
CHAPTER - II

KINETICS OF ION EXCHANGE OF Mg, Ca, Sr AND Ba ON AMBERLITE IR-120 (NH₄)⁺ IN AQUEOUS ACETONE-AMMONIUM CITRATE MEDIA

EARLIER WORK

Kinetics of exchange reactions in aqueous medium has been studied by many workers¹⁻³, but only a few studies have been made in mixed solvents⁴⁻⁷. Wilson et al⁴ studied hydrogen n-butyl ammonium exchange on variously cross linked exchangers (Permutit Q) in ethanol-water mixtures, ranging from 71 to 92% ethanol at 0.2 M solution. The diffusion coefficients (\bar{D}) were found to decrease in magnitude with increase in the ethanol content and increased cross linking. Gorshkov et al⁵ studied alkali metal hydrogen exchange in aqueous and 60% methanol-water using KU-2 resin and the shallow bead-technique (infinite bath), \bar{D} values of Li^+/H^+ exchange decreased slightly and for Na^+/H^+ and K^+/H^+ systems increased in 60% methanol as compared to the aqueous systems. This was explained on the basis of much greater increase in selectivity for Na^+ and K^+ ions in 60% methanol, Shankar and Ghate⁶ investigated Li^+/H^+ exchange in 0-80% methanol water using Amberlite IR-120 at various solution concentrations. They have shown that the particle diffusion controlled rates at concentrations above 0.05M.

Diffusion coefficients(\bar{D}) decreased at methanol content increased. Bhatnagar and Garde⁷ studied $\text{Ca}^{2+}/\text{H}^+$ exchange in anhydrous and aqueous ethanol solutions. Rates in systems involving water were higher, Shukla and Bhatnagar⁸ studied the kinetics of the exchange reaction of

copper ions in non-aqueous solvents. The exchange reaction of copper ion in ethyl alcohol and acetone at 30.5° and 40.1°C were carried out using Amberlite IR-50 and IR-120 as cation exchange resins. The rate constant K were calculated for all systems and it was reported that the reaction did not obey first or second order.

The kinetic behaviour of alkali metal-hydrogen exchanges on Dowex W x 8 resin was investigated in aqueous and in methanol-water and acetone-water by DeokiNandan et al^{9,10}. The studies were carried out under conditions of intraparticle diffusion and infinite bath. K^+/H^+ exchanges are the fastest and Li^+/H^+ are the slowest in the water-acetone mixtures. However, on adding acetone to the extent of 44.2%, D^- values decrease by 33% for Li^+/H^+ and by 20% for Na^+/H^+ , K^+/H^+ exchanges. The rates for Na^+/H^+ and K^+/H^+ exchanges in acetone-water were found to be higher than those in methanol-water system. The viscosities of these mixtures were proved to play an important role in those systems. The kinetics of exchange of Ca^{2+}/H^+ was reported⁸ in absolute and aqueous-ethanol. Kinetics of exchange of Li^+/H^+ was studied in absolute and aqueous ethanol solutions. The formal overall reversible second order rate constant was reported¹¹. The rates in general are slower in perfectly non aqueous systems and slightly faster in systems containing air dried or dehydrated resin.

Most of the studies on the kinetics of ion-exchange deal with organic resins, leaving the inorganic counter parts still to be exploited. Mention must be made of the work on zeolites¹², hydrous zirconium oxide¹³, zirconium phosphate¹⁴⁻¹⁶ zirconium-antimonate¹⁷, tin-antimonate¹⁸, tantalum arsenate¹⁹, iron-antimonate²⁰. Kinetics of ion exchange of Rb^+ , Cs^+ and Ag^+ with H^+ on titanium vanadophosphate, employing the limited bath technique have been investigated by Singh et al²¹. The slow step which determines the rate of exchange of these ions is the diffusion through the exchanger particle. The values for inter-diffusion coefficients, energy of activation and entropy of activation were observed to approach to those on organic resins. The kinetics of exchange reactions of Ag^+ , Cu^{2+} , Mg^{2+} , Ca^{2++} , Sr^{2+} , Ba^{2+} and Y^{3+} exchange on Sn(IV) arseno phosphate double salt have been studied by varshney and premdas²². At a concentration 0.1N, rate of exchange was found to be independent of the metal ion concentration.

The kinetics of exchange reactions of Cu, Co, Ni, Zn, Ca, Mg, Pb, Cd and Mn in solution containing aqueous acetone carboxylic acids such as acetic, chloroacetic, dichloroacetic, trichloroacetic and succinic acid on Dowex 50 W x 8 (H^+) resin were carried out in our laboratory²³⁻²⁵. The rate constants and the kinetic parameters were found out. The data was useful to know the optimum conditions of

separations. It was concluded that the particle diffusion mechanism was predominant in the process of exchange kinetics.

The esterification of amyl and isoamyl alcohol²⁶ with propionic and butyric acid concluded that the rate of reaction increased with increasing the branching of the side chain of both alcohol and acid due to the sterichindrance. The same conclusion was established²⁷ for esterifying ethanol with acetic and isobutyric acid in presence of cation exchanger. The esterification of methanol²⁸ with a homologous series of aliphatic organic acids such as formic, acetic, propionic, butyric and valeric in presence of Amberlite IR-120 (H⁺ form) as a catalyst was studied. The effect of the structure of reactant has been investigated by application of Tatt's equation.

EXPERIMENTAL

Solution

- 1) 0.1M stock solutions of Ca, Mg, Sr and Ba wre prepared from A.R. grade salts of BDH and SRL (India), by using double distilled water.
- 2) Acetone%, 0, 30, 50, 70.
- 3) Ammonium citrate solution.
- 4) EDTA : 0.001M

THERMODYNAMIC ARRANGEMENT

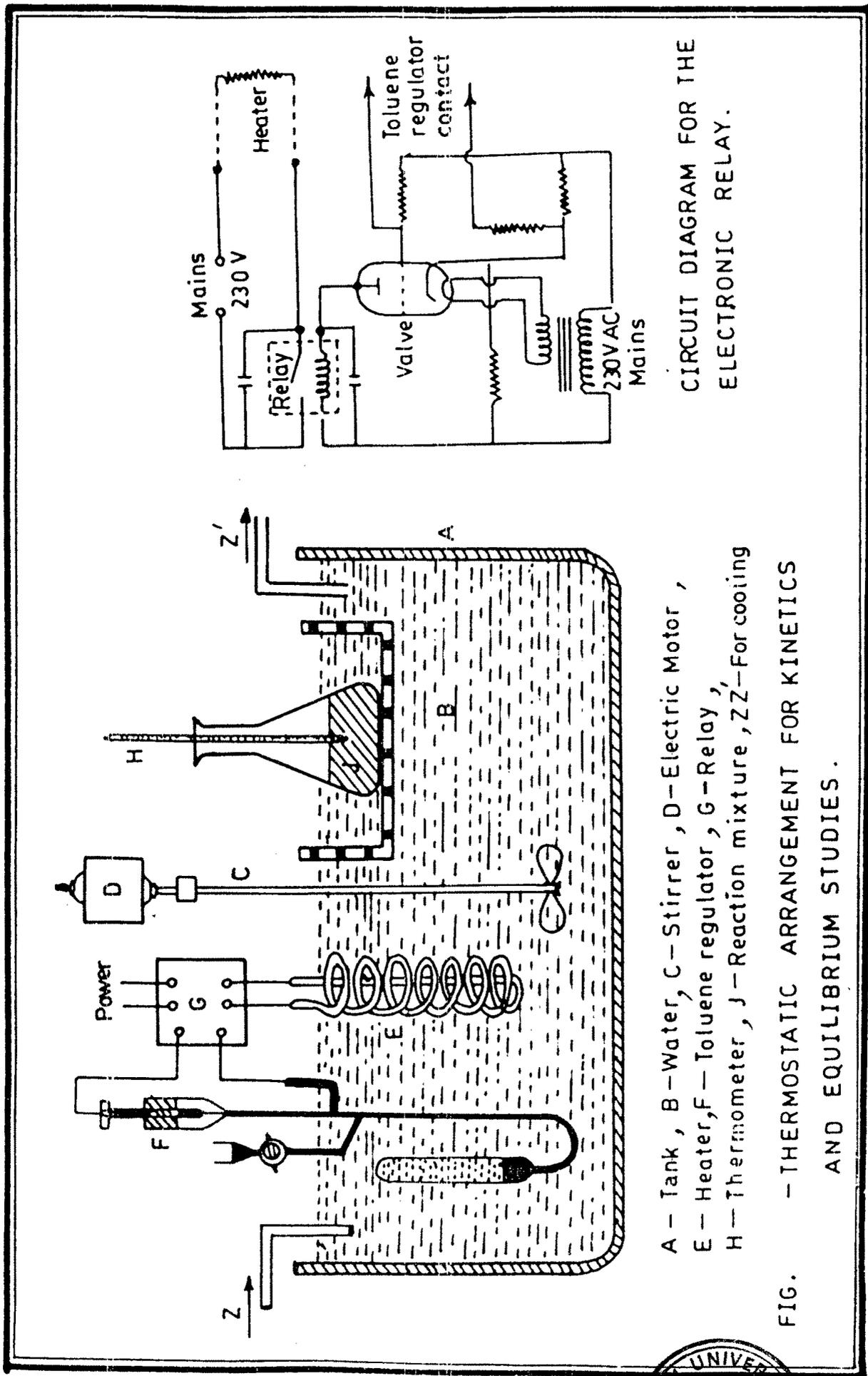
A schematic diagram of the thermostatic arrangement which maintains the temperature constant within $\pm 0.5^{\circ}\text{C}$ is shown in fig. The copper tank A contains bath liquid B (water) which is vigorously stirred using stirrer C, driven by electric motor D. The desired constant temperature is maintained by means of a heater E and a regulator F, connected to relay G. The temperature of the reaction mixture was recorded by the thermometer H.

PROCEDURE

Exactly 2 g of air dried Amberlite IR-120 (NH_4^+ form) was taken in an erlenmeyer flask. The mixture containing 0.02M Ammonium citrate, water and various percentage of acetone. Appropriate quantity of metal ion solution was poured into it at noted time so that the total volume of the mixture becomes 100 ml. The amount of metal ions exchanged on the resin was estimated at different time intervals from the concentration difference before and after the ion exchange. The studies were carried out at 303° , 308° , 313° and 318°K resp.

PRESENT WORK

Kinetic studies of exchange reactions of Mg, Ca, Sr and Ba ions with NH_4^+ ion of Amberlite IR-120 in aqueous



A - Tank, B - Water, C - Stirrer, D - Electric Motor,
 E - Heater, F - Toluene regulator, G - Relay,
 H - Thermometer, J - Reaction mixture, Z, Z' - For cooling

FIG. - THERMOSTATIC ARRANGEMENT FOR KINETICS
 AND EQUILIBRIUM STUDIES.

CIRCUIT DIAGRAM FOR THE
 ELECTRONIC RELAY.



acetone ammonium citrate media were carried out. The kinetic parameters such as interdiffusion coefficient(D), half exchange time($t_{\frac{1}{2}}$), parabolic diffusion constant(K) were found out. The effect of concentration of metal ions, acetone and ammonium citrate on these kinetic parameters are reported in this chapter. The plots of Bt Vs t leads to probable mechanism of diffusion. The variations of rate constant (K) with percentages of acetone and molarities of metal ions were studied. The value of energy of activation (E_a). The pre-exponential constant(D_0) and entropy of activation (ΔS^\ddagger) were obtained by the studies of kinetic exchange reactions at different temperatures.

Table 2.1 : Reichenberg Table for Interpreting 'F' in
Terms of Bt

F	Bt	F	Bt	F	Bt	F	Bt
0.00	0.00000	0.25	0.0623	0.50	0.301	0.75	0.905
0.01	0.00009	0.26	0.0678	0.51	0.316	0.76	0.944
0.02	0.00036	0.27	0.0736	0.52	0.332	0.77	0.985
0.03	0.00076	0.28	0.0797	0.53	0.348	0.78	1.028
0.04	0.00141	0.29	0.0861	0.54	0.365	0.79	1.073
0.05	0.00219	0.30	0.0928	0.55	0.382	0.80	1.120
0.06	0.00320	0.31	0.0998	0.56	0.400	0.81	1.171
0.07	0.00440	0.32	0.1027	0.57	0.419	0.82	1.224
0.08	0.00570	0.33	0.1147	0.58	0.438	0.83	1.280
0.09	0.00730	0.34	0.1226	0.59	0.458	0.84	1.340
0.10	0.00910	0.35	0.1308	0.60	0.479	0.85	1.404
0.11	0.01110	0.36	0.1391	0.61	0.500	0.86	1.468
0.12	0.01320	0.37	0.1485	0.62	0.522	0.87	1.543
0.13	0.01560	0.38	0.1577	0.63	0.545	0.88	1.623
0.14	0.01830	0.39	0.1670	0.64	0.569	0.89	1.710
0.15	0.02100	0.40	0.1700	0.65	0.594	0.90	1.800
0.16	0.02410	0.41	0.1880	0.66	0.620	0.91	1.910
0.17	0.02740	0.42	0.1990	0.67	0.647	0.92	2.030
0.18	0.03090	0.43	0.2100	0.68	0.675	0.93	2.160
0.19	0.03460	0.44	0.2220	0.69	0.703	0.94	2.320
0.20	0.03860	0.45	0.2340	0.70	0.734	0.95	2.500
0.21	0.04280	0.46	0.2460	0.71	0.765	0.96	2.720
0.22	0.04730	0.47	0.2590	0.72	0.789	0.97	3.010
0.23	0.05200	0.48	0.2730	0.73	0.832	0.98	3.410
0.24	0.05700	0.49	0.2870	0.74	0.868	0.99	4.110

Table 2.2.1: Dependence of Fractional Attainment of Equilibrium(F) with time(t).

System: Mg (0.002 and 0.004M) on Amberlite IR-120 (NH₄)⁺
in Aqueous Acetone Ammonium Citrate (0.02M) at 303°K

Time in min	Mg (0.002M) Acetone %, V/V				Mg (0.004M) Acetone %, V/V			
	00	30	50	70	00	30	50	70
000	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
005	0.02	0.04	0.05	0.06	0.05	0.07	0.08	0.10
010	0.04	0.05	0.06	0.08	0.13	0.15	0.17	0.20
040	0.10	0.12	0.15	0.18	0.17	0.21	0.25	0.33
070	0.25	0.33	0.41	0.58	0.26	0.30	0.36	0.45
130	0.43	0.50	0.61	0.74	0.41	0.46	0.53	0.61
190	0.56	0.64	0.72	0.84	0.51	0.58	0.65	0.73
250	0.66	0.74	0.81	0.91	0.62	0.70	0.75	0.82
310	0.73	0.81	0.86	0.94	0.71	0.78	0.82	0.88
370	0.80	0.86	0.92	0.96	0.78	0.84	0.88	0.92
430	0.86	0.90	0.95	0.97	0.84	0.90	0.93	0.96
490	0.92	0.94	0.96	0.99	0.89	0.94	0.97	0.98
550	0.97	0.98	0.99	1.00	0.96	0.97	0.98	0.99
610	0.98	0.99	1.00	-	1.00	1.00	1.00	1.00
670	1.00	1.00	-	-	-	-	-	-

Table 2.2.2: Dependence of Fractional Attainment of Equilibrium(F) with time(t).

System: Mg (0.006 and 0.008M) on Amberlite IR-120 (NH₄⁺)
in Aqueous Acetone Ammonium Citrate (0.02M) at 303°K

Time in min	Mg (0.006M) Acetone %, V/V				Mg (0.008M) Acetone %, V/V			
	00	30	50	70	00	30	50	70
000	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
005	0.04	0.05	0.07	0.09	0.05	0.07	0.08	0.082
010	0.07	0.09	0.10	0.12	0.06	0.07	0.08	0.096
040	0.16	0.26	0.36	0.54	0.19	0.26	0.37	0.56
070	0.28	0.38	0.48	0.65	0.25	0.37	0.53	0.68
130	0.45	0.55	0.65	0.80	0.46	0.55	0.71	0.83
190	0.58	0.68	0.76	0.87	0.60	0.70	0.82	0.93
250	0.69	0.77	0.84	0.92	0.71	0.80	0.89	0.97
310	0.78	0.83	0.89	0.95	0.80	0.86	0.92	0.98
370	0.84	0.89	0.94	0.97	0.86	0.90	0.94	0.99
430	0.90	0.93	0.96	0.98	0.91	0.93	0.96	1.00
490	0.95	0.97	0.99	1.00	0.94	0.95	0.96	-
550	0.97	0.99	1.00	-	0.96	0.98	0.99	-
610	1.00	1.00	-	-	1.00	1.00	1.00	-
670	1.00	1.00	-	-	-	-	-	-

Table 2.3.1: Dependence of Fractional Attainment of Equilibrium(F) with time(t).

System: Ca (0.002 and 0.004M) on Amberlite IR-120 (NH₄⁺)
in Aqueous Acetone Ammonium Citrate (0.02M) at 303°K

Time in min	Ca (0.002M) Acetone %, V/V				Ca (0.004M) Acetone %, V/V			
	00	30	50	70	00	30	50	70
000	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
005	0.01	0.03	0.042	0.05	0.01	0.02	0.08	0.19
010	0.08	0.12	0.15	0.22	0.07	0.12	0.22	0.33
030	0.19	0.24	0.29	0.35	0.21	0.30	0.39	0.49
090	0.44	0.49	0.54	0.59	0.52	0.61	0.67	0.75
150	0.64	0.68	0.72	0.76	0.72	0.79	0.83	0.88
210	0.78	0.82	0.86	0.90	0.84	0.88	0.92	0.95
270	0.90	0.93	0.95	0.98	0.93	0.95	0.96	0.98
330	0.97	0.98	0.99	1.00	0.97	0.97	0.98	0.99
390	1.00	1.00	1.00	-	1.00	1.00	1.00	1.00

Table 2.3.2: Dependence of Fractional Attainment of Equilibrium(F) with time(t).

System: Ca (0.006 and 0.008M) on Amberlite IR-120 (NH₄⁺)
in Aqueous Acetone Ammonium Citrate (0.02M) at 303°K

Time in min	Ca (0.006M) Acetone %, V/V				Ca (0.008M) Acetone %, V/V			
	00	30	50	70	00	30	50	70
000	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
005	0.04	0.06	0.06	0.07	0.07	0.11	0.14	0.20
010	0.09	0.12	0.13	0.18	0.15	0.20	0.25	0.35
030	0.24	0.30	0.35	0.47	0.34	0.39	0.50	0.61
090	0.54	0.63	0.69	0.83	0.63	0.67	0.84	0.90
150	0.72	0.81	0.86	0.93	0.78	0.82	0.93	0.96
210	0.84	0.91	0.95	0.98	0.88	0.91	0.95	0.98
270	0.92	0.96	0.98	1.00	0.95	0.96	0.98	0.99
330	1.00	1.00	1.00	-	1.00	1.00	1.00	1.00
390	-	-	-	-	-	-	-	-

Table 2.4: Dependence of Fractional Attainment of Equilibrium(F) with time(t).

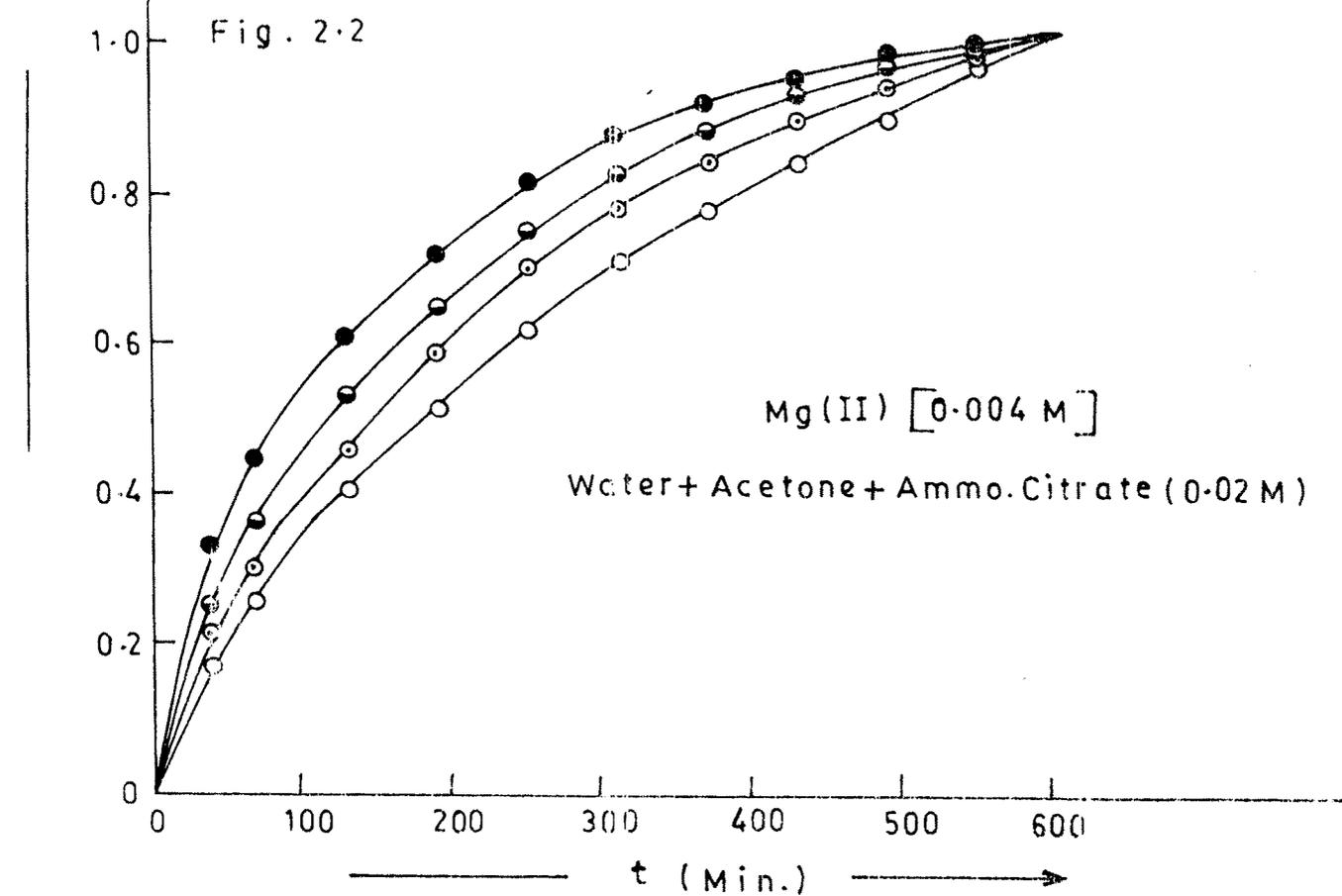
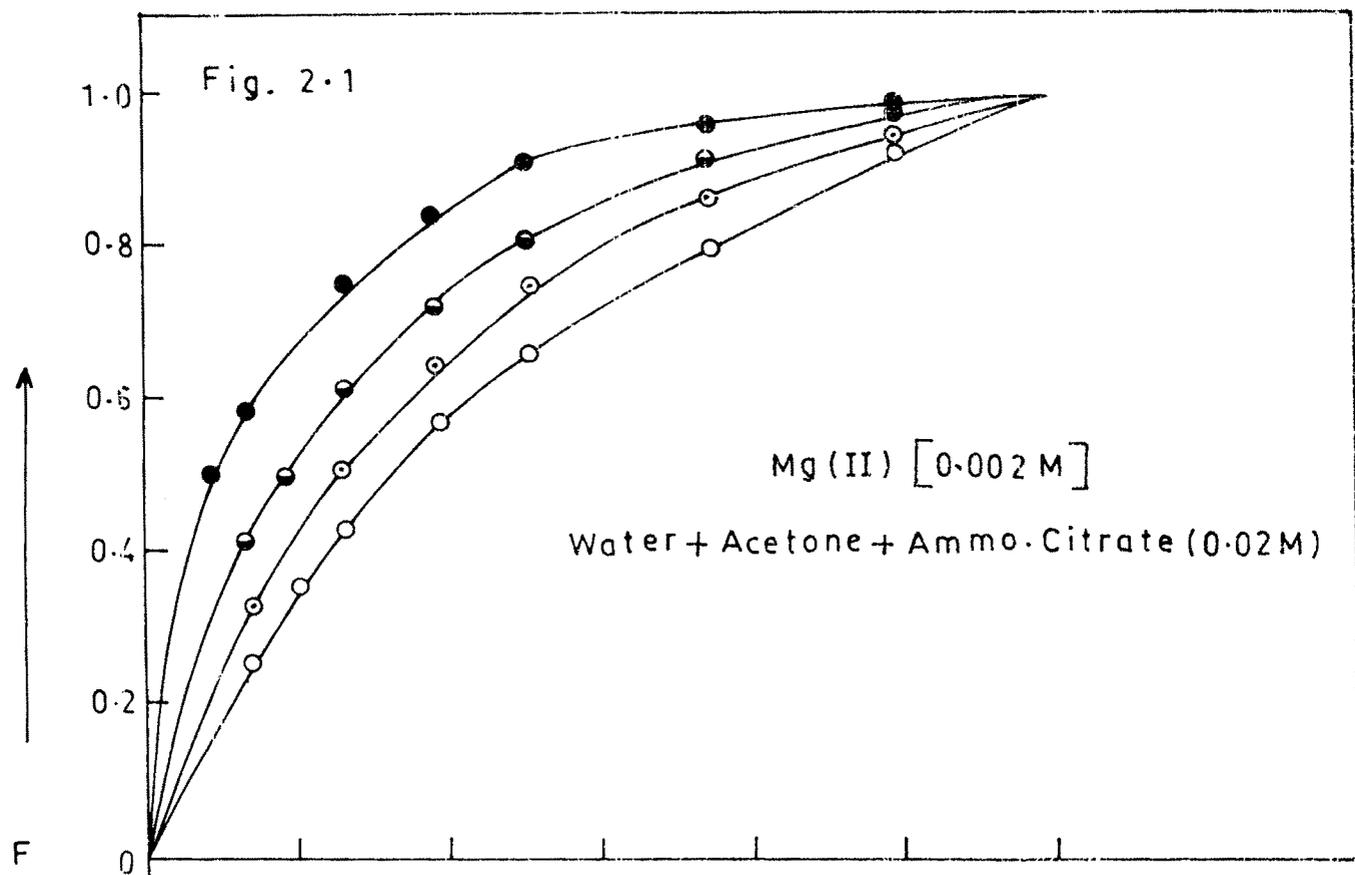
System: Sr (0.002 and 0.004M) on Amberlite IR-120 (NH₄⁺) in Aqueous Acetone Ammonium Citrate (0.02M) at various temperatures.

Time in min	Sr (0.002M)				Sr (0.004M)			
	Temperature in °K							
	303	308	313	318	303	308	313	318
000	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
005	0.01	0.02	0.03	0.03	0.02	0.02	0.03	0.03
010	0.04	0.06	0.07	0.12	0.04	0.06	0.06	0.14
030	0.12	0.16	0.19	0.27	0.11	0.15	0.20	0.30
090	0.33	0.39	0.45	0.56	0.29	0.40	0.46	0.53
150	0.51	0.59	0.66	0.72	0.49	0.53	0.62	0.69
210	0.65	0.75	0.82	0.90	0.62	0.69	0.74	0.78
270	0.73	0.86	0.91	0.94	0.75	0.81	0.84	0.87
330	0.85	0.94	0.96	0.99	0.86	0.90	0.92	0.94
390	0.96	0.98	0.99	-	0.95	0.97	0.98	0.99
450	1.00	1.00	1.00	-	1.00	1.00	1.00	1.00

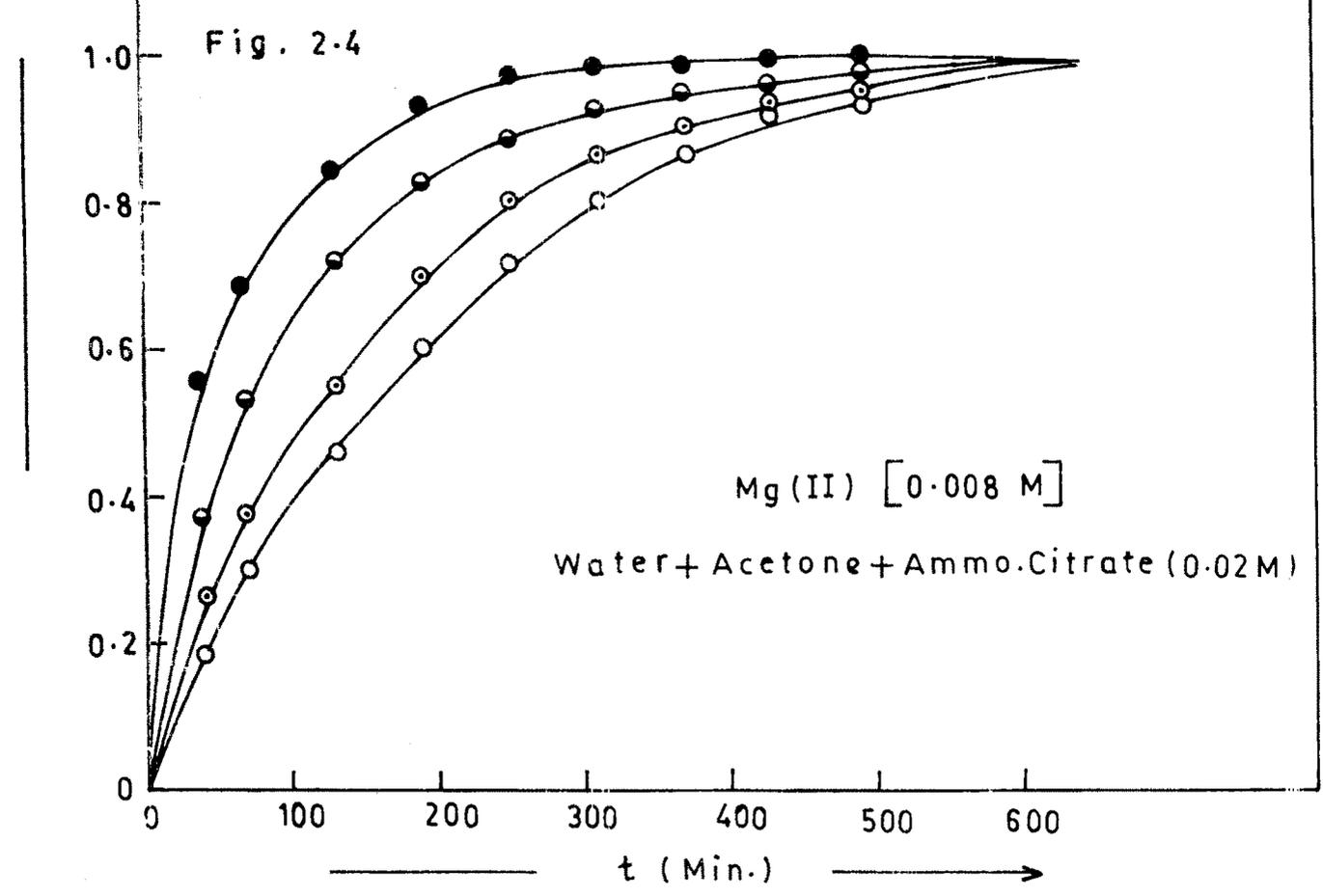
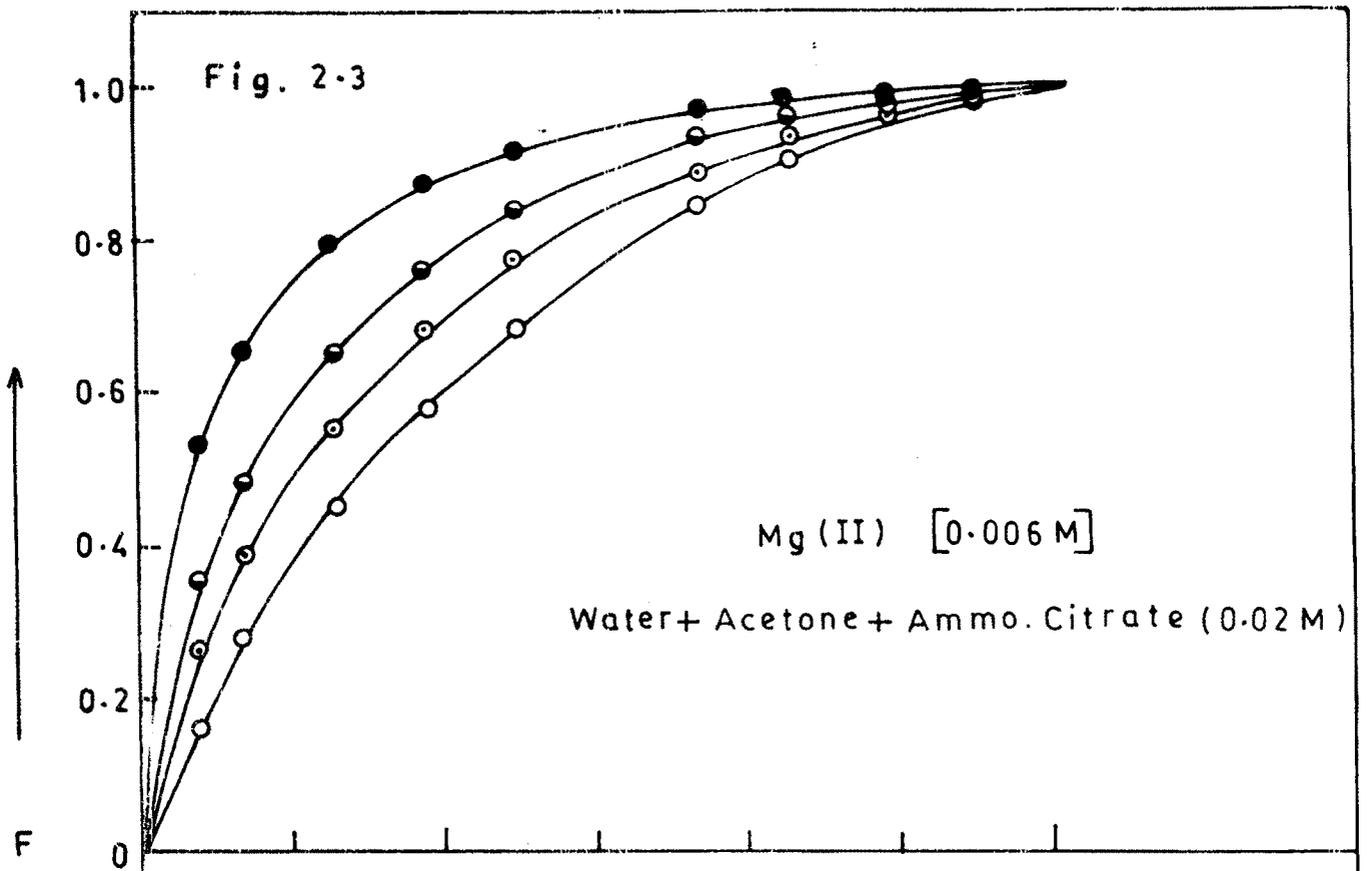
Table 2.5: Dependence of Fractional Attainment of Equilibrium(F) with time(t).

System: Ba (0.002 and 0.004M) on Amberlite IR-120 (NH₄⁺) in Aqueous Acetone Ammonium Citrate (0.02M) at various temperatures.

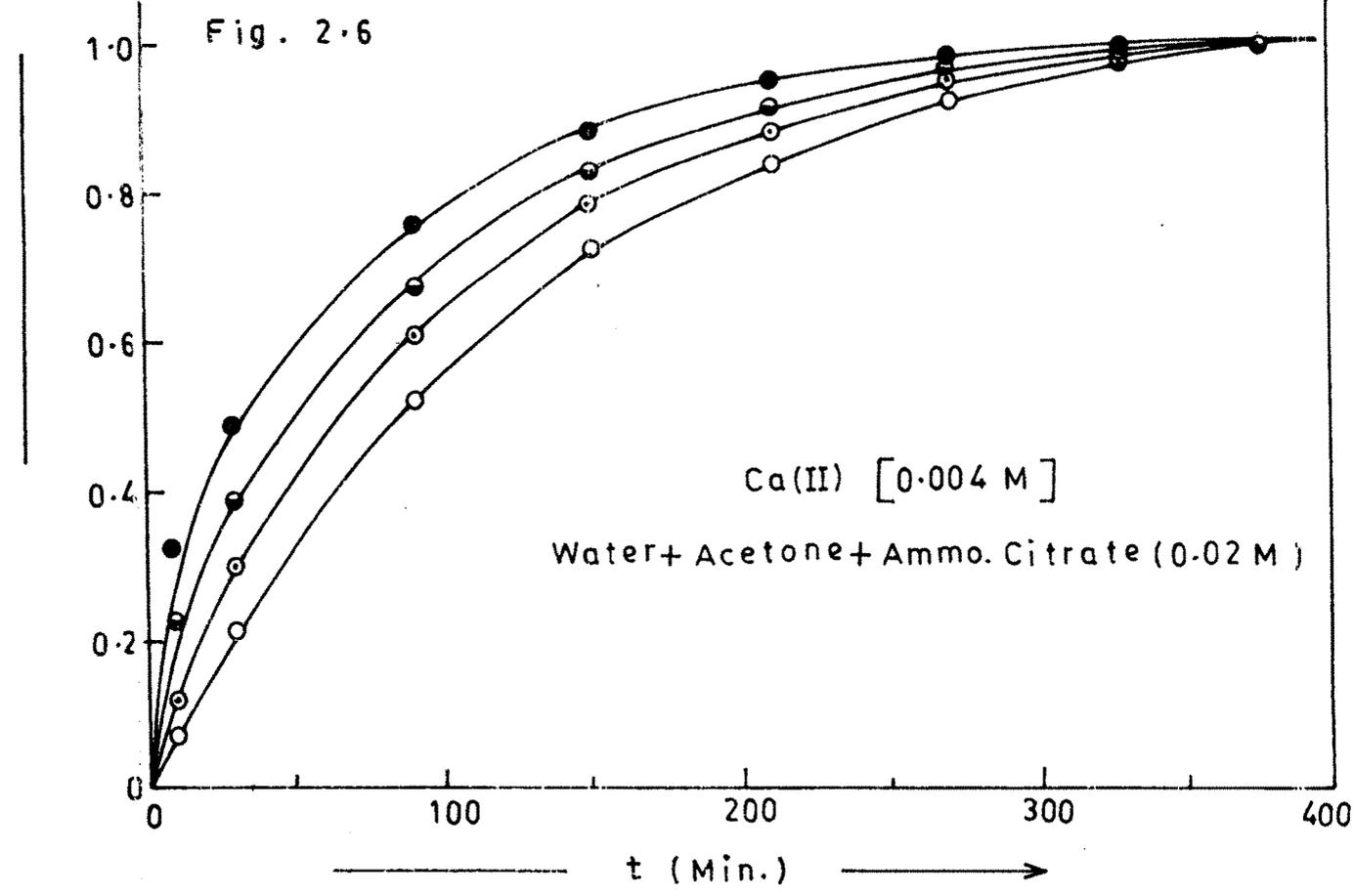
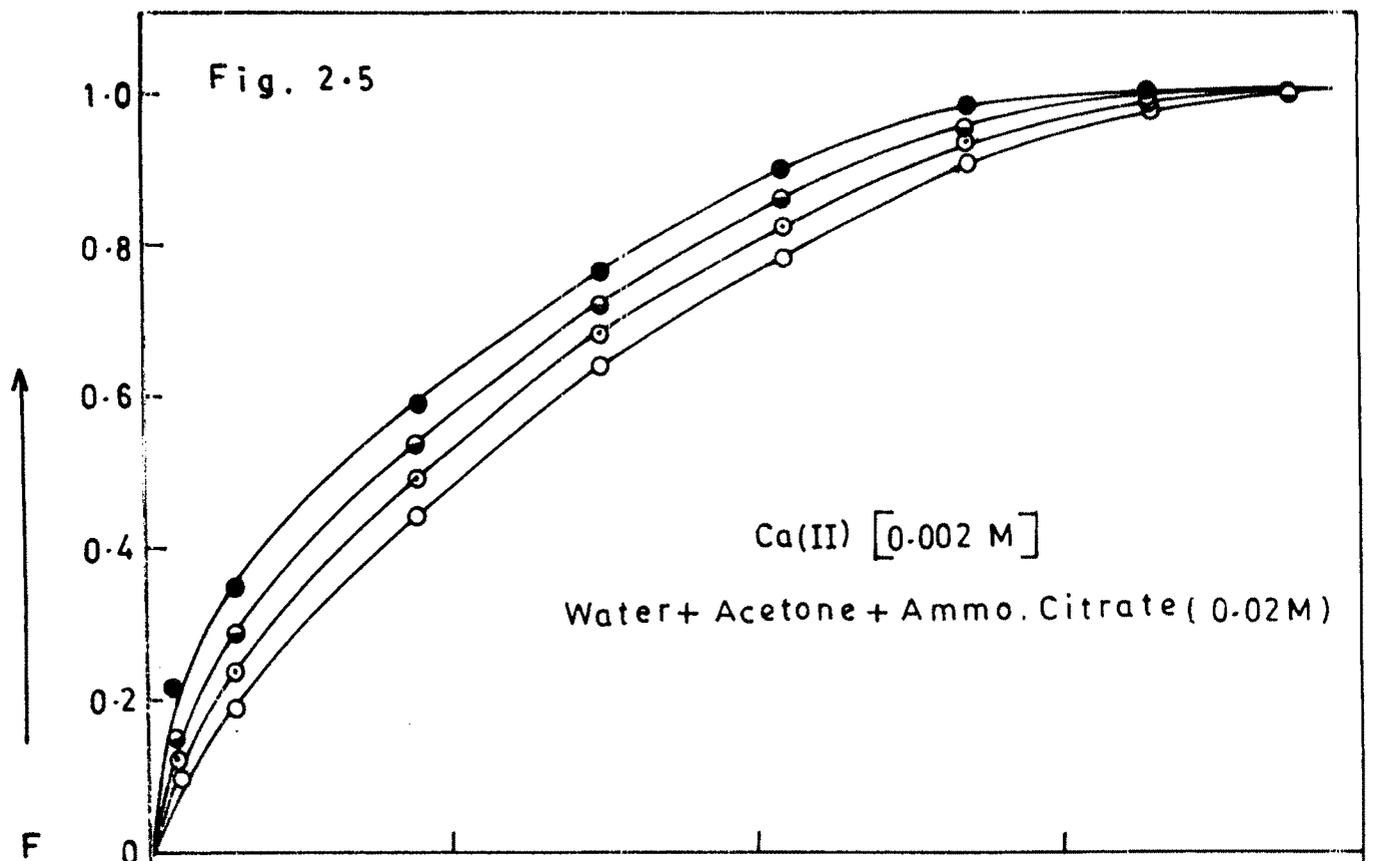
Time in min	Ba (0.002M)				Ba (0.004M)			
	Temperature in °K							
	303	308	313	318	303	308	313	318
000	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
005	0.01	0.02	0.04	0.05	0.02	0.03	0.03	0.04
010	0.03	0.04	0.06	0.11	0.04	0.08	0.08	0.13
030	0.10	0.15	0.24	0.32	0.13	0.15	0.21	0.32
090	0.28	0.35	0.44	0.54	0.35	0.42	0.50	0.59
150	0.43	0.52	0.60	0.68	0.52	0.61	0.67	0.72
210	0.58	0.64	0.72	0.79	0.67	0.74	0.78	0.83
270	0.70	0.75	0.82	0.88	0.79	0.84	0.87	0.91
330	0.82	0.85	0.90	0.95	0.88	0.92	0.94	0.96
390	0.92	0.94	0.97	0.99	0.96	0.97	0.98	0.99
450	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00



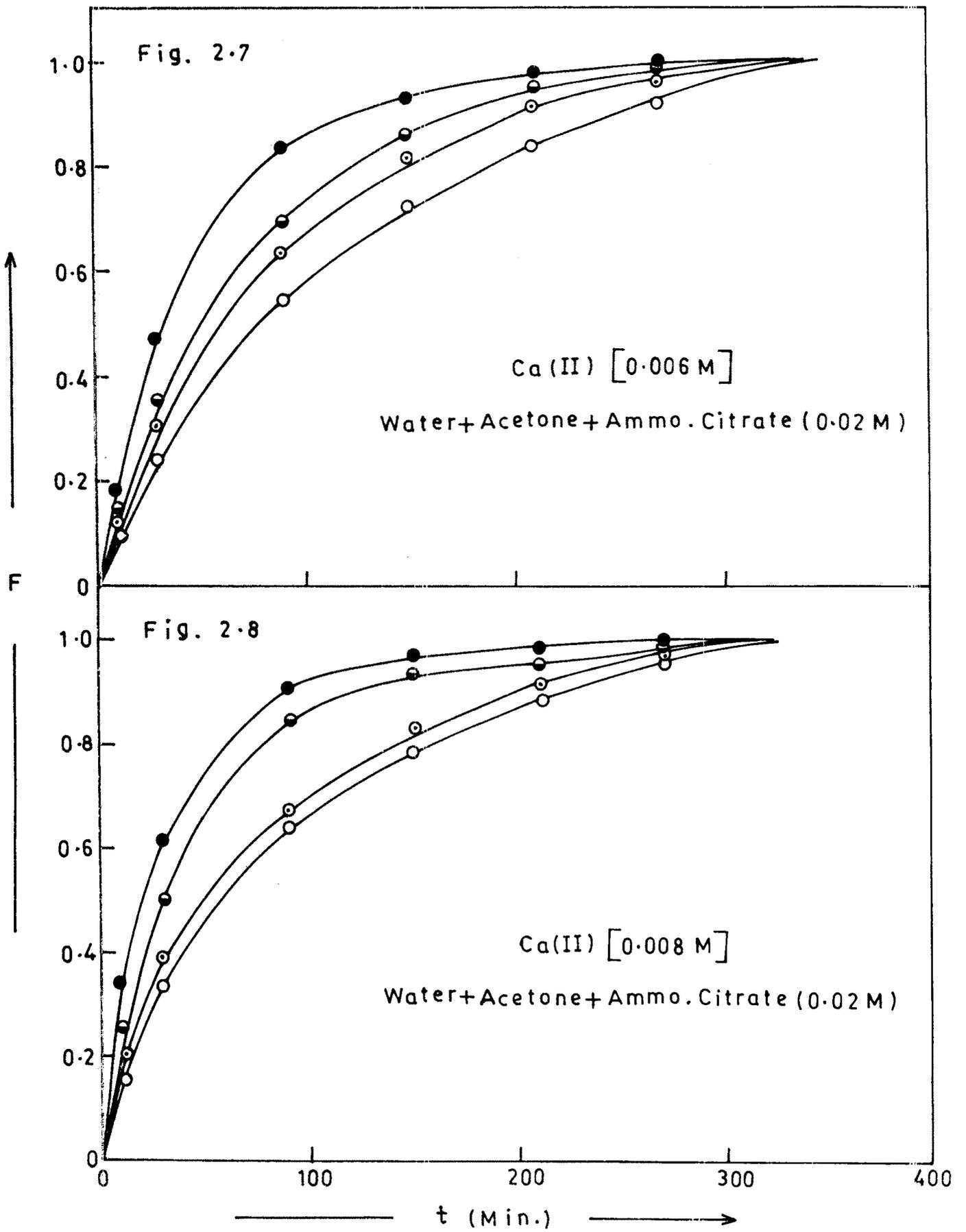
Acetone % v/v ; 0 (○), 30 (◐), 50 (◑), 70 (●) .



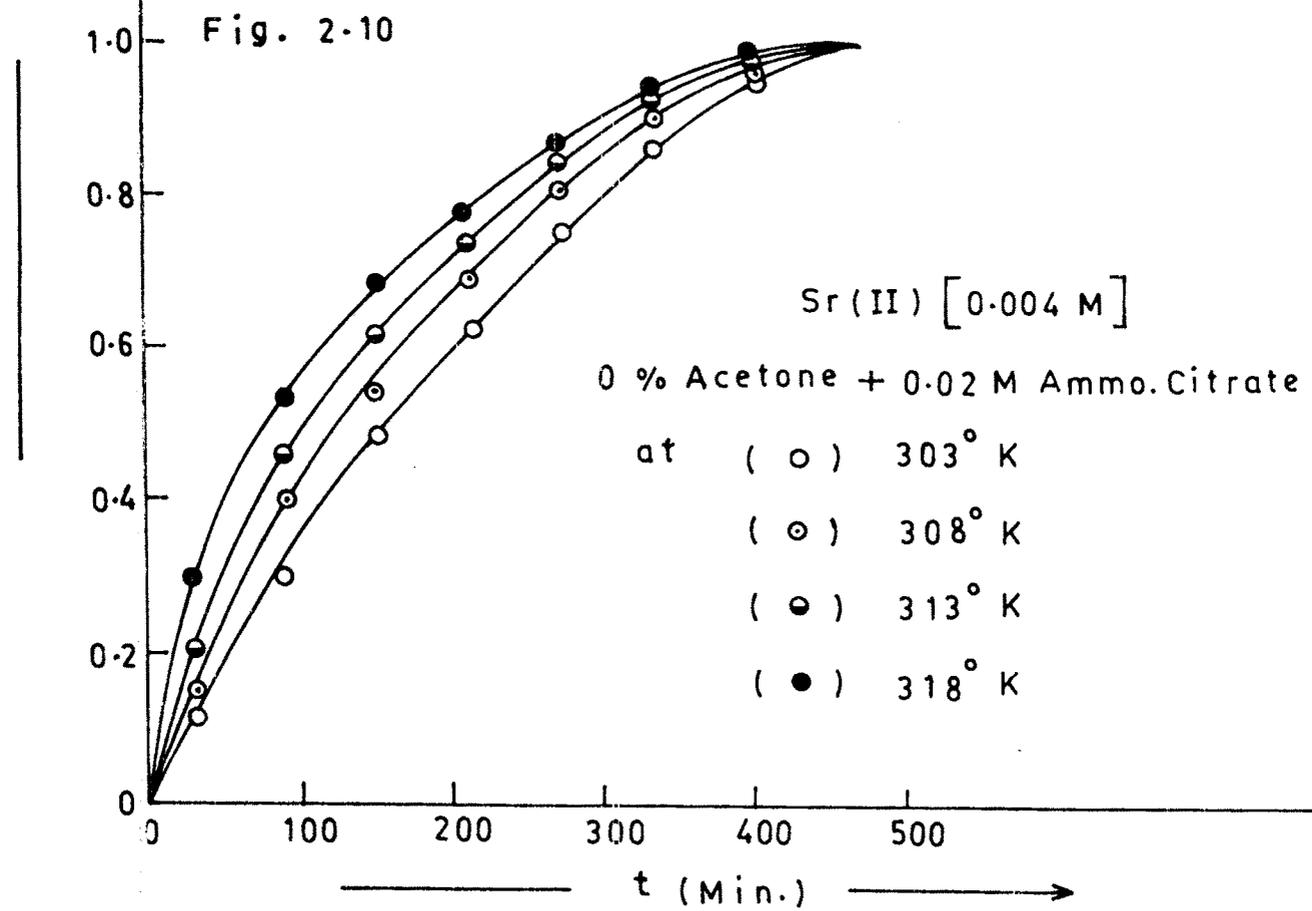
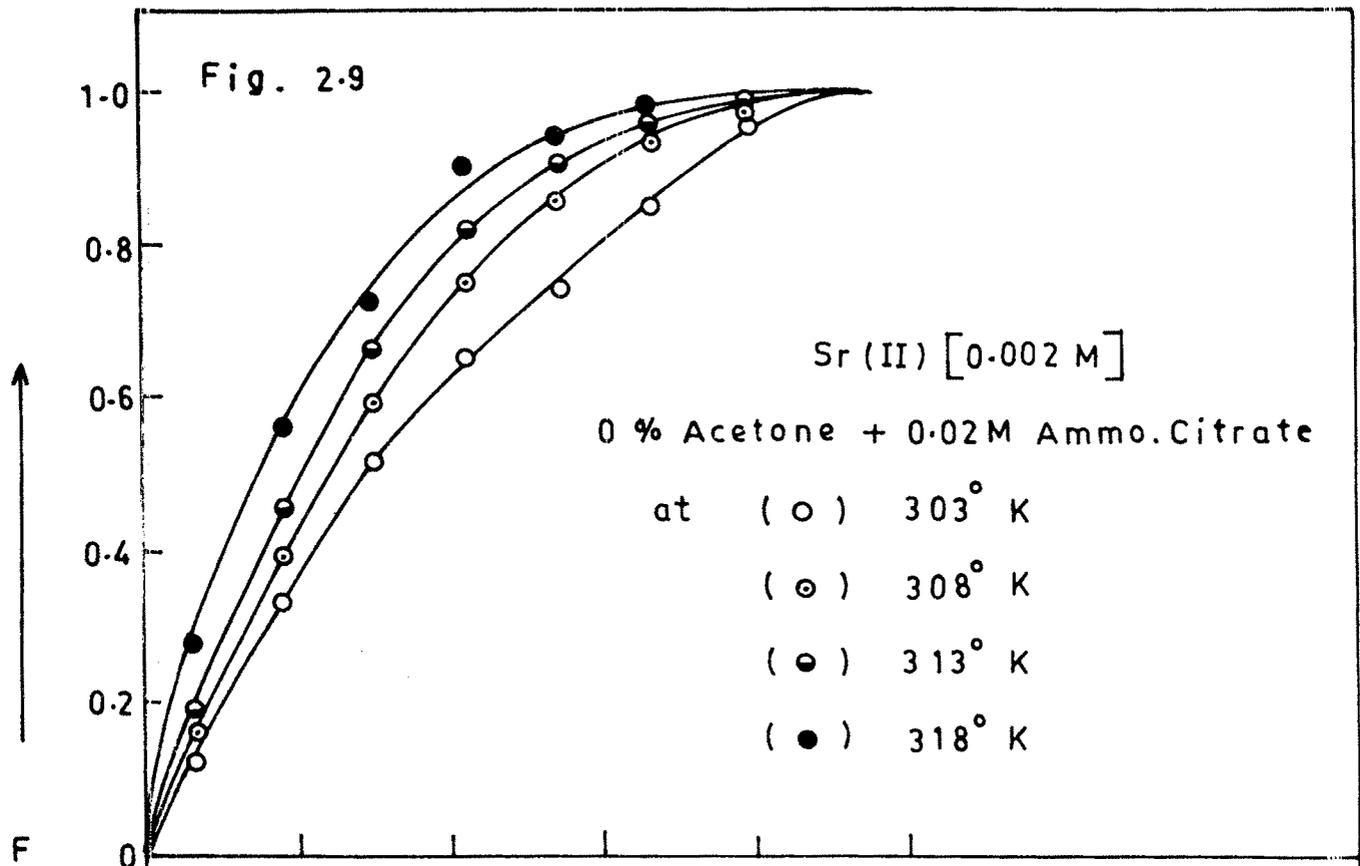
Acetone % v/v ; 0 (○), 30 (◐), 50 (◑), 70 (●) .



Acetone % v/v ; 0 (○) , 30 (⊙) , 50 (●) , 70 (●) .



Acetone % v/v ; 0 (o) , 30 (⊙) , 50 (⊖) , 70 (●) .



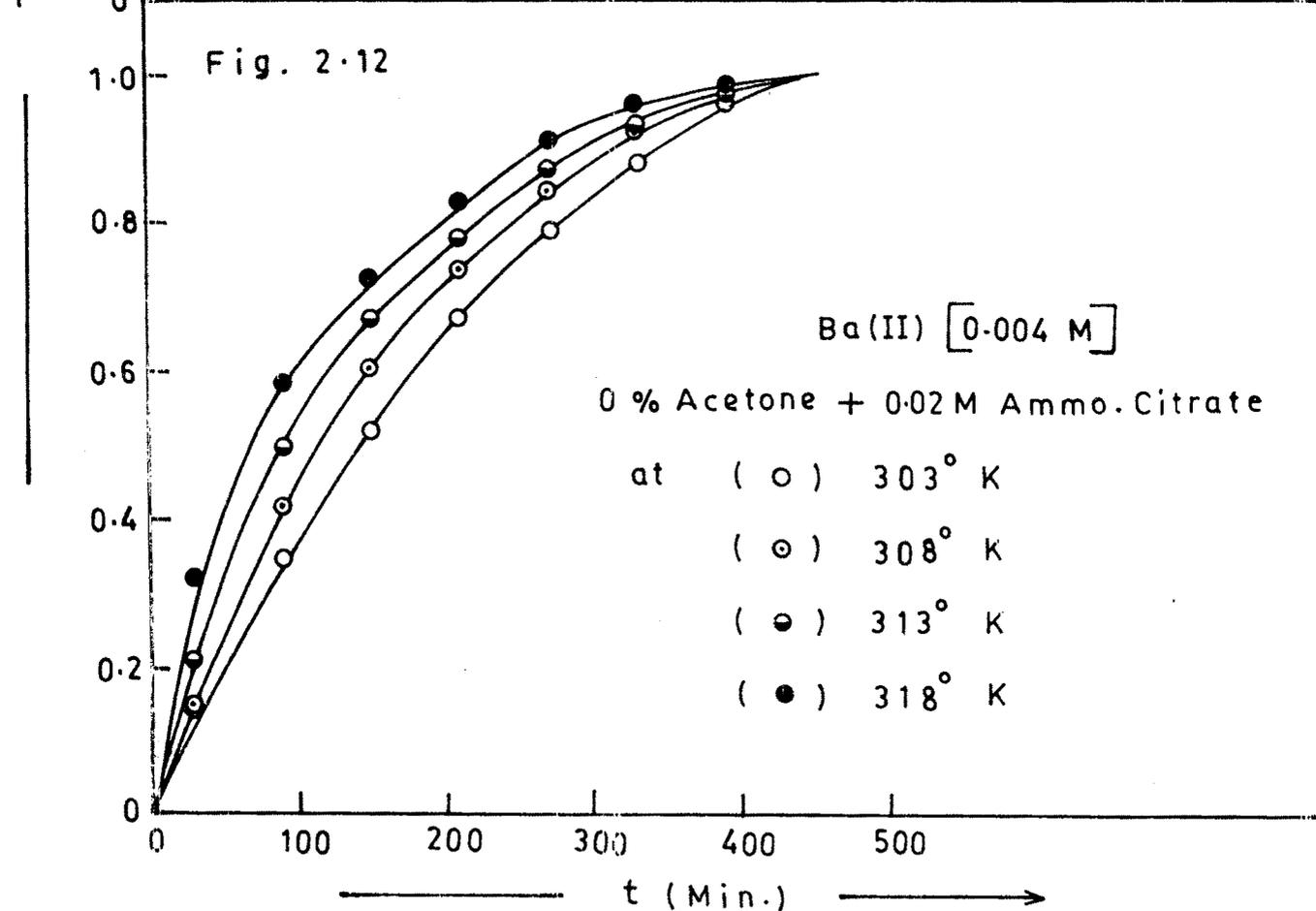
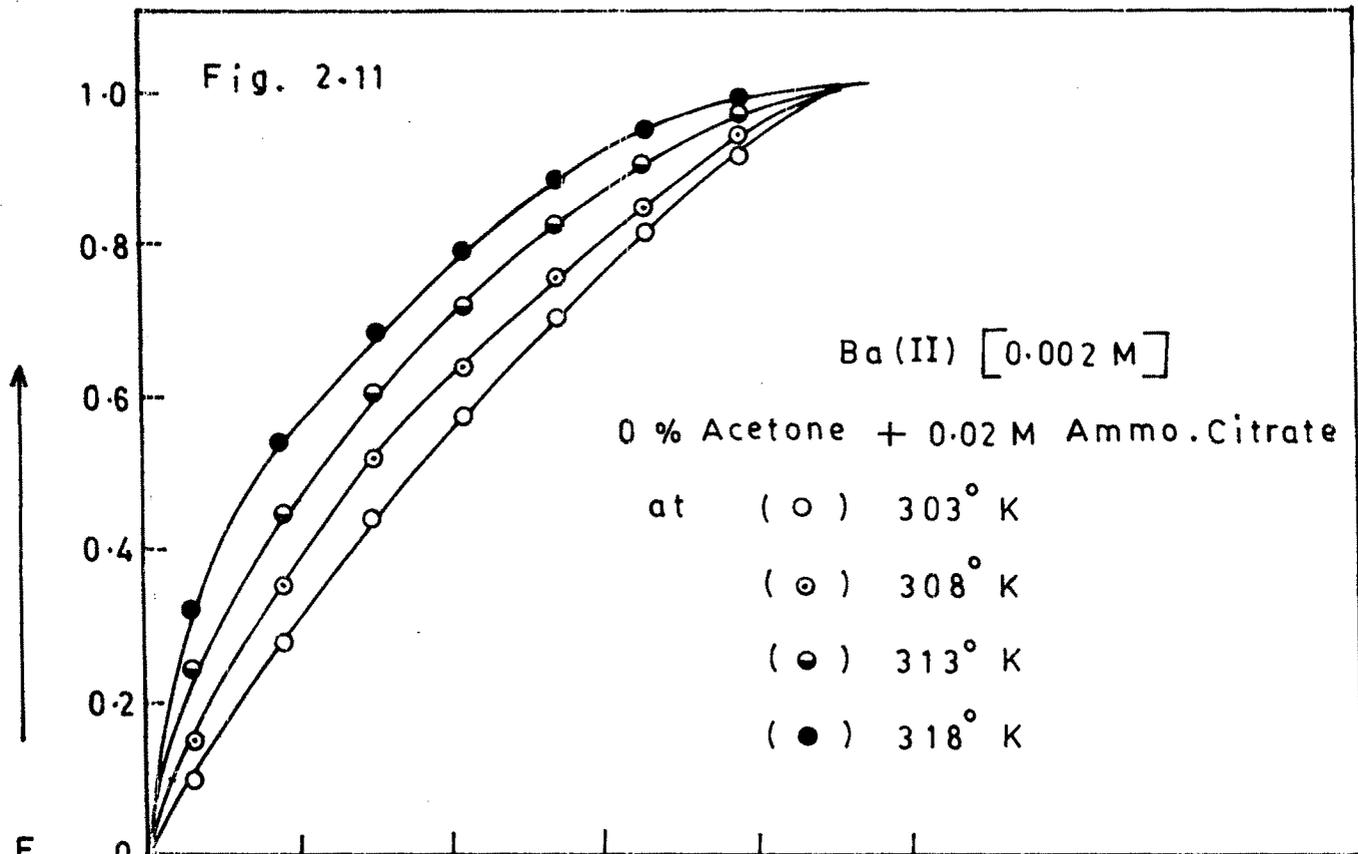


Fig. 2-13

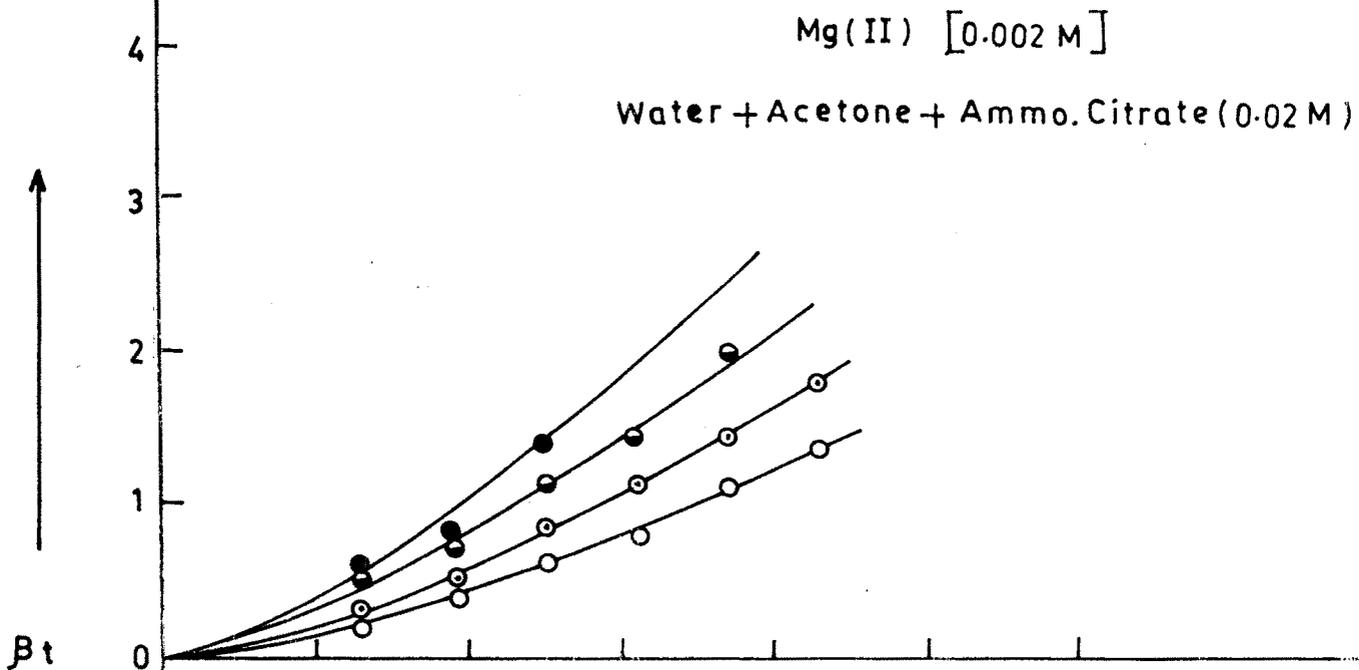
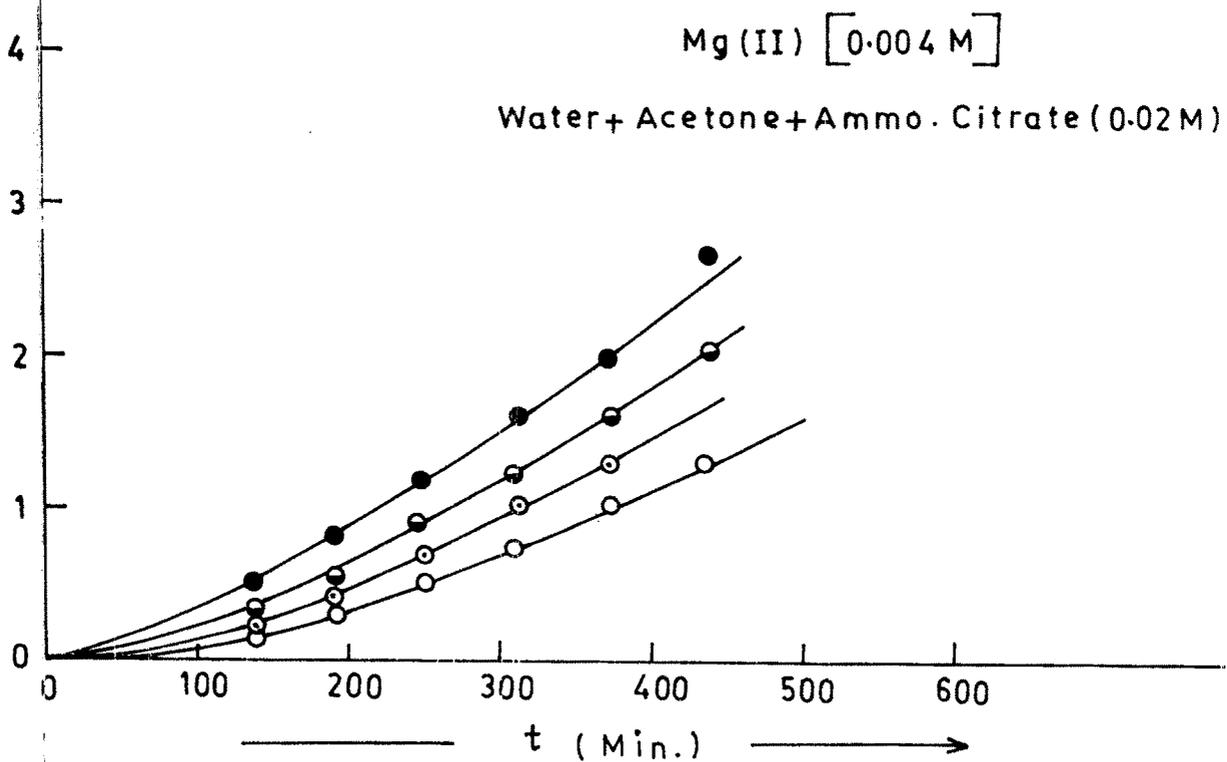


Fig. 2-14



Acetone % v/v ; 0 (o) , 30 (⊙) , 50 (●) , 70 (●) .

Fig. 2-15

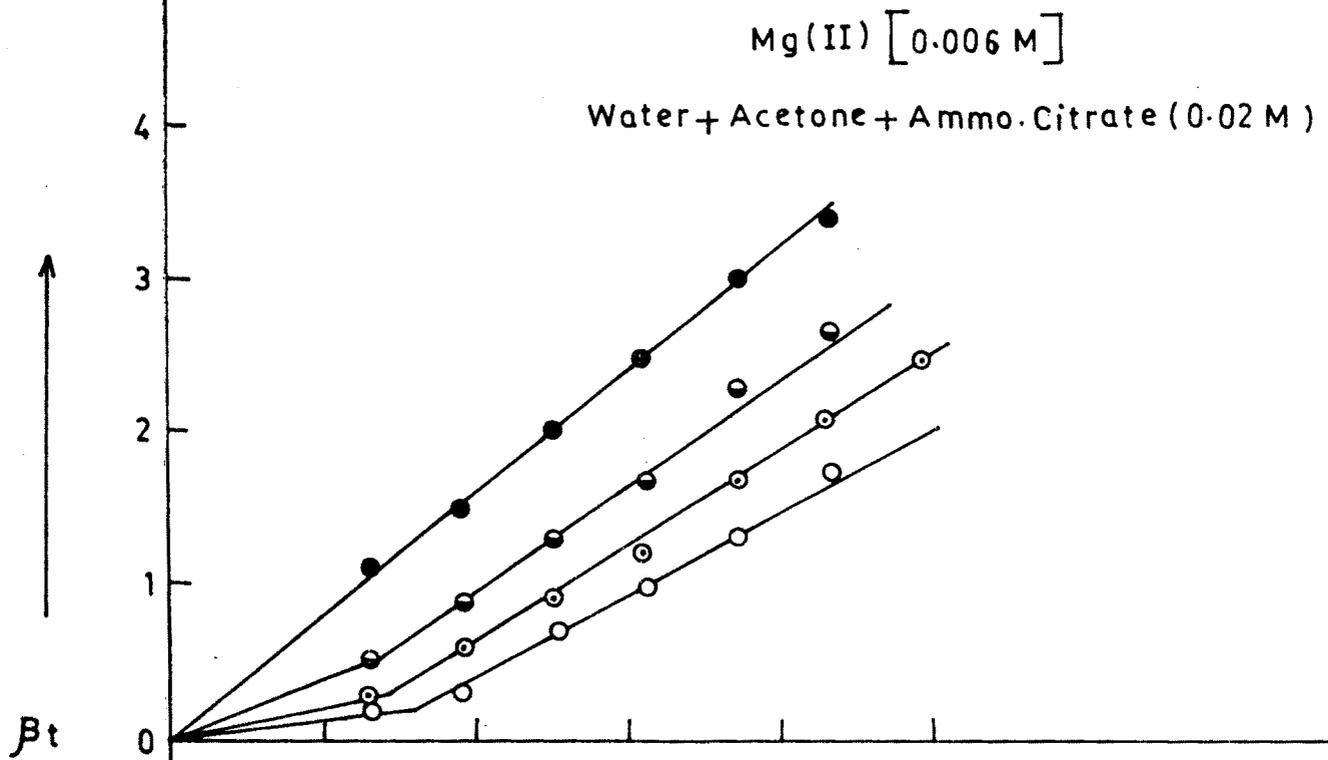
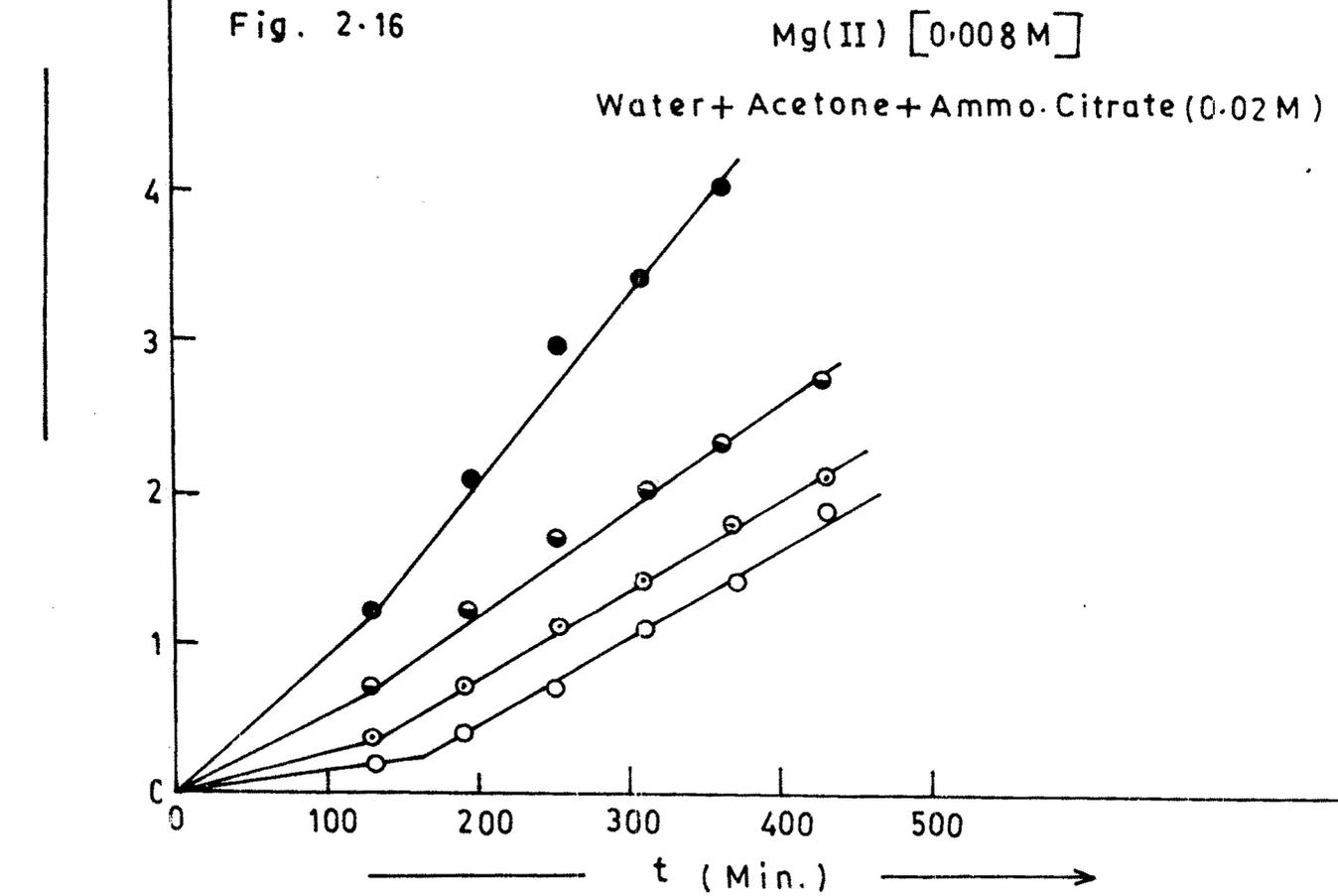
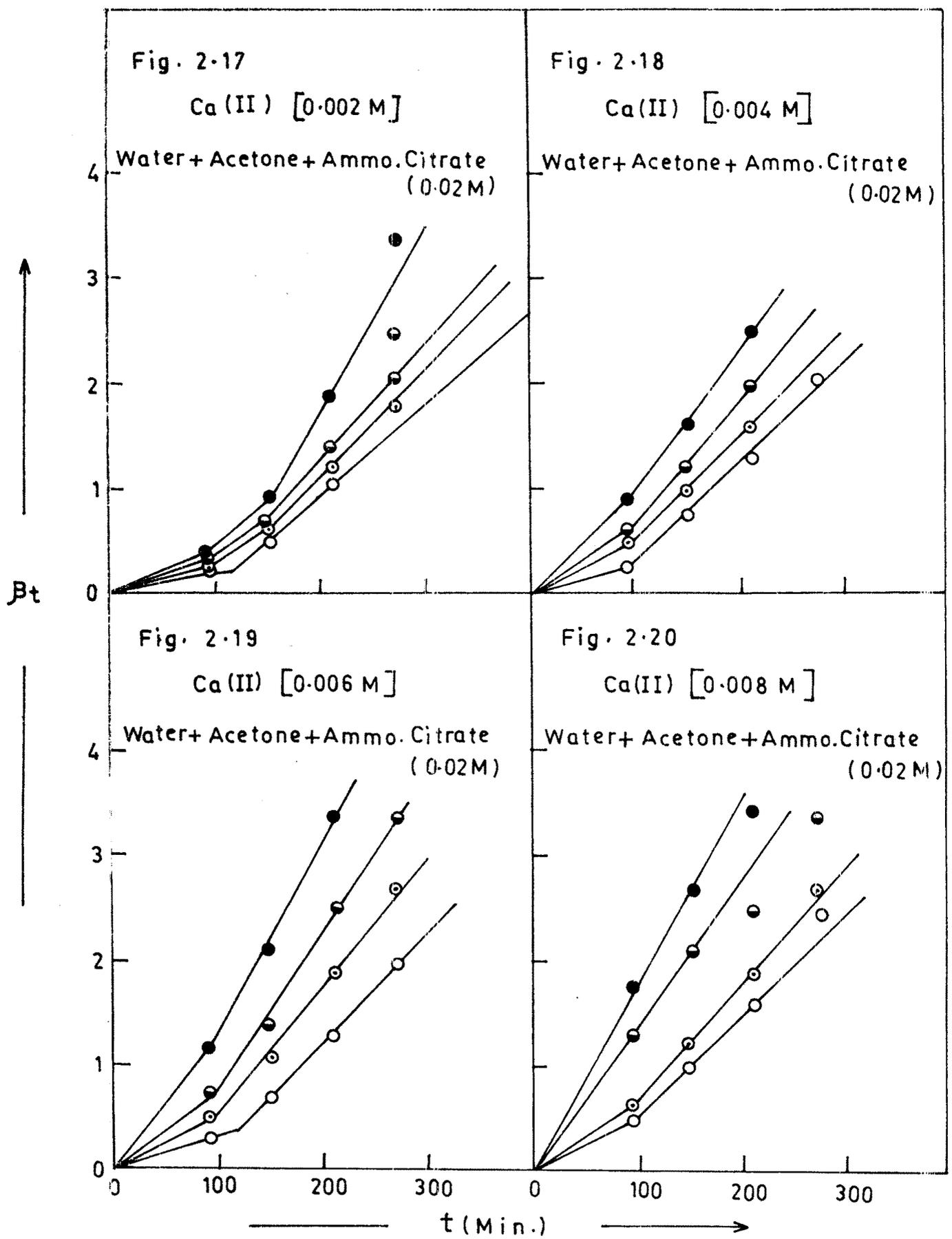


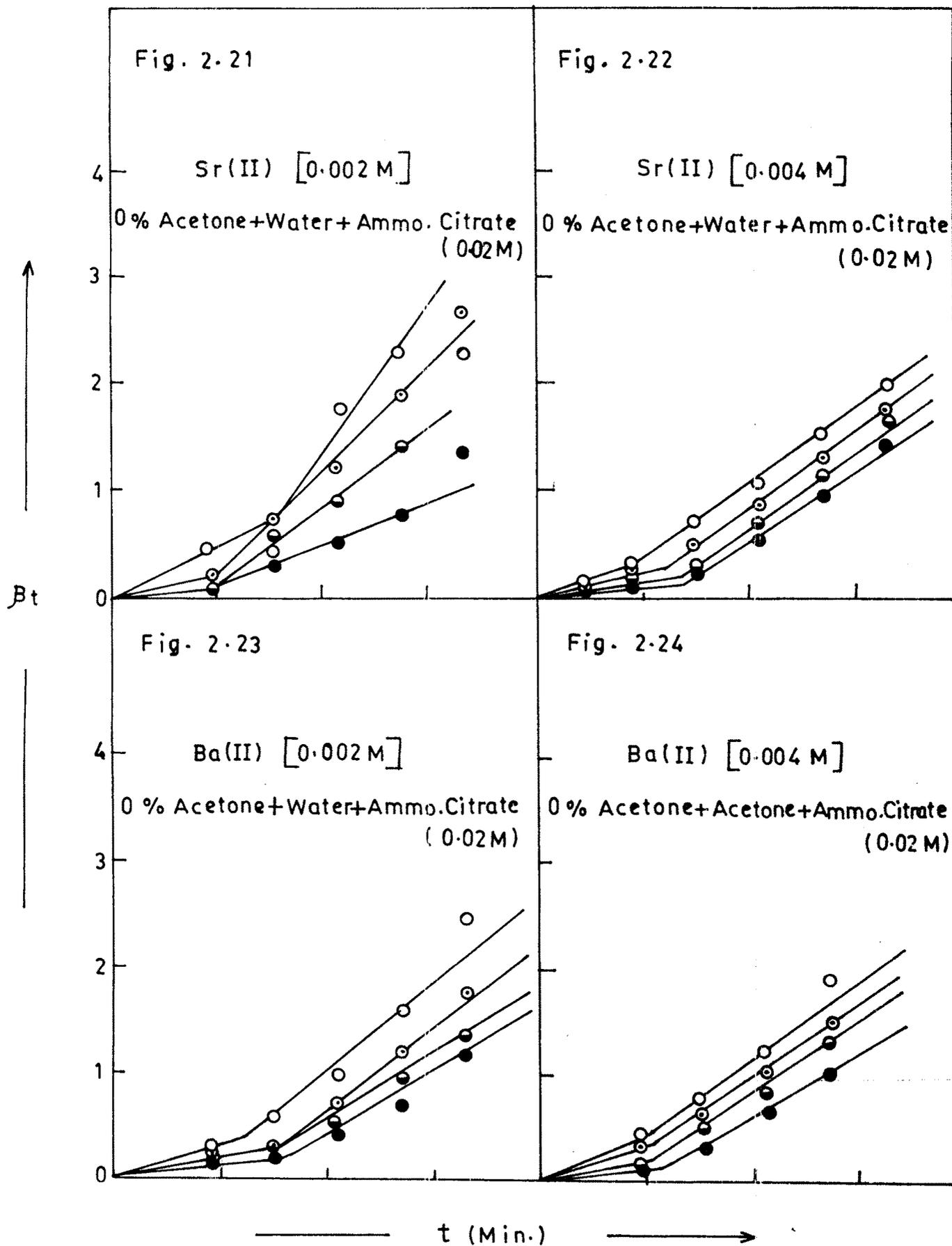
Fig. 2-16



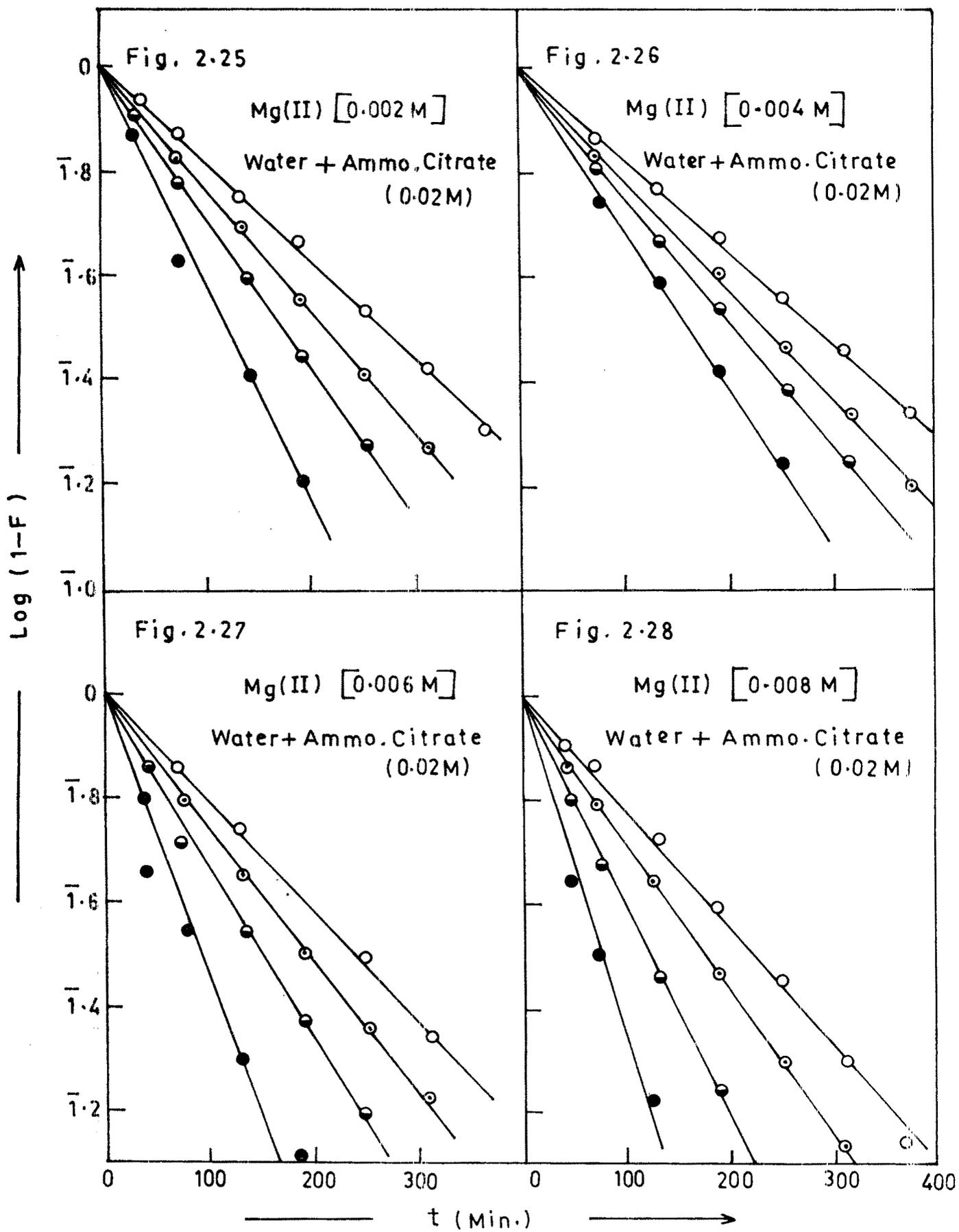
Acetone % v/v ; 0 (○), 30 (◉), 50 (●), 70 (●) .



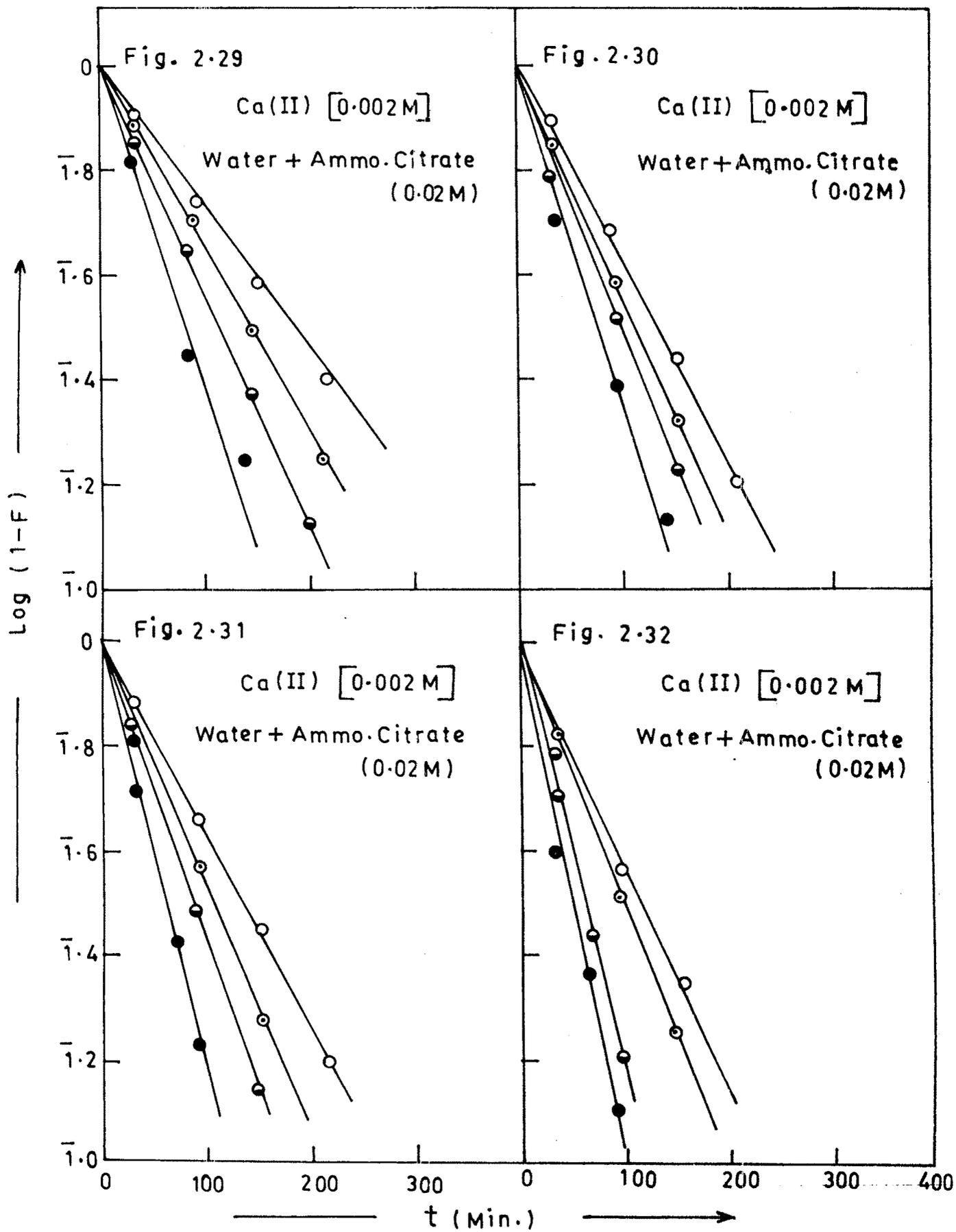
Acetone % v/v ; 0 (○), 30 (◐), 50 (◑), 70 (●) .



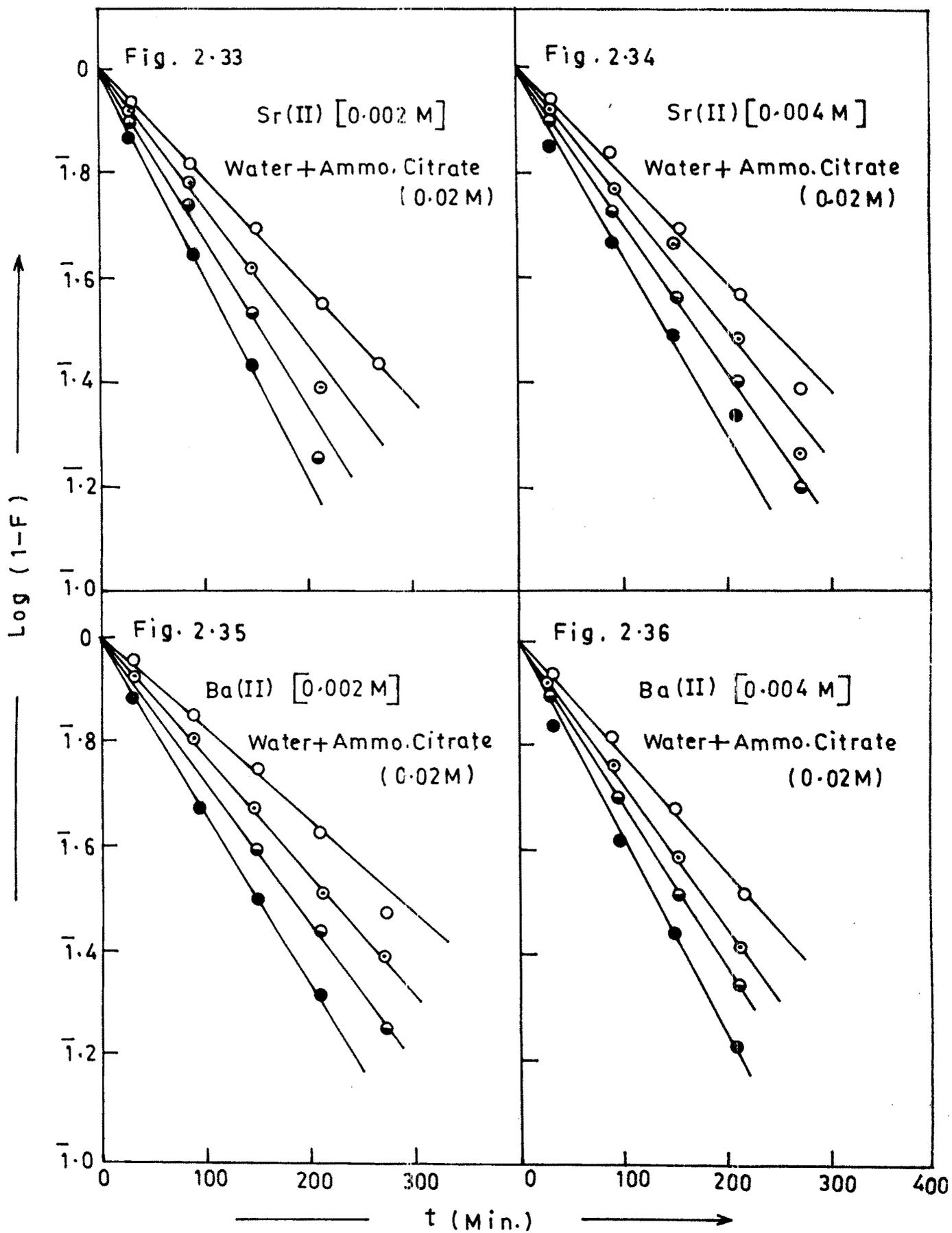
Temp. °K — 303 (○), 308 (⊙), 313 (◐), 318 (●).



Temp. °K — 303 (○), 308 (◐), 313 (◑), 318 (●).



Temp. °K — 303 (○), 308 (◐), 313 (◑), 318 (●).



Temp. °K — 303 (○), 308 (◐), 313 (◑), 318 (●).

Table 2.6 : Kinetic parameters calculated for the Exchange of Mg(0.002, 0.004, 0.006, 0.008 M) on Amberlite IR-120 (NH₄⁺) in Aqueous-Acetone Ammonium Citrate (0.02M) at 303°K.

Acetone %, V/V	t _{1/2} min.	D x 10 ¹⁰ M ² sec ⁻¹	B x 10 ² sec ⁻¹	K x 10 ³ min ⁻¹
Mg (0.002M)				
0	165	0.155	0.87 0.57	2.303
30	125	0.209	0.60 0.33	3.070
50	90	0.300	0.50 0.33	3.220
70	45	0.520	0.50 0.25	4.606
Mg (0.004M)				
0	180	0.150	0.66 0.16	1.919
30	150	0.180	0.66 0.142	2.870
50	115	0.230	0.50 0.16	3.070
70	85	0.330	0.40 0.20	3.220

Table 2.6: Contd...

Acetone %, V/V	$t_{\frac{1}{2}}$ min.	$D \times 10^{10}$ $M^2 \text{ sec}^{-1}$	$B \times 10^2$ sec^{-1}	$K \times 10^3$ min^{-1}
Mg (0.006M)				
0	150	0.180	0.85 0.85	2.630
30	110	0.240	0.75 0.37	2.960
50	75	0.360	0.75 0.20	3.610
70	85	0.330	0.58 0.125	5.750
Mg (0.008M)				
0	145	0.195	1.33 1.00	2.303
30	110	0.245	0.66 0.50	3.280
50	65	0.420	0.50 0.28	4.600
70	30	0.780	0.25 0.16	6.500

Table 2.7: Kinetic parameters calculated for the Exchange of Ca(0.002, 0.004, 0.006, 0.008 M) on Amberlite IR-120 (NH₄⁺) in Aqueous-Acetone Ammonium Citrate (0.02M) at 303°K.

Acetone %, V/V	$t_{\frac{1}{2}}$ min.	$D \times 10^{10}$ M ² sec ⁻¹	$B \times 10^2$ sec ⁻¹	$K \times 10^3$ min ⁻¹
Ca (0.002M)				
0	100	0.245	1.50 0.60	3.280
30	90	0.300	0.66 0.50	4.600
50	75	0.360	1.50 0.50	4.900
70	65	0.420	1.50 0.25	7.200
Ca (0.004M)				
0	85	0.330	1.30 1.00	4.600
30	65	0.420	1.16 0.75	4.900
50	50	0.540	1.00 0.60	5.750
70	30	0.780	0.90 0.30	7.480

Table 2.7 : Contd.....

Acetone %, V/V	$t_{\frac{1}{2}}$ min.	$D \times 10^{10}$ $M^2 \text{ sec}^{-1}$	$B \times 10^2$ sec^{-1}	$K \times 10^3$ min^{-1}
Ca (0.006M)				
0	85	0.330	1.60 1.50	5.750
30	60	0.450	1.50 0.75	6.330
50	50	0.540	1.20 0.61	6.900
70	30	0.780	1.05 0.40	9.200
Ca (0.008M)				
0	55	0.490	1.80 1.80	5.060
30	50	0.540	1.33 1.33	5.520
50	30	0.780	1.09 0.60	9.200
70	20	0.820	1.00 0.50	9.590

Table 2.8: Kinetic parameters calculated for the Exchange of Sr(0.002, 0.004 M)

on Amberlite IR-120 (NH₄⁺) in Aqueous-Acetone Ammonium Citrate (0.02M) at various temperatures.

Temp. ° K	t _{1/2} min.	D x 10 ¹⁰ M ² sec ⁻¹	B x 10 ² sec ⁻¹	K x 10 ³ min ⁻¹
Sr (0.002M)				
303	145	0.195	1.33 0.30	2.303
308	120	0.225	1.00 0.55	3.070
313	105	0.257	0.83 0.125	4.030
318	75	0.360	0.40 0.120	4.180
Sr (0.004M)				
303	155	0.162	0.70 0.312	2.303
308	125	0.209	0.80 0.17	3.450
313	100	0.270	0.66 0.11	3.580
318	75	0.360	0.72 0.16	3.680

Table 2.9: Kinetic parameters calculated for the Exchange of Ba(0.002, 0.004 M)

on Amberlite IR-120 (NH₄⁺) in Aqueous-Acetone Ammonium Citrate (0.02M) at various temperatures.

Temp. ° K	t _{1/2} min.	D x 10 ¹⁰ M ² sec ⁻¹	B x 10 ² sec ⁻¹	K x 10 ³ min ⁻¹
Ba (0.002M)				
303	175	0.154	0.83 0.33	2.303
308	140	0.192	0.85 0.20	2.090
313	110	0.245	0.62 0.20	1.530
318	75	0.360	0.66 0.21	1.381
Ba (0.004M)				
303	145	0.195	0.75 0.50	2.600
308	115	0.230	0.75 0.375	3.450
313	90	0.300	0.66 0.20	3.600
318	65	0.420	0.62 0.21	4.000

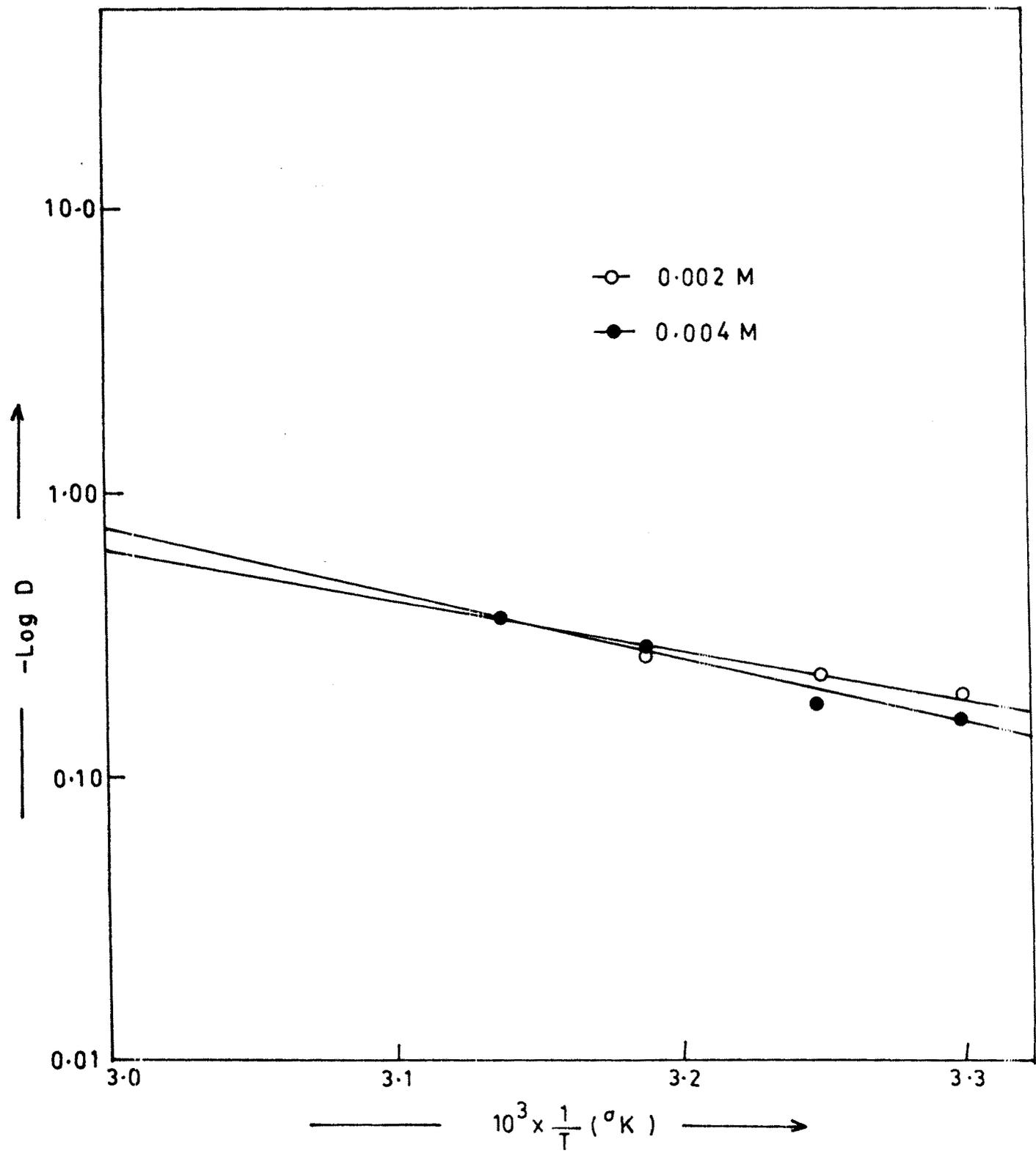


Fig. 2.38 Plots of $\text{Log } D$ Vs $\frac{1}{T}$ for Kinetics of Sr (0.002 M) and (0.004 M) on Amberlite IR 120 (NH_4^+) in aqueous Ammo. Citrate (0.02 M) medium.

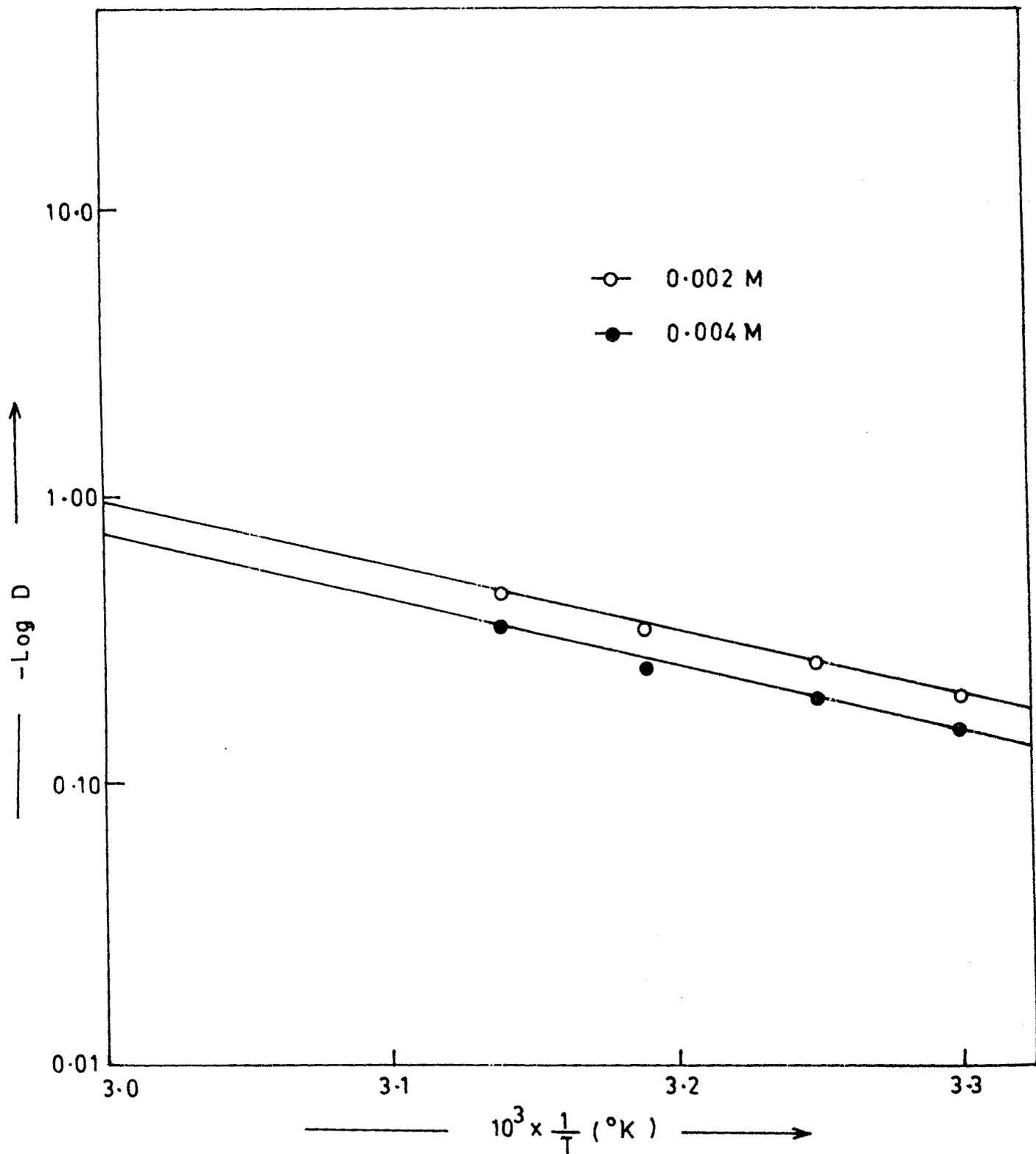


Fig. 2.37-Plots of $\text{Log } D$ Vs $\frac{1}{T}$ for Kinetics of Ba (0.002 M) and (0.004 M) on Amberlite IR 120(NH_4^+) in aqueous Ammonium Citrate (0.02 M) medium.

Table 2.10: Values of pre-exponential constant (D_0) Energy of Activation (E_a) and Entropy of Activation (ΔS^*)

Metal ion	Conc. M	$D_0 \times 10^{10}$ $\text{cm}^2 \text{sec}^{-1}$	E_a KJ mole ⁻¹	ΔS^* J mol ⁻¹ deg ⁻¹
Sr	0.002	0.65	25	-29.58
Sr	0.004	0.78	30	-29.28
Ba	0.002	0.99	24	-29.01
Ba	0.004	0.75	30	-29.41

RESULTS AND DISCUSSIONS

The kinetics of exchange of Mg(II) and Ca(II) ions on Amberlite IR-120 (NH_4^+ form) in queous acetone ammonium citrate (0.02M) was studied. The experiments were carried out at 0, 30, 50 and 70 percentages of acetone and at 0.002, 0.004, 0.006 and 0.008 M of metal ion concentrations.

The kinetics of exchange of Sr(II) and Ba(II) ions on Amberlite IR-120 (NH_4^+ form) in aqueous acetone ammonium citrate (0.02M) was studied. The experiments were carried out at 303°, 308°, 313° and 318°K temperature and at 0.002 and 0.004M of metal ion concentrations.

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 $CV > C\bar{V}$, where C is the concentration of the metal ion in the solution, V is the volume of the solution \bar{C} is the concentration of the metal ion in exchanger 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 varified by Reichenberg²⁹, Helfferich³⁰ and Blickenstaff³¹ in their studies. Hence,

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

where

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

r = radius of the fully swollen resin bead and

D = the effective diffusion coefficient of the two ion undergoing exchange within the exchanger.

n = an integer having any value from 1 to ∞ .

The experimental values of F at various time intervals for the exchange of Mg, Ca, Sr and Ba ions are presented in different tables. The behaviour of F with time t for Mg-metal ion is presneted graphically by figures.



The values of half exchange time $t_{\frac{1}{2}}$ were found out from F Vs t graphs. The interdiffusion coefficient D for the concerned ion exchange systems was calculated from the equation²⁹.

$$D = 0.03 \frac{r^2}{t_{\frac{1}{2}}}$$

Where r is the radius of the resin particles. The values of D are given in Tables. The fractional attainment of equilibrium 'F' is interpreted in terms of Bt by using Reichenberg²⁹ (Table 2.1). Bt Vs t plots are presented for various systems and from the slopes of these curves the values of B are obtained.

The variation of interdiffusion coefficient with time was studied by the plots of log D Vs 1/T. The values of energy of activation Ea were obtained by applying the Arrhenius equation

$$D = D_0 \exp \left(- \frac{E_a}{RT} \right)$$

Where 'D' is interdiffusion coefficient, 'R' is gas constant and 'T' is temperature. The values of Ea are calculated from the slopes of linear plots of log D Vs 1/T and the values of pre-exponential constant D₀ were obtained from the intercepts on these curves. The values of Ea and D₀ are presented in tables.

D_0 is related with the entropy of activation ΔS^* as follows³²,

$$D_0 = 2.72 \frac{d^2KT}{h} \exp\left(\frac{\Delta S^*}{R}\right)$$

where, d = ionic jump distance taken as 5\AA , between two successive positions of ion in the process of diffusion, K = Boltzman constant, $T = 303^\circ\text{K}$, h = planck constant and R = gas constant.

The calculated values of ΔS^* are presneted in tables.

The ion exchange process might be considered to follow the formal kinetics showing the relationship between the order of reaction and its rate. The plots of $\ln(1-F)$ Vs time are linear and satisfy the first order equation

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

Where, K represents the exchange rate constant. The values of K were computed from the slopes of these linear plots and are recorded in tables.

Kinetics of exchange of Mg and Ca on Amberlite IR-120 (NH_4^+) at 0.002, 0.004, 0.006 and 0.008M concentration and at 0, 30, 50 and 70 percentages of acetone were studied. The results of dependence of fractional attainment of

equilibrium (F) with time (t) are presented in tables 2.2 and 2.3 and by figs. 2.1 to 2.12.

It is generally observed that the exchange is quick to begin with and becomes slower and slower towards the equilibrium. Nearly 10% coverage is in 10 minutes, 30% in 30 minutes and 50% in approximately 70 to 90 minutes. These can be viewed by the graphs of F versus t, the nature of the initial part of the graphs is steep in the beginning, then the curve becomes concave towards time axis and later on becomes parallel to time axis. It can therefore be concluded that the exchange is fast initially and remains time independent at equilibrium. The figures of F versus t indicate more that the adsorption isotherms are of 'L' type as defined by Giles³³ which may be due to the fact that vacant sites become less accessible with the progressive covering of adsorption surface. Bansal³⁴ studied the adsorption of cadmium on agricultural soil. The results are giving L type curves. The initial nature of curve indicates that Cd met no strong competition for adsorption sites of water. Adsorption capacity, cation exchange capacity and organic water content were positively correlated. In the present studies the initial nature of isotherms indicates that $[M(H\text{ cit})^+]$ where M=Mg, Ca, Sr, Ba met no strong competition for adsorption sites from the medium containing water and acetone.

It is generally observed that the values of half exchange time $t_{\frac{1}{2}}$ decreases slowly with the rise in percentage of acetone from 0 to 70. It indicates that the process becomes faster by the presence of acetone. The findings are supported by the values of first order rate constant ($K \text{ min}^{-1}$) for the corresponding studies. The rate constants are calculated from the graphs of $\log(1-F)$ versus t (fig 2.25 to 2.36) and the results are presented in tables 2.6 to 2.7. Plots of $\log(1-F)$ Vs. t are linear showing that the exchange of Ca, Mg citrate with Amberlite IR 120 resin in NH_4^+ follows first order rate equation.

$(1-F) = \exp(-Kt)$, wher K represents the exchange rate constant.

B Values

The plots of Bt versus t are represented by figs 2.13 to 2.24. B vlaues obtained from the slopes of these lines are presneted in table 2.6 to 2.9, Bt values were obtained from the Reichenberg's table ²⁹. Bt Vs. t graphs show two segments, the first segment is a straight line, passing through the origin, supports the mechanism of particle diffusion³⁵.

INTERDIFFUSION COEFFICIENT (D)

Interdiffusion coefficient (D) is inverse of half-



exchange time ($t_{\frac{1}{2}}$). It is observed that the values of D increase with the percentage of acetone. It may be concluded that the process of exchange is enhanced by the acetone content.

Kinetics of exchange of Sr and Ba in ammonium citrate media, not containing acetone with Amberlite IR-120 (NH_4^+) resin are studied at 303, 308, 313 and 318°K. The kinetic parameters $t_{\frac{1}{2}}$, D , B , K are presented in tables 2.8 and 2.9. The values of half exchange time $t_{\frac{1}{2}}$ increase with the rise in temperature. It can be concluded that the rate of exchange is accelerated by temperature. This is also confirmed by the values of first order rate constants K presented in the same tables. The values of interdiffusion coefficients increase and those of B decrease at higher temperatures. The process of exchange is thus accelerated by the temperature. The values of energy of activation E_a for the exchange of Sr and Ba are presented in table 2.10.

Energies of activation of diffusion in resin are usually some what higher than in aqueous solution, probably because of the additional effect of higher flexibility of the resin skeleton. The rate of exchange in the particle diffusion controlled processes increases by 4 to 8% °c corresponding to 4-10 K Cal mol⁻¹ in activation energy³⁶.

In present studies Sr and Ba have equal mean radius of the particle = 99.7 (μ m) and hence the values of

E_a are found to be nearly equal 25, 30 KJ mole⁻¹ for 0.002 & 0.004 M respectively. There is no measurable change in the values of energy of activation at different concentrations of metal ions. The values of E_a for particle diffusion mechanism in standard ion exchange resins were found to be^{37,38} 25.1 to 41.84 KJ mole⁻¹.

The values of entropy of activation are in part associated with the change of hydration states of the ions as they leave the aqueous solution and the solid phase and vice versa. It is observed that the values of entropy of activation are practically same (-29.01 to -29.58 KJ mole⁻¹) for Sr and Ba.

The values of entropy are found to be negative and are not measurably affected by acetone. According to Frank and Evans ionisation of natural molecules into charged species accompany a decrease in entropy due to the immobilisation of a large number of solvent molecules, around the charged species. The negative values of entropy were also observed by the behaviour of the dissociation of acetic acid in methanol³⁹.

REFERENCES

- 1) F.C. Nachod and W. Wood,
J. Am. Chem. Soc., 66, 1380 (1944).
- 2) W. Judda and Carron, M.
Paper presented before the Division of Physical and
Inorganic Chemistry American Chemical Society, Sept.
1947.
- 3) H.C. Thomas,
J. Am. Chem. Soc., 66, 1664 (1944).
- 4) S. Wilson and L. Lapidus,
Ind. Engg. Chem., 48, 992 (1956).
- 5) V.I. Gorshkov, G.M. Pahchenkov and T.V. Ivanova,
Russ J. Phys. Chem. 36, 911 (1962).
- 6) J. Shankar and M.R. Ghate,
Ind. J. Chem., 3, 212 (1965).
- 7) R.P. Bhatnagar and S.L. Garde,
J. Ind. Chem. Soc., 43, 259 (1966).
- 8) R.P. Shukla and R.P. Bhatnagar,
J. Ind. Chem. Soc., 32(1), 39 (1955).
- 9) Deoki-nandan, A.R. Gupta and J. Shankar,
Ind. J. Chem., 10, 931 (1972).
- 10) Deoki-nandan and A.R. Gupta,
Ind. J. Chem., 14-A, 75 (1976).
- 11) R.P. Bhatnagar and R.G. Trivedi,
J. Jiwaji Univ., 2(1), 11 (1974).

- 12) L.V. Ress,
Ann. Rep. Prog. Chem. Soc., A-67, 207 (1970).
- 13) E. Hallaba, Z. Mirak and H.N. Saloma,
Ind. J. Chem., 11, 580 (1973).
- 14) G.H. Nacollas and R.P. Paterson,
J. Inorg. Nucl. Chem., 22, 259 (1961).
- 15) S.J. Harvie and G.H. Nacollas,
J. Inorg. Nucl. Chem., 30, 223 (1968).
- 16) S.J. Harvie and G.H. Nacollas,
J. Inorg. Nucl. Chem., 32, 3923 (1970).
- 17) J. Mathew and S.N. Tandon,
Can. J. Chem., 35, 3857 (1977).
- 18) J. Mathew, N.J. Singh, C.B. Gupta and S.N. Tandon,
Ind. J. Chem., 20-A, 841 (1981).
- 19) J.P. Rawat and P.S. Thind,
J. Phys. Chem., 80, 1383 (1976).
- 20) J.P. Rawat and D.K. Singh,
J. Inorg. Nucl. Chem., 40, 897 (1978).
- 21) N.J. Singh, S.N. Tandon and J. Mathew,
Ind. J. Chem., 19-A, 416 (1980).
- 22) K.G. Varshney and A. Premdas,
Ind. J. Chem., 20-A, 841 (1981).
- 23) S.B. Jadhav,
M.Sc. thesis, Shivaji University, Kolhapur (1980).
- 24) A.V. Desai,
M.Sc. thesis, Shivaji University, Kolhapur (1981).

- 25) V.S. Ganbawale,
M. Phil. thesis, Shivaji University, Kolahpur (1984).
- 26) O.N. Karpove and L.I. Somova,
Khim. Tekhnol (Kiev)5, 61 (1974).
- 27) F. Zidan and M.R. EL Nahas,
Indian J. Tech., 19, 187 (1981).
- 28) Y.A. EL Ewady, A.M. EL Wakil, M.R. EL Nahas and M.N.H.
Moussa,
J. Indian Chem. Soc., 61, 517 (1984).
- 29) D. Reichenberg,
J. Am. Chem. Soc., 75, 589 (1953).
- 30) F. Helfferich,
J. Phys. Chem. 69, 1178 (1965).
- 31) R.A. Blickenstaff, J.D. Wagner and J.S. Dranoff,
J. Phys. Chem., Ithaca, 71, 1665 (1967).
- 32) R.M. Barrer, R.F. Bartholomew and L.V.C. Ress,
J. Phys. Chem. Solids 12, 21 (1961).
- 33) C.H. Giles, T.H. Macevan, S.N. Nakhwa and D. Smith,
J. Chem. Soc., 3973 (1960).
- 34) O.P. Bansal,
J. Indian Chem. Soc., LXV, 183 (1988).
- 35) G.E. Boyd and B.A. Saldano,
J. Am. Chem. Soc., 75, 6091, 6105 (1953).
- 36) S. Fronaeus,
Acta. Chem. Scand., 5, 8859 (1951).

- 37) I.A. Kunin and A.M. Semushin,
J. Phys. Chem., 36, 205 (1962).
- 38) E.D. Kieselva and A.M. Semushin,
J. Phys. Chem., 49(8), 212 (1975).
- 39) D.C. Bhattacharya, A.K. Basu and Aditya,
J. Indian Chem. Soc., LX1, PP 956-959 (1984).