	8
Cu(II)	30	170	135	1.43	1.8	0.065	0.045
	35	60	25	4.06	9.47	0.07	0.081
	40	65	60	3.74	4.06	0.074	0.085
	45	170	107	1.43	2.27	0.043	0.077
Zn(II)	30	16	10	15.22	24.36	0.061	0.13
	35	22.5	4	10.83	60.91	0.12	0.14
	40	15	4	16.24	60.91	0.143	0.1955
	45	12.5	10	19.49	24.36	0.16	0.225
Mg(II)	30	135	35	1.8	6.96	0.064	0.065
	35	70	60	3.48	4.06	0.08	0.078
	40	12.5	82.5	19.49	2.95	0.1525	0.113
	45	5	52.5	48.73	4.64	0.17	0.13
Ca(II)	30	120	27	2.03	9.0	0.0775	0.0875
	35	30	57	8.1	4.2	0.09	0.0875
	40	45	65	5.4	3.7	0.085	0.18
	45	65	5	3.74	48.7	0.14	0.245
Pb(II)	30	55	3	4.43	81.22	0.08	0.115
	35	50	30	4.87	81.22	0.1	0.12
	40	10	5	24.3	48.73	0.11	0.16
	45	50	10	4.87	24.36	0.07	0.22

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1	2	3	4	5	6	7	8
Th(IV)	30	2.5	4.0	97.47	60.91	0.115	0.098
	35	56.0	5.0	4.35	48.73	0.125	0.175
	40	4.0	7.0	60.91	34.81	0.135	0.19
	45	32.0	5.0	7.61	48.73	0.17	0.255
Cd (II)	30	115.0	4.0	2.11	60.9	0.165	0.31
	35	65.0	6.0	3.74	40.61	0.125	0.23
	40	70.0	5.0	3.48	48.73	0.125	0.205
	45	45	7.0	5.41	34.81	0.125	0.21
Co(II)	30	210.0	65.0	1.16	3.74	0.055	0.075
	35	100.0	32.0	2.43	7.61	0.075	0.068
	40	135.0	55.0	1.80	4.43	0.044	0.0637
	45	95.0	60.0	2.56	4.06	0.053	0.058
Mn(II)	30	50.0	7.0	8.12	34.81	0.081	0.11
	35	150.0	5.0	6.96	48.73	0.145	0.235
	40	3.0	2.0	6.09	121.83	0.285	0.345
	45	100.0	40.0	5.41	60.91	0.075	0.17

a= 20 %Acetone

b= 20 % Acetone + 0.5 SA

The half exchange time $t_{\frac{1}{2}}$ (table $3C_{22}$) increases as the percentage of acetone is increased. As per equation $t_{\frac{1}{2}} = 0.03\frac{r^2}{D}$, $t_{\frac{1}{2}}$ is inversely proportional to D and hence the values of D decreases with the rise in concentration of acetone. The values of D from (table $3C_{22}$) show similar behaviour .

The various possible factors contributing to this observation are (i) the swelling and solvent fraction behavious of H^+ as well as metal forms of Dowex 50 W-X8 in mixed media. (ii) the solv-ated size of ions in these media (iii) selectivities of the resin for various ions in various media, and (iv) the viscosities of the solvent mixtures and electrolyte solutions in these solvent mixtures.

The solvated size of the ions under study are governed by the overall solvation of the ions in the specific solvent medium. In mixed solvent, cations are usually preferentially solvated by water ; the extent to which the organic solvent is excluded from the solvation shell depends upon the ability of the organic solvent to solvate the cation. In this context, a study by Zipp[13] shows that alkali metal cations are solvated almost equally by acetone and methanol. The similarity in the solvating tendency of these organic solvents for alkali metal ions implies that the cations in aqueous acetone or aqueous methanol solvents would have a solvation shell consisting of water molecules and more or less, the same number of organic solvent molecules, depending upon the composition of the mixed solvent.

In the mixed solvent systems ionic selectivities of the resins have also been considered as a factor influencing the rates.

The viscosities of the aqueous-acetone-carboxylic acid solutions are generally not available in the literature. However, the viscosities of the aqueous - acetone itself, may give an indication of the general variations of the viscosities of the various solutions. The viscosities in acetone water system at 0, 20, 44% acetone are reported[15] as 8.95, 10.7, 10.0 millipoise respectively.

It can be seen that the viscosities[15] of the water-acetone mixtures are significantly higher than that of water and seen to be responsible for the lowering of rates in these media as compared to aqueous medium. The variations of D for the same types of exchange $M^{n}({}_{n}SA)^{n+}/H^{+}$ acetone water mixtures as a function of percentage of acetone does not correlate with the viscosity variations. This emphasizes that all the factors mentioned above should be taken in to consideration. Similar conclusion that the role of viscosities of acetone-water and methanol-water mixtures in Li^{+}/H^{+}, Na^{+}/H^{+} and K^{+}/H^{+} exchanges on cationic resin was studied by Nandan and Gupta[16] and the values of F was found to be decreasing with rise in concentration of acetone (from 0-44.2%)

The curves F versus t for Cu(II), Zn(II) , Ca(II) Pb(II), Th(IV), Al(III), Hg(II), Ni(II), Cd(II), Co.(II), Mn(II), and Mg(II) exchanges on Dowex 50 W-X8H^+ resin in aqueous acetone, aqueous acetone-SA are presented by figs. 3.1 to 3.12. The curves show that almost complete exchange takes place for the whole range of mixed solvent (H_2O-$CH_3CO.CH_3$) composition. The attainment of exchange equilibrium in water is faster than $\left[H_2O\cdot CH_3\ CO\ CH_3\right]$ media.

The rate-determining step in ion exchange is, as a rule, interdiffusion of the counter ions either in the resin itself or across an adherent liquid film. The slower of these two processes controls the over-all rate. In systems with organic solvents, the mobilities of the counter ions in the resin are usually lower than in aqueous system because swelling is less pronounced and electrostatic interactions with fixed changes are stronger. Particle diffusion thus is relatively slow and usually is the rate-controlling mechanism[17].

In the process of ion exchange in mixed aqueous-organic solvents, the resin accumulates water in its pores. Electrolyte sorption may be particularly strong. At the same time , the mobilities of the counter ions in the resin remain relatively high because the presence of water guarantees at least moderate swelling and ionic-dissociation. This shows that , in many cases, ion exchange rates can be considerably increased by addition of water to the organic solvent[18, 19, 20].

Values of Bt versus t plots are shown in figs 3.41 to 3.48.

B values

$B = \frac{\pi^2 D}{r^2}$, where D is the interdiffusion coefficient for exchanging ion inside the exchanger particle and r, the radius of exchanger particle. The experimental data can be tested to determine whether or not they confirm to equation.

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-n^2 Bt}$$

by plotting Bt values corresponding to experimentally determined F values from Reichenberg's table (table $3B_1$), against time. The plots of Bt versus time for the exchange between positively charged complexes of Zn, Cu, Mg, Co with H^+ of Dowex 50 W-X8 in aqueous acetone, aqueous acetone succinic acid are presented by figures 3.41 to 3.48. It is generally observ-ed that these plots of Bt versus t are linear passing through the origin, with constant value of inter diffusion coefficient. For the systems studied at 20 percentage of acetone and 20% acetone and 0.5 M SA, the rate of diffusion is controlled by particle diffusion. Some of the curves show slight deviations at later part indicating that in the final stages of the exchange the diffusion is not controlled by particle diffusion alone. The linear nature of Bt versus t plots indicate that the process of exchange is controlled by particle diffusion and the values of B show the following sequence

$$Cd > Zn > Pb \simeq Mn > Th(IV) > Mg \simeq Ca > Co > Cu$$

Parabolic diffusion constant 'k':-

The work of Boyd[21,13] et al and Kunin and Mayers[22] indicates that the rate of cation exchange in cation exchange resin is diffusion controlled. Boyd has distinguished between two diffusion processes. First at concentrations of less than 0.003 M, the diffusion of ions through a film of solution about each particle is considered to be the rate-determining process. Second, at concentration above 0.1M, the diffusion of ions throughout the particle becomes the rate determining step. The film diffusion must be controlling for the strong acid resins in very dilute solution and particle diffusion must be controlling in solutions of moderate concentrations.

The parabolic diffusion law[23] is,

$$F = k\sqrt{t} ,$$

Where F is the fractional attainment of equilibrium and k is a constant and may be called as the parabolic diffusion constant. The values of k were ontained from the slope of F versus $\sqrt{t}$ plots. Fig. 3.13 to 3.22 at room temperature and fig. 3.31 to 3.40 for different temperatures. The values of k for Ca, Mg, Mn, Pb, Cd, Cu, Co, Zn, Ni, Al(III), Th(IV), Hg at various percentages of acetone and at various temperatures (excluding Al(III), Hg and Ni) are presented in table $3C_{22}$.

The values of k in aqueous acetone succinic acid media were found to be greater than those in aqueous acetone media. As the temperature increases the values of k were found to be increased.

Effect of temperature:-

The values of diffusion coefficients (D) and half exchange time $t_{\frac{1}{2}}$ for exchange reactions of Cu, Zn, Cd, Co, Mn, Mg, Pb and Th(IV) with H^+ ions on Dowex 50 W-X8 in aqueous acetone, aqueous acetone-SA at 30, 35, 40, 45° C are represented in tables $3C_{23}$ and in fig. 3.31 to 3.40. It is observed that the values of D increase and those of $t_{\frac{1}{2}}$ decrease with the increase in temperature.

The problem of diffusion in porous media is usually approached with the use of either of two rather different types of models. In the model of the first type, the medium is considered as consisting of two phases, namely the solid frame work and the intersticial pore phase. Diffusion is viewed as taking place in the pores only. In such models, diffusion is necessarily slower than in the corresponding homogeneous systems having the same composition as the pore phase. In the models of the second type, the medium is considered as a single homogeneous phase, analogous to an ordinary solution. Diffusion in ion exchange resins is assumed to be no different from that in solutions of analogous organic electrolytes. Be-nzyltrimethyl ammonium chloride has been used as a model electrolyte for Dowex 1 anion exchanger in Cl^- form[24].

As in ordinary solutions, diffusion coefficients in ion exchangers increase with increasing temperature. As a rule, the increase in mobility with the temperature is some what

TABLE- $3C_{24}$

THERMODYNAMIC PARAMETERS CALCULATE-D FOR THE EXCHANGE $M^{n}(nSA)^{n+}/H^{+}$

Metal	Temperature °K	D_o cm^{2}min^{-1} $D_o \times 10^{-7}$		Ea kJ mole^{-1}		S JK mole^{-1} deg^{-1}	
		a	b	a	b	a	b
Mg(II)	303	11.89	5.754	22.8	4.918	3.737	3.995
Zn(II)	303	3.236	3.388	12.865	7.342	4.2	4.208
Co(II)	303	2.951	5.495	3.557	5.644	4.233	5.644
Cu(II)	303	19.95	15.49	29.05	22.133	3.552	3.554
Th(IV)	303	15.49	12.02	11.11	11.71	3.642	3.733
Pb(II)	303	5.012	7.079	5.76	6.384	4.044	3.92
Cd(II)	303	12.59	1.0	21.84	13.28	3.716	3.798
Ca(II)	303	6.457	15.86	14.29	26.81	3.954	3.634

a = Aqueous acetone 20 %

b = Aqueous acetone + 0.5 SA (20 %)

TABLE- $3C_{25}$

'B' VALUES

Metal	Temperature °C	B x 10^{-3}	
		a	b
1	2	3	4
Cu(II)	30	1.37	1.37
	35	4.0	4.75
	40	2.75	4.25
	45	1.75	2.37
Zn(II)	30	6.5	15.5
	35	5.75	17.6
	40	1.28	11.8
	45	4.37	9.0
Mg(II)	30	1.5	6.0
	35	4.5	3.33
	40	9.0	5.55
	45	6.5	4.62
Ca(II)	30	1.75	6.25
	35	3.0	5.0
	40	4.0	5.0
	45	2.75	6.75
Pb(II)	30	6.25	9.0
	35	3.75	8.0
	40	4.87	11.0
	45	5.25	12.0

Contd. on next page

1	2	3	4
Th(IV)	30	6.25	6.0
	35	3.5	10.6
	40	7.87	8.37
	45	4.62	7.5
Cd(II)	30	2.75	18.7
	35	3.75	26.2
	40	3.5	12.5
	45	4.87	11.5
Co(II)	30	8.75	3.25
	35	2.62	7.0
	40	3.75	4.25
	45	2.0	4.0
Mn(II)	30	5.37	11.5
	35	1.5	5.25
	40	4.75	8.25
	45	2.25	4.62

[a] a= 20%Acetone

b= 20% Acetone + o.5 M SA

TABLE- $3C_{26}$

RATE CONSTANT 'k' FOR M^{2+} ON DOWEX 50 W-X8 H^+ FORM

Metal Ion	Temperature, °C	k min^{-1} Water + Acetone 20% (v/v) k X 10^{-3}	k min^{-1} Water + Acetone + 0.5 M SA (20% v/v) k X 10^{-3}
1	2	3	4
Cu(II)	30	0.668	4.8
	35	5.05	5.6
	40	2.41	4.19
	45	2.09	1.58
Zn(II)	30	8.94	5.43
	35	0.95	9.74
	40	4.56	4.31
	45	3.71	5.59
Mg(II)	30	3.625	7.95
	35	6.23	6.144
	40	3.166	3.477
	45	4.6	6.24
Ca(II)	30	1.66	4.6
	35	0.31	6.1
	40	0.619	1.35
	45	2.58	6.1
Pb(II)	30	4.02	7.22
	35	5.9	7.36
	40	0.88	7.6
	45	4.3	5.75

Contd. on next page

1	2	3	4
Th(IV)	30	1.91	7.31
	35	4.76	7.46
	40	7.88	7.72
	45	4.45	7.31
Cd(II)	30	3.16	10.0
	35	5.45	237.0
	40	4.72	8.44
	45	4.02	11.0
Co(II)	30	0.79	4.68
	35	2.71	8.32
	40	1.64	6.68
	45	5.08	5.15
Mn(II)	30	0.504	41.0
	35	1.72	3.45
	40	2.25	4.39
	45	2.46	5.33

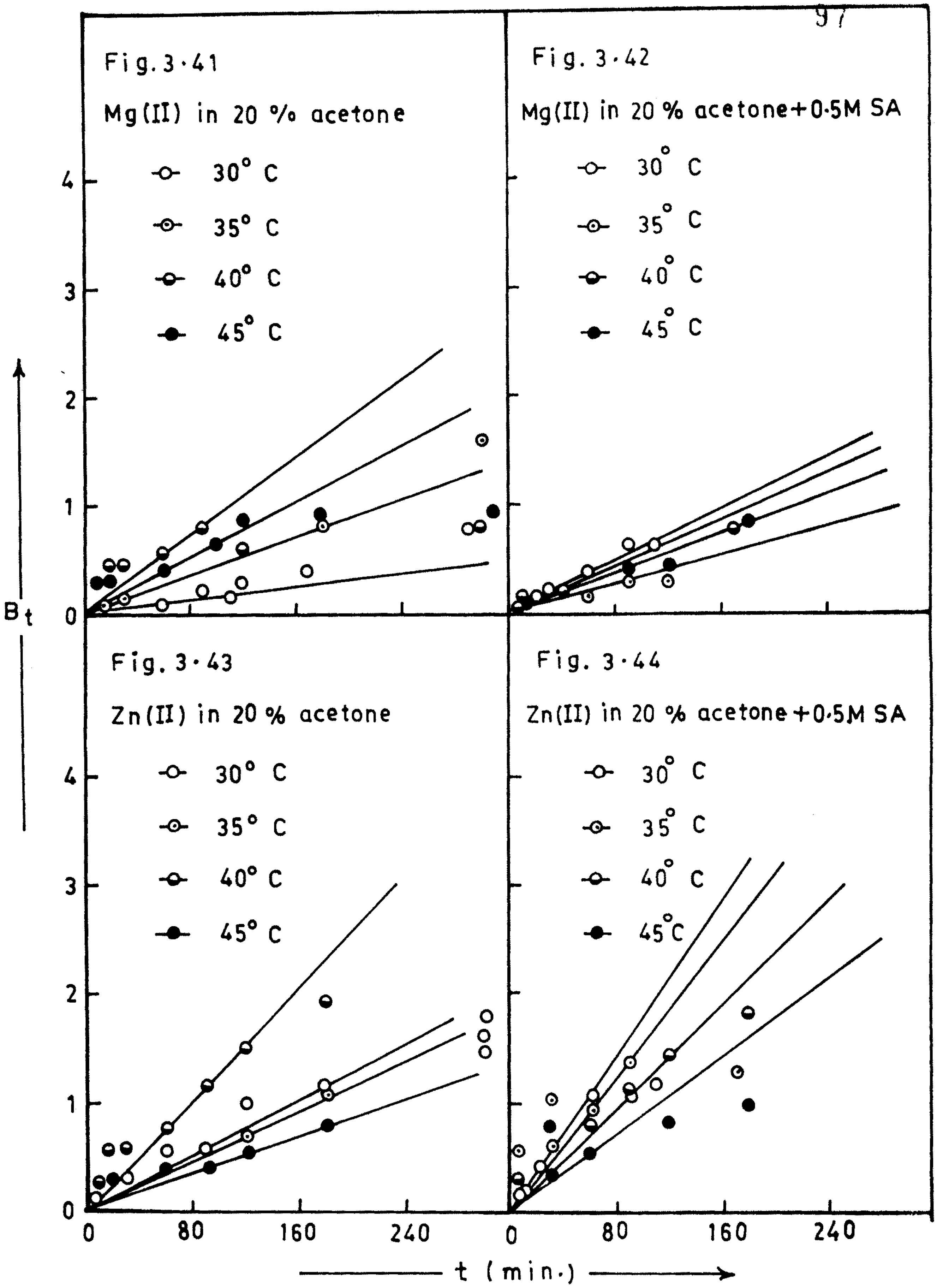


Fig. 3·41
Mg(II) in 20 % acetone
30° C
35° C
40° C
45° C
Fig. 3·42
Mg(II) in 20 % acetone+0·5M SA
30° C
35° C
40° C
45° C
Fig. 3·43
Zn(II) in 20 % acetone
30° C
35° C
40° C
45° C
Fig. 3·44
Zn(II) in 20 % acetone+0·5M SA
30° C
35° C
40° C
45°C
B_t
0
1
2
3
4
0
80
160
240
t (min.)

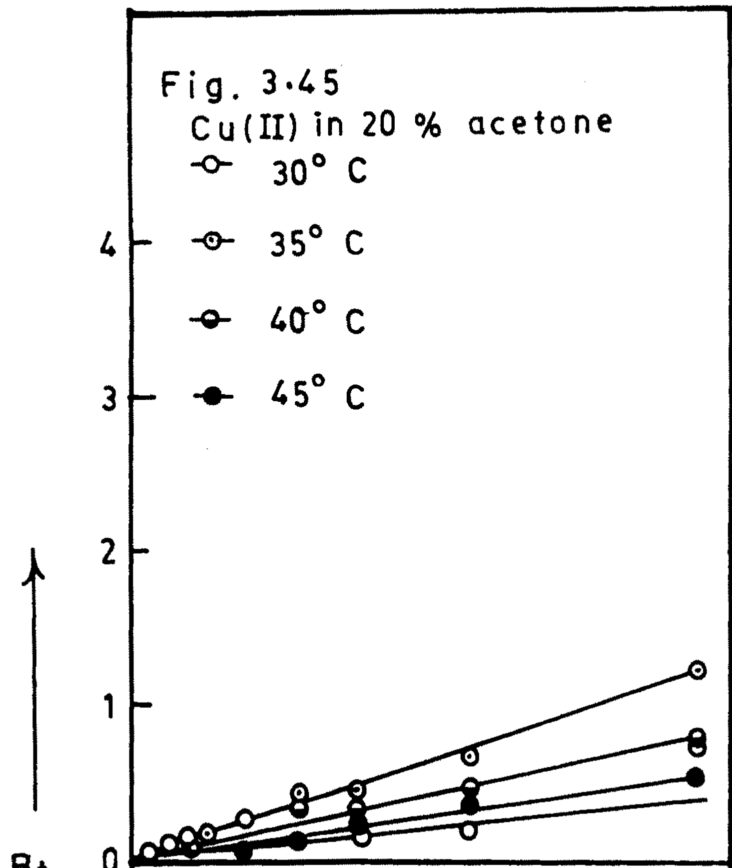


Fig. 3.45
Cu(II) in 20 % acetone

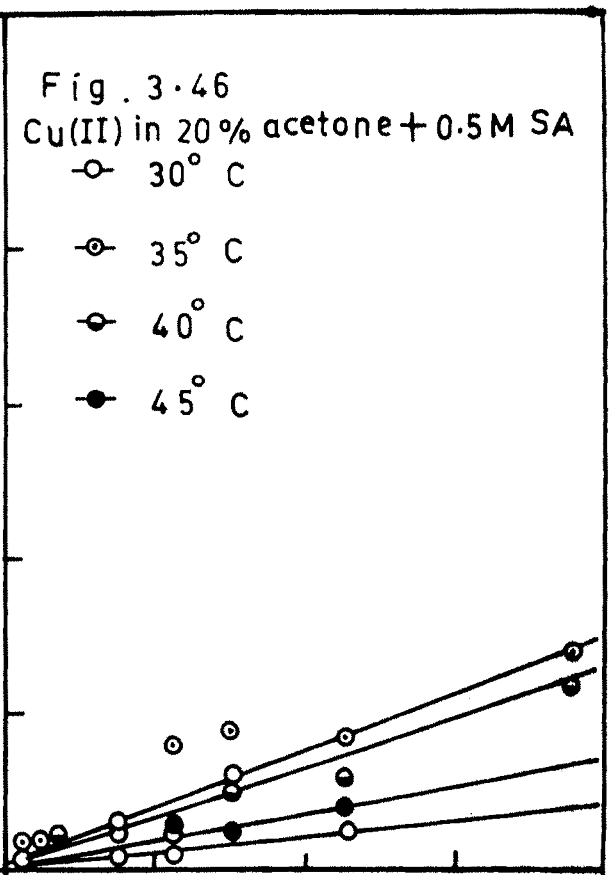


Fig. 3.46
Cu(II) in 20 % acetone + 0.5M SA

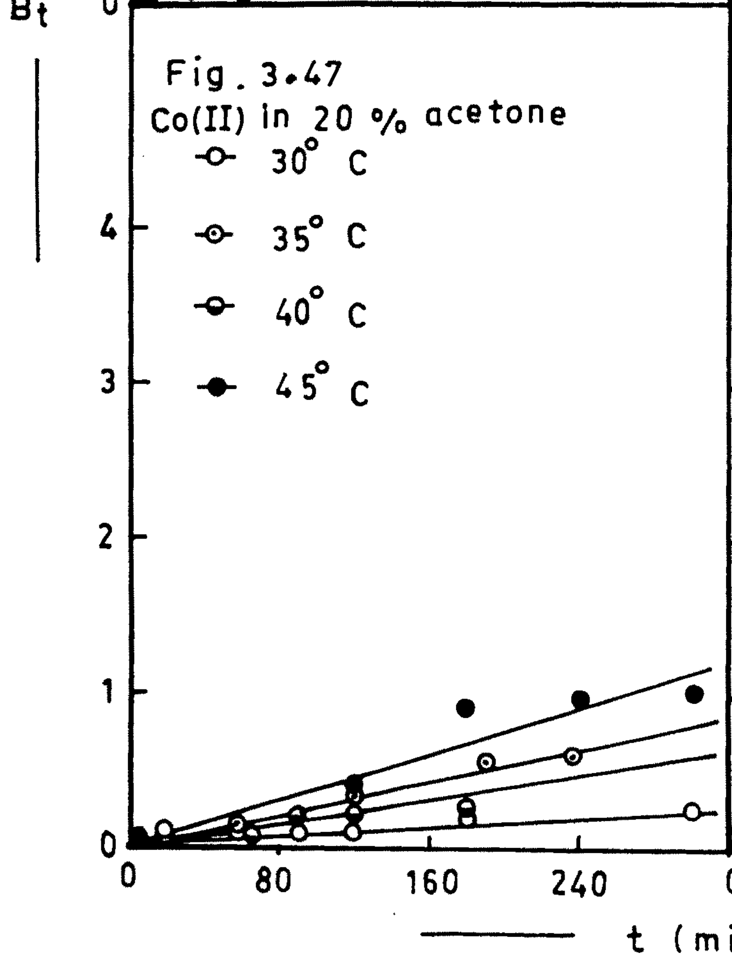


Fig. 3.47
Co(II) in 20 % acetone

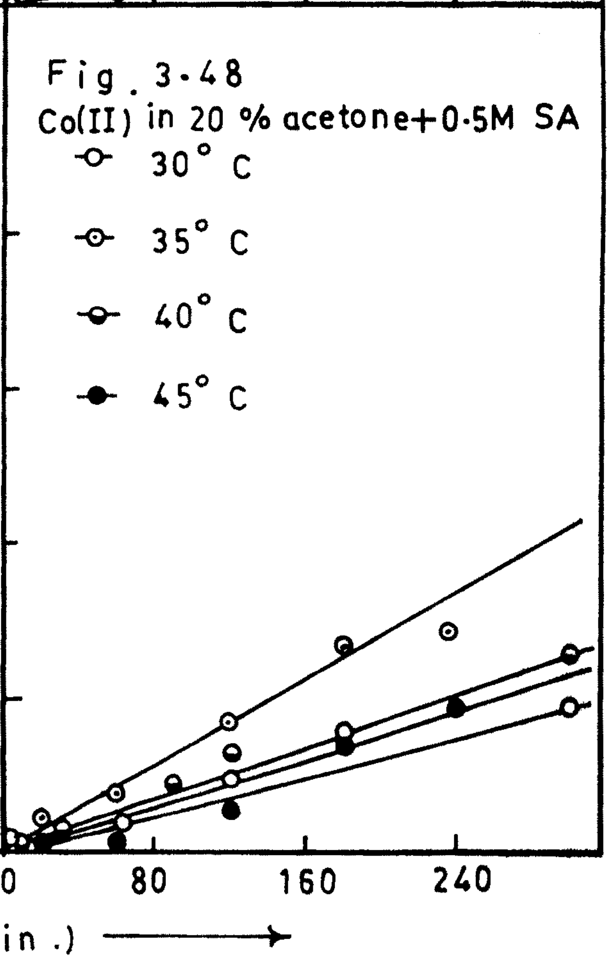


Fig. 3.48
Co(II) in 20 % acetone + 0.5M SA

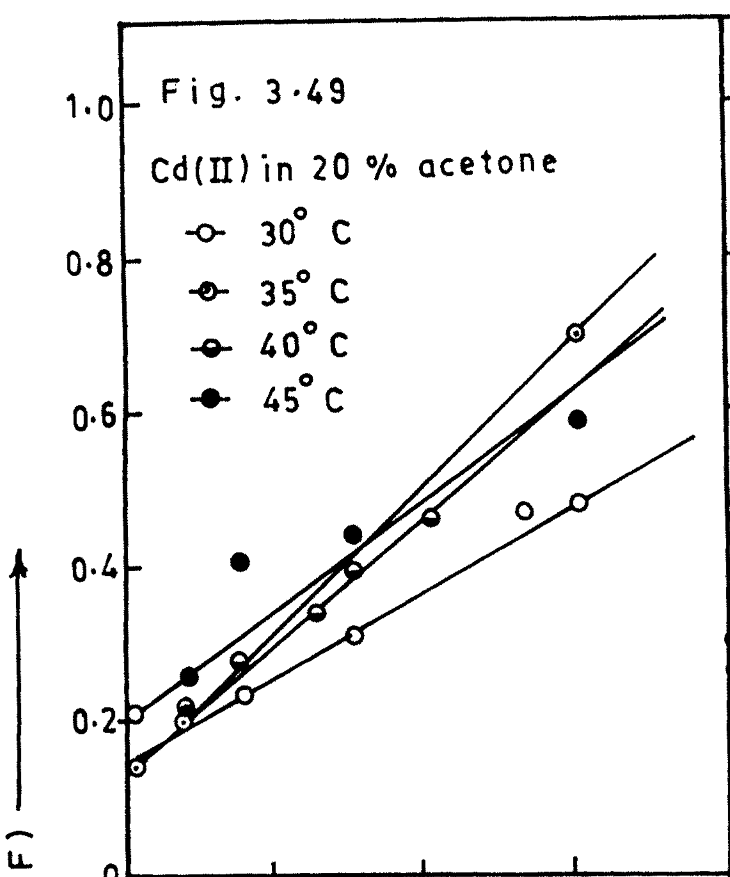


Fig. 3·49

Cd(II) in 20 % acetone

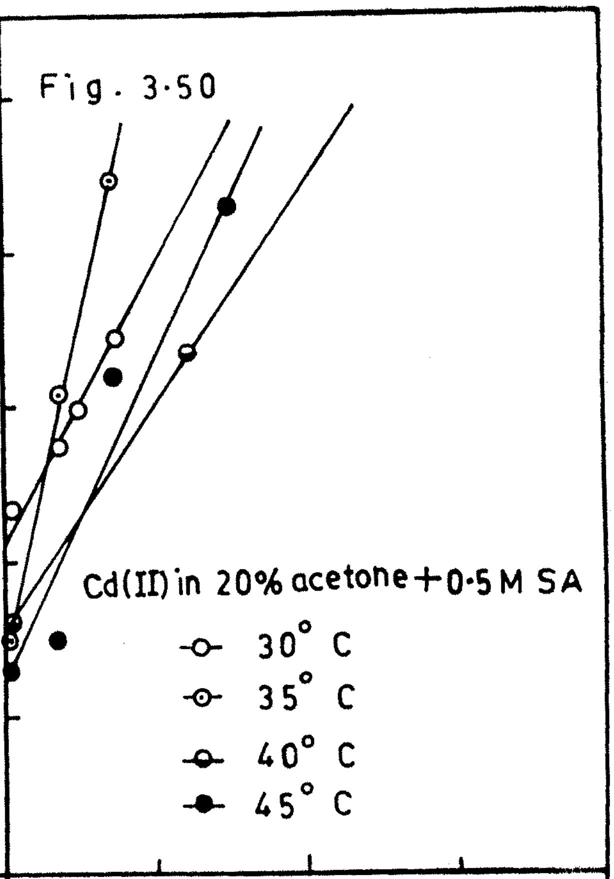


Fig. 3·50

Cd(II) in 20% acetone + 0·5 M SA

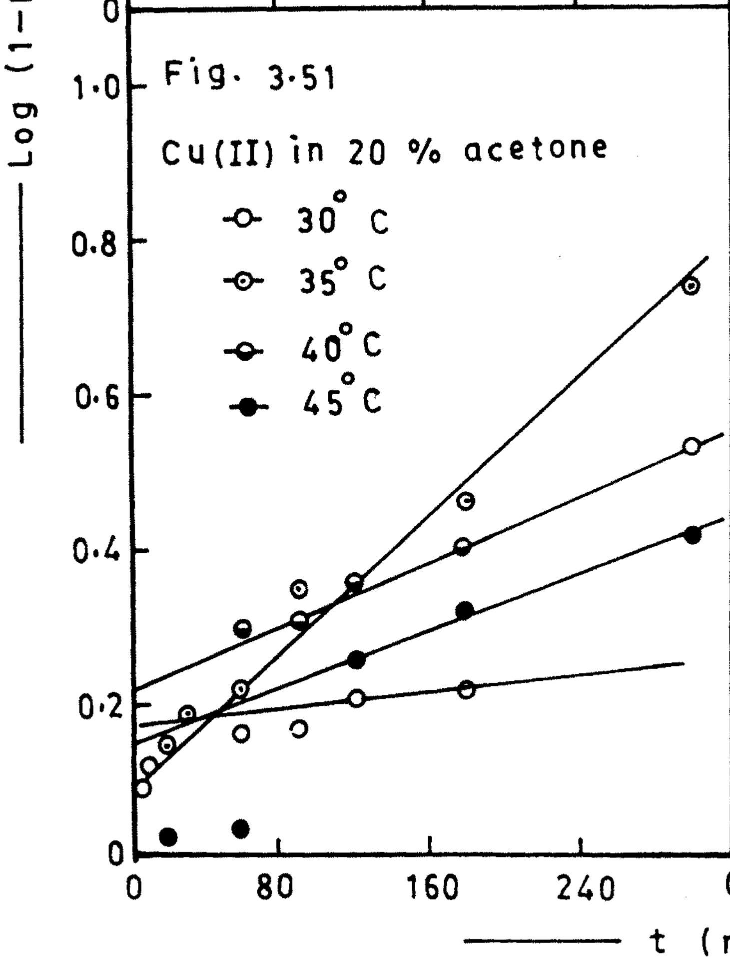


Fig. 3·51

Cu(II) in 20 % acetone

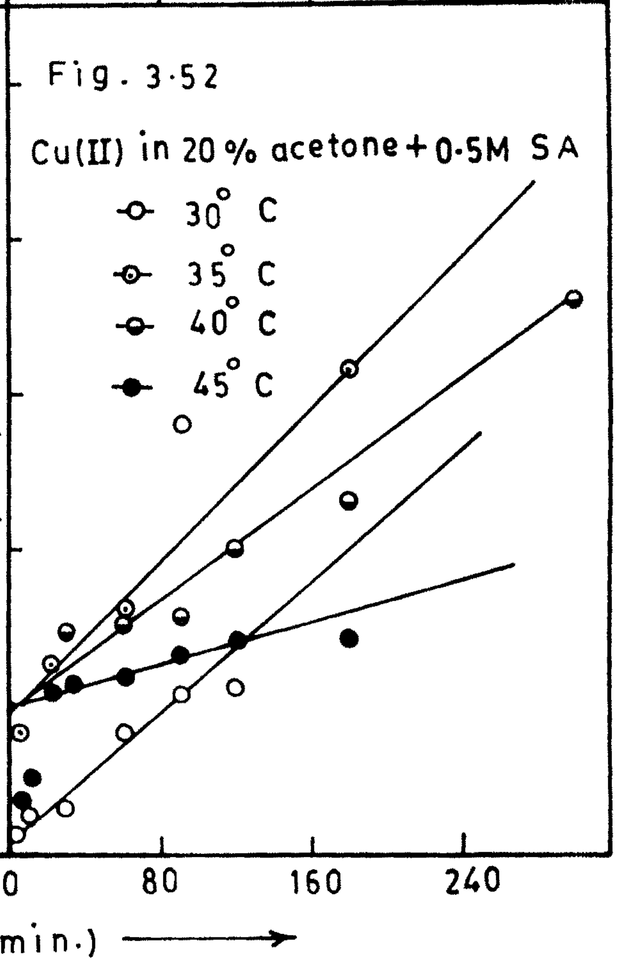


Fig. 3·52

Cu(II) in 20 % acetone + 0·5M SA

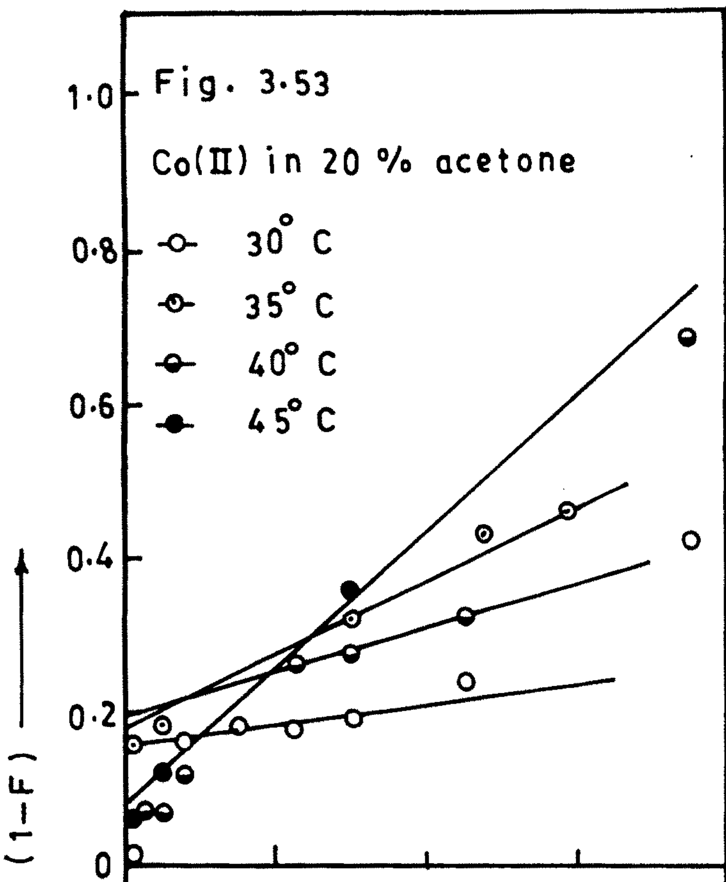


Fig. 3.53

Co(II) in 20 % acetone

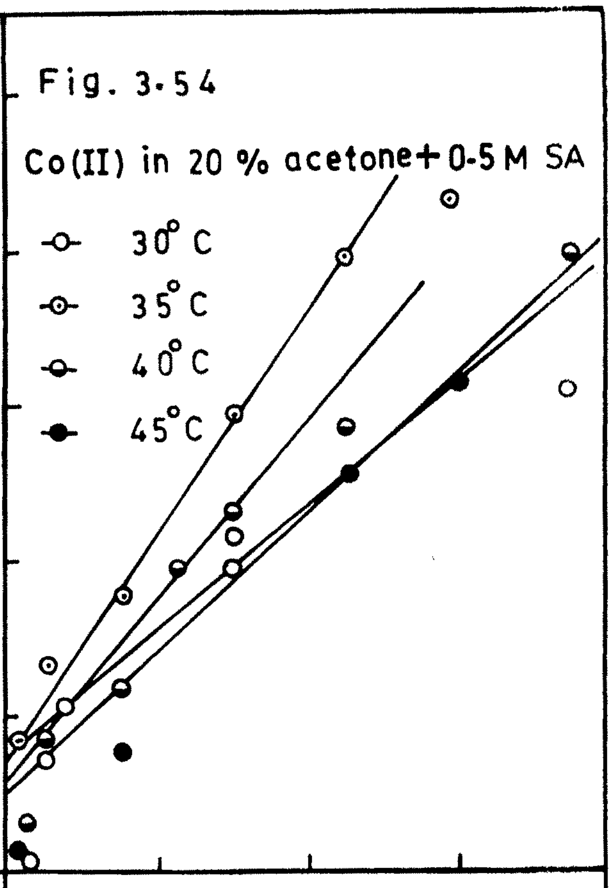


Fig. 3.54

Co(II) in 20 % acetone+0.5 M SA

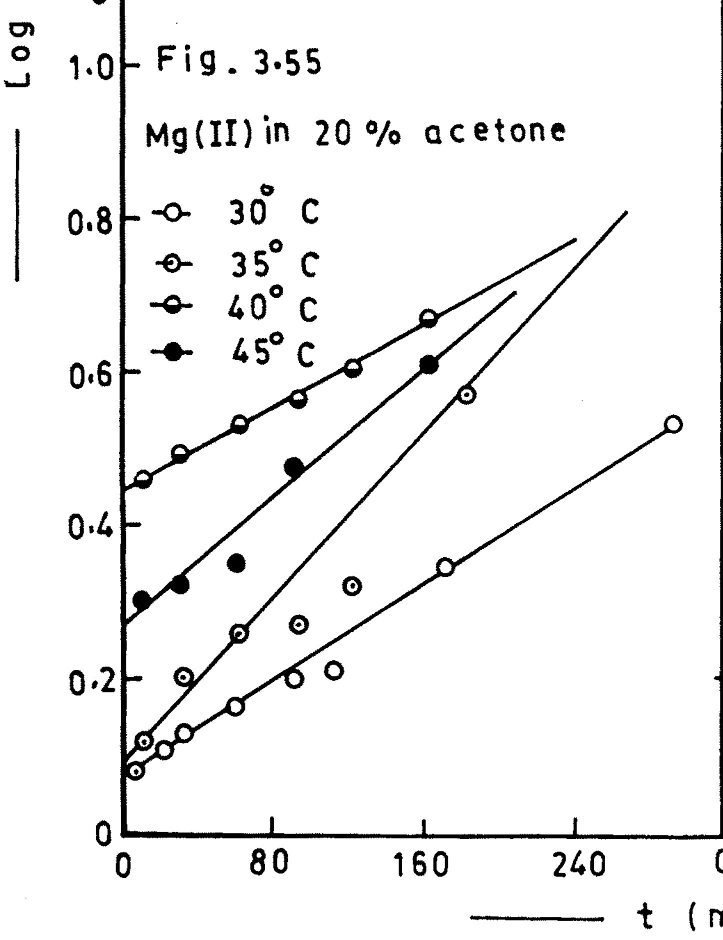


Fig. 3.55

Mg(II) in 20 % acetone

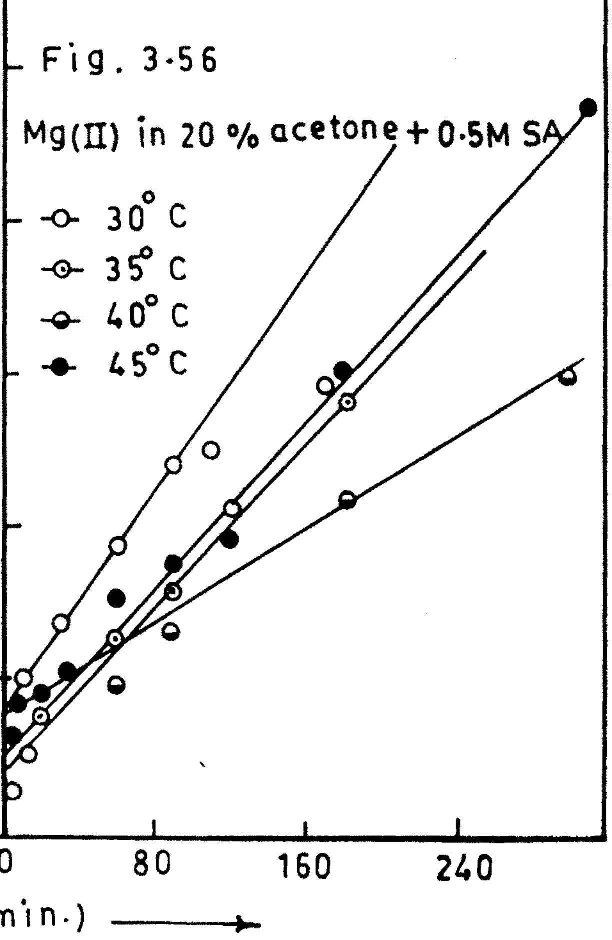


Fig. 3.56

Mg(II) in 20 % acetone+0.5M SA

Fig. 3.57

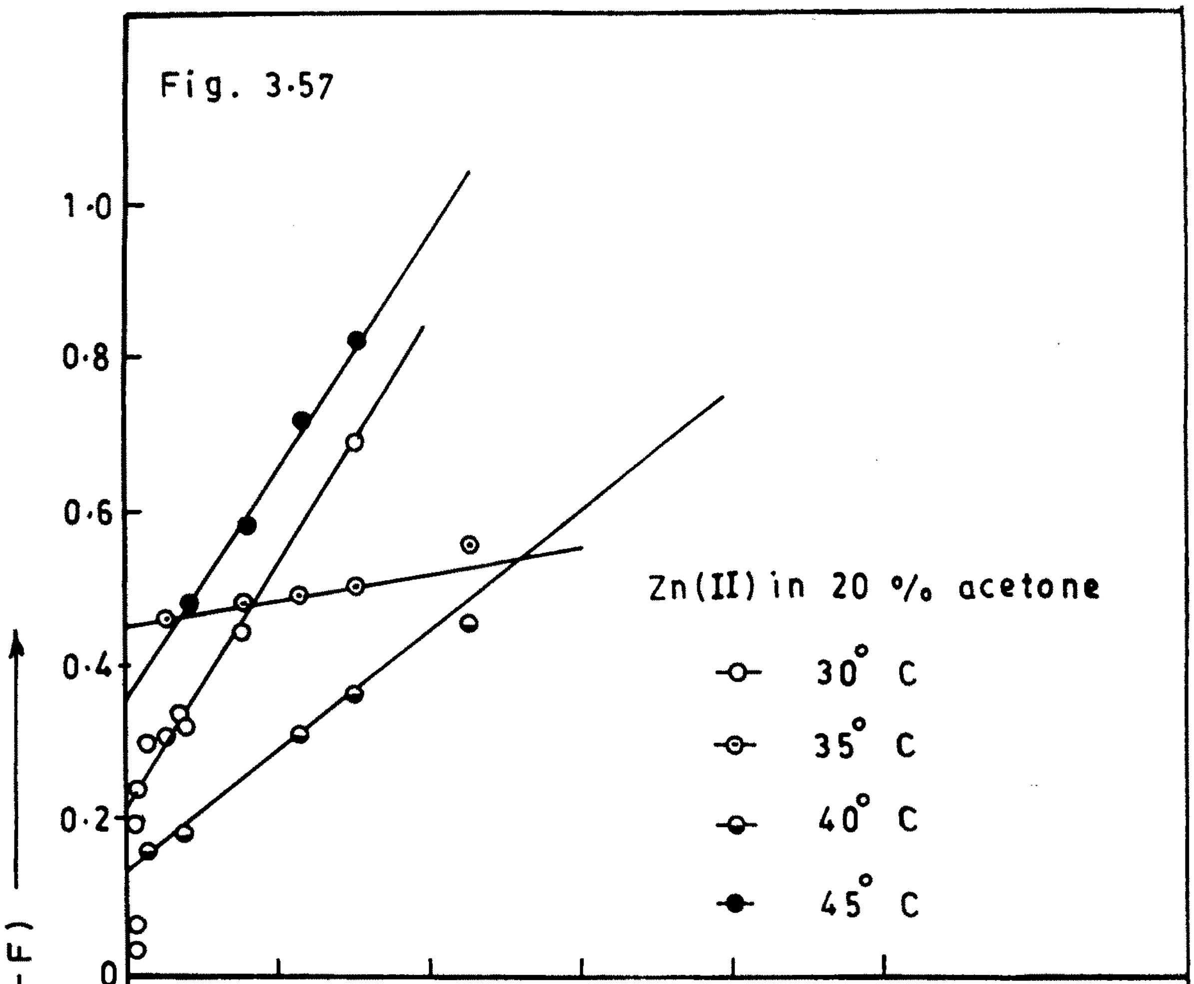
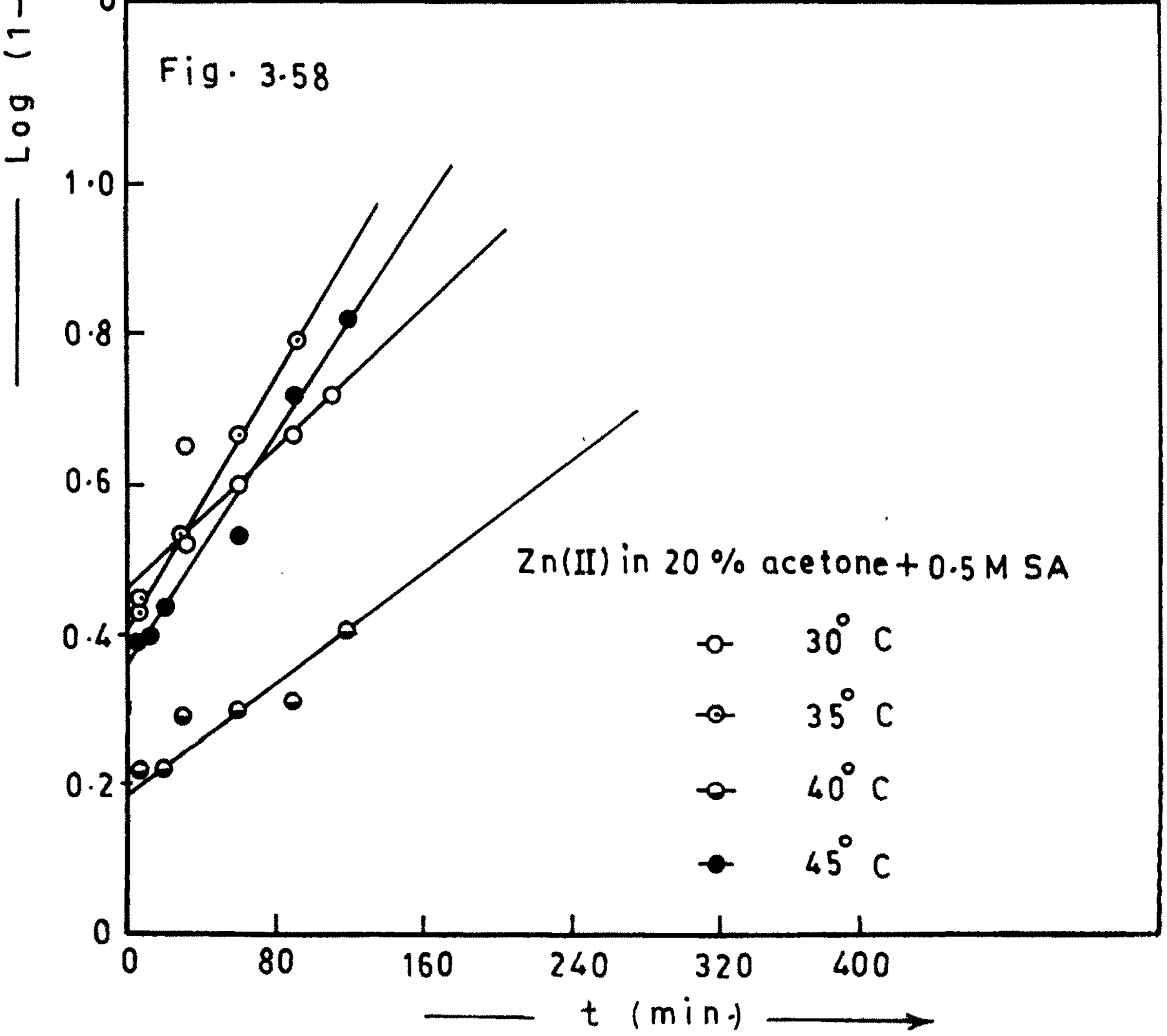


Fig. 3.58



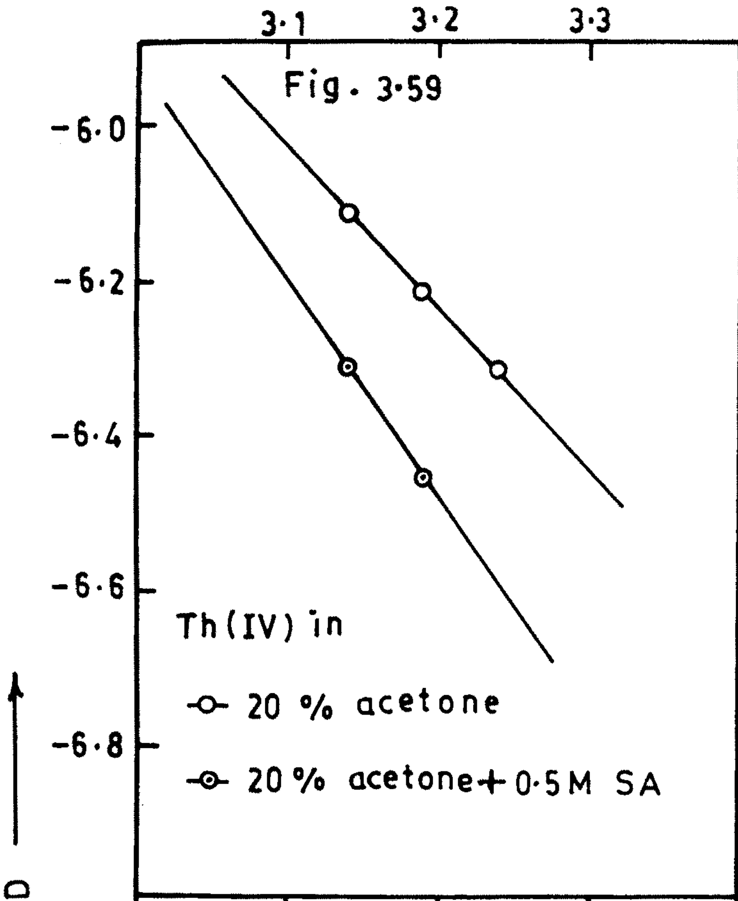


Fig. 3·59

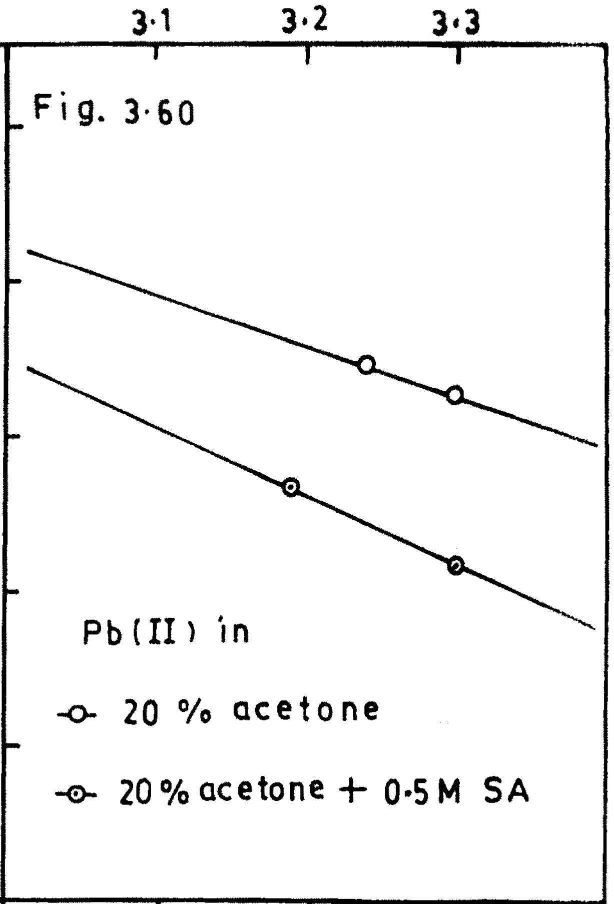


Fig. 3·60

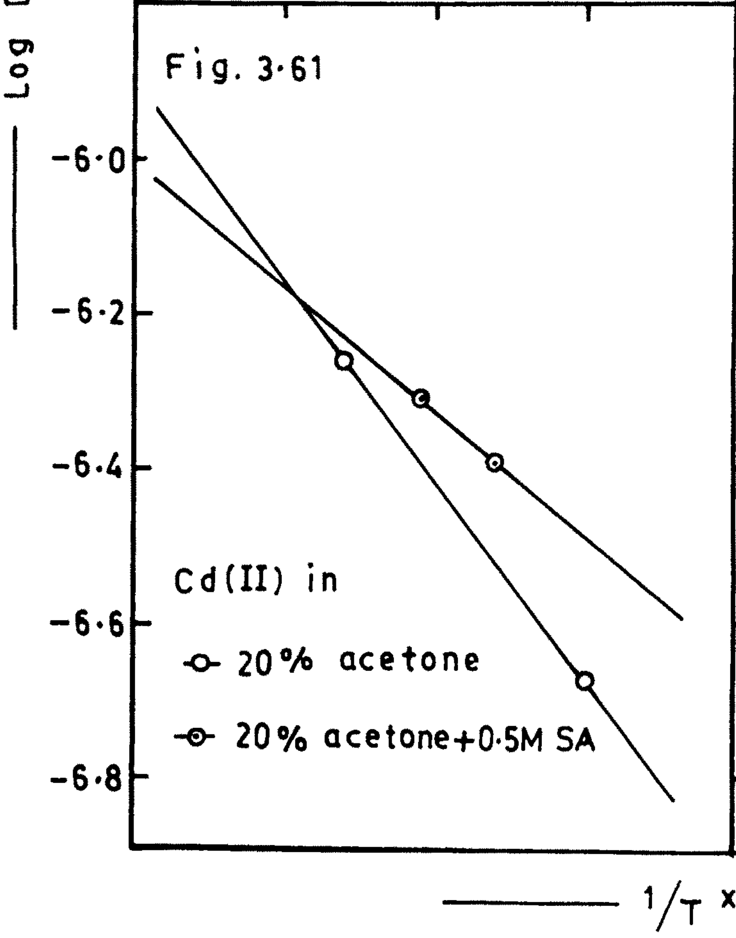


Fig. 3·61

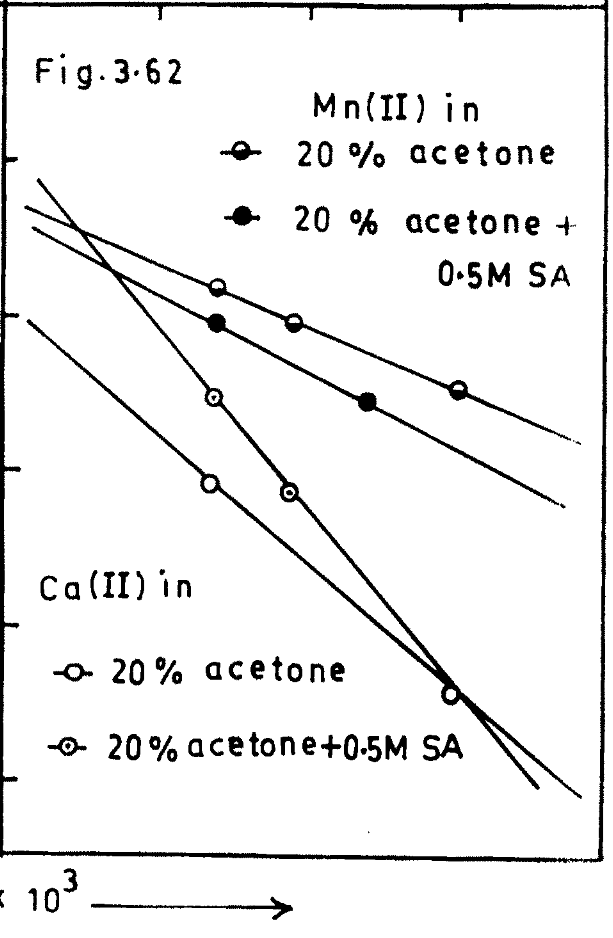


Fig. 3·62

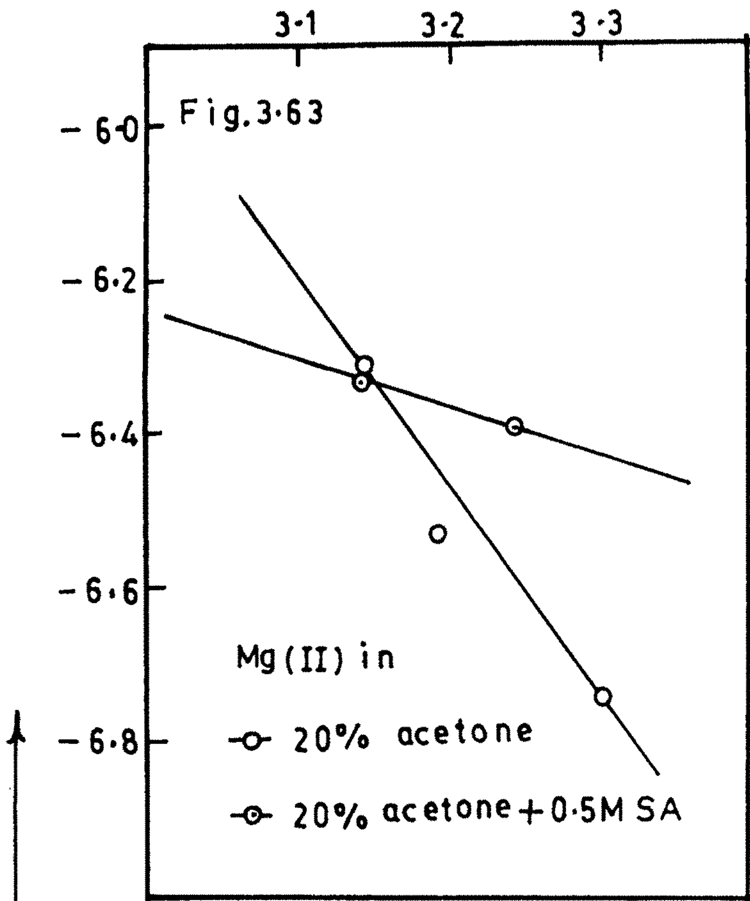


Fig. 3·63

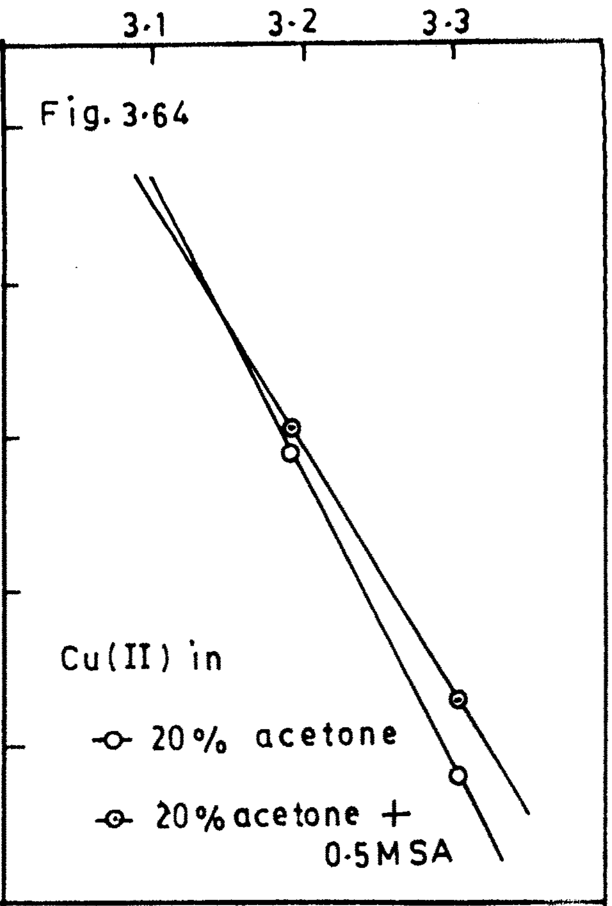


Fig. 3·64

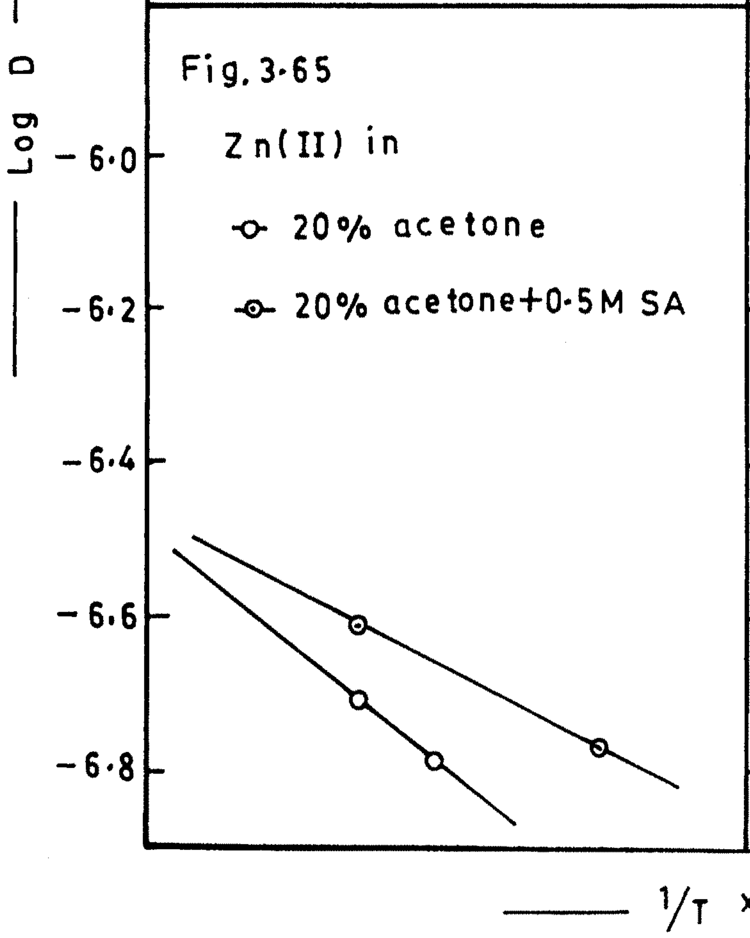


Fig. 3·65

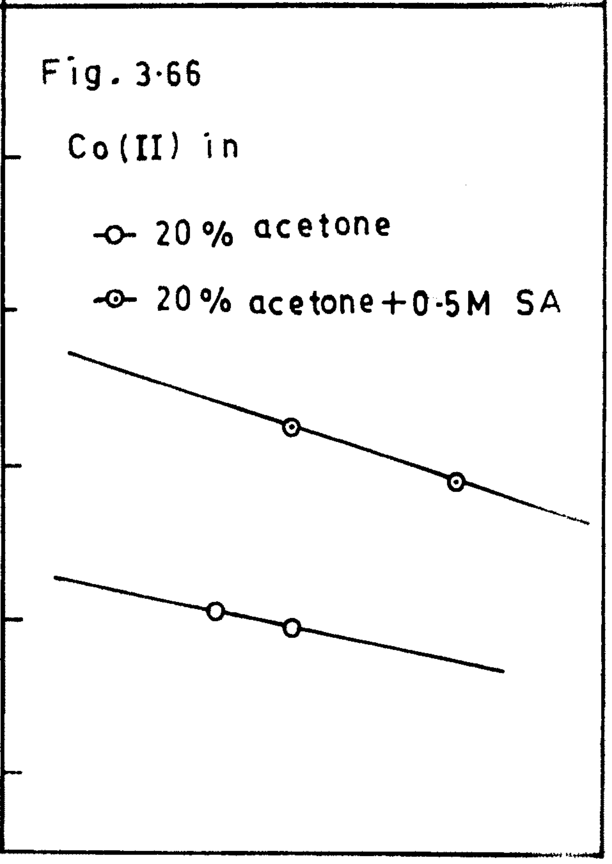


Fig. 3·66

greater in ion exchanger than in ordinary aqueous solutions. Activation energy of diffusion in standard ion exchange resins is about 6 to 10 K. cal.mole^{-1}, as compared to about 3 to 6 K.Cal. mole^{-1} in solutions.[25, 26, 27]. It can be explained because the retarding specific or electrostatic interactions become weaker, the matrix becomes more flexible and the ions become smaller as solvation is reduced. In the standard anion exchangers, the values of diffusion coefficients are about ½ to 1/10 of the corresponding coefficients in water and depends much less on the counter-ion valence.

Plot of log D versus $\frac{1}{T}$ is a straight line for all the metal ions used, as shown in fig. 3.59 to 3.66. The values of Ea, energy of activation, were obtained by applying the Arrhenius equation $D = Do \exp(-Ea/RT)$. The values of Ea for the exchange reactions understudy are presented in table $3C_{24}$. The values of Ea are in good agreement with that found in literature [28,29] for particle diffusion mechanism in standard ion exchange resins (25.1 to 41.84 KJ mole^{-1}). Varshney and Premdas[30] observed that the values of energy of activation encreases with a decrease in the hydrated radii for alkaline earths. The hydrate ionic radii contribute to the mechanism of exchange in two ways. (a) by affecting the position of equilibrium, and (b) by affecting the rate of attainment of equilibrium.

The pre-exponential constants, Do is related with the entropy of activation ΔS^* as follows[31],

$$Do = 2.72\,(K_B T\, d^2/h)\, \exp(\Delta S^*/R)$$

where K_B = Boltzmann constant, $T = 303^{\circ}K$, d = ionic jump, distance between two successive positions of ion in the process of diffusion taken[31] as equal to 5×10^{-10}m, h = Plank's constant and R = gas constant.

The values of entropy of activation are in part associated with the change in hydration states of the ions as they leave the aqueous solution and enter the solid phase and vice-versa. Table 3C$_{24}$ summerises the calculated values of ΔS^* which are negative as observed in tantalum, arsenate[32], ferric antimonate[33], Sn(IV) arsenophosphate[30]. The negative values of ΔS^* observed may be in part due to an overall increase in the hydration as the hydrogen ions-replace larger counter ions in solution, indicating thereby certain degree of dehydration of cations while diffusing into the solid p-hase. This is in agreement with the observation of Harvie and Nancollas [34] who pointed out that Li^+ and Na^+ diffuse as hydrated species with the possibility of K^+ being anhydrous on zirconium phosphate.

Rate constants : 'k' :

The range of validity of a simplified rate equation can only be established by a series of experiments under various conditions[35] or by comparison with more rigrous solutions. log (1-F) versus time t for the exchange systems are plotted. A representative set of the plots for Cu, Co, Cd, Mg, Zn, Ca exchange systems have shown in fig (3.49 to 3.58). The plots are linear showing that the exchange systems follow the first order kinetic equation.

$$(1 - F) = \exp(-kt)$$

Where k values for the exchange process have been computed from the slopes of three linear plots and recorded in table ($3C_{26}$). The values of the rate constant k are in agreement with the following overall relations.

(a) The values of k for the metal ions in aqueous acetone, aqueous acetone + 0.5 M S A media are in following sequence.

Cd > Zn > Th > Mg > Pb > Co > Ca > Cu > Mn.

(b) k increases at high temperatures. The rate of ion exchange increases with the increase in temperature from 30 to 50° C, suggesting that the mobility of the ion increases with increasing temperature. The uptake decreases with time. These findings are similar to the findings of the distribution coefficients (chapter - 4) of the metal ions in these media. The distribution coefficients increase with rise in perc-entage of acetone. In case of Zn and Cd the distribution coefficients are higher than those of Co, Cu, Ca, Mg and hence the rates of exchange of Zn and Cd are found to be greater than those of Co, Cu, Ca and Mg. The distribution coefficients of the metal ions showed the following order.

Th > Pb > Ca > Cu > Co > Cd > Zn > Mg > Mn

Similarly the order is observed by rate constants. As the distribution coefficients of the metal ions in various acidic media showed the sequence.

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