
CHAPTER-II

KINETICS OF ION-EXCHANGE OF

Cu, Mg and Pb ,

ON

AMBERLITE IR-120

IN

AQUEOUS ACETONE AMMONIUM TARTRATE

MEDIUM.

INTRODUCTION

Rates of exchange can be measured in both static and dynamic systems. Although vigorous treatments relating the kinetics of ion exchange and column performance are lacking as yet, these rate measurements are of considerable aid in comparing various ion exchange systems.

It is of interest to speculate on the mechanism of exchange by considering how an individual ion in the bulk solution exchanges with an ion within the resin phase. As the ion approaches the resin phase, it first diffuses through the bulk solution until it reaches a stagnant solution layer near the resin surface. It then must diffuse through this surface film. It is this film that is referred to in the film diffusion rate theory.¹⁻⁵ Once in the resin structure, the ion must diffuse through restricted and water-filled porous pores until it reaches an exchange site. At this point, exchange takes place and ion replaced covers the path taken by the entering ion. Each step of the diffusion, whether in the resin or solution phase, must be accompanied in the presence of an ion of the opposite charge, for the law of electroneutrality must be obeyed at all times. This type of diffusion is known as particle diffusion.

Kinetics of exchange reactions has been studied by many workers in aqueous media, only a few studies have been made in mixed solvents.

Turse and Rieman concluded that the rate determining step of the ion exchange reaction for several bivalent metals on Dowex A₁ was chemical reaction.⁶ However, later workers could not verify this conclusion.^{7,8.}

Matsueuru and Wadachi have reported that the rate determining steps for the sorption of Co(II) and Co(III) on anion exchanger Dowex A₁ were particle diffusion and chemical reaction respectively.⁹

The differences in the conclusions concerning the rate determining step show that the kinetic studies of the ion exchange process are difficult. Attempts have been made to study the various ion exchange systems to test as to which of the mechanism are applicable.

Cation exchange chromatographic studies of manganese on Dowex 50W-X8 are recently reported in our laboratory.¹⁰ The distribution coefficients for Cu, Zn, Mg, Ni, Cd, Co, Mn, Ca, Pb, Th, Al, Hg, Sr and Ba were found out in aqueous acetone - succinic acid media. The effect of varying concentrations of acetone and the acid on distribution coefficients were studied to find out the suitable conditions for the separations. The quantitative separations of manganese from other elements were carried out.

A systematic study of the cation exchange behaviour of metals on R-NH₄ type resin in aqueous-ammonium acetate and ammonium acetate containing other solvents (mixed media) has been reported by some workers. Minami and Ishimori¹¹ explored the possibility of separating barium from lead on a cation-exchanger by first eluting the adsorbed lead with ammonium acetate at pH 6 and then barium, with 10% ammonium chloride solution. The difference in the stability of the anionic complexes of barium

and lead with ethylenediaminetetraacetic acid at pH 4.5 and 10.5 respectively has been utilised for their separation.¹² Lead (pH = 4-5) passed out of bed and adsorbed barium was eluted with EDTA (disodium salt) at pH 10.5. Khopkar and De¹³ studied the cation exchange behaviour of barium on Dowex 50W-X8 (H⁺). Nitric acid, hydrochloric acid, ammonium chloride, sodium nitrate, sodium chloride, ammonium acetate, citric acid, tartaric acid and EDTA has been used as the eluting agents. Barium has been separated from U(VI), Cu(II), Hg(II), Cs, Zn, Cd, Ag, Co(IV), Zr, Th, Fe(III) and Bi(III) by 4 M ammonium acetate.

PRESENT WORK :-

Kinetic studies of exchange reactions of Cu, Pb, and Mg ions with NH₄⁺ ion of Amberlite IR-120 resin in aqueous acetone ammonium tartrate media were carried out. The kinetic parameters such as interdiffusion coefficient (D), half exchange time ($t_{1/2}$), parabolic diffusion constant (k), were found out. The effect of concentration of metal ions, acetone and ammonium tartrate on these kinetic parameters are reported in this chapter. The plots of Bt versus t leads to probable mechanism of diffusion. The variations of rate constant (k) with percentage of acetone and molarities of metal ions were studied. The values of energy of activation (Ea), the pre-exponential constant (Do) and entropy of activation (ΔS^\ddagger) were obtained by the studies of kinetics of exchange reactions at different temperatures.

EXPERIMENTAL

Solutions

1. Chloride solutions of copper(II), Lead (II) and Magnesium (II) = 0.1 M
2. Acetone % - 0, 10, 30, 50, 70 and 80
3. Ammonium tartrate 0.06 M and 0.4 M.

Procedure

Exactly 1 g of air dried resin Amberlite-IR-120 (NH_4^+) form was taken in an erlynmeyer flask. 50 ml of mixture containing acetone water Ammonium tartrate was added. Appropriate quantity of metal ion solution was added into it at noted time so that the overall metal concentration would be 0.002, 0.0004, 0.006, 0.008 M or as desired. The change in metal ion concentration was noted at different time intervals titrimetrically.

DISCUSSION

The kinetics of exchange of Cu^{2+} , Pb^{2+} , and Mg^{2+} ions on Amberlite IR-120 (NH_4^+) resin in aqueous acetone Ammonium tartrate media was studied. The studies represent the mechanism of exchange of Cu, Mg, and Pb with the Amberlite IR-120 (NH_4^+). The pH of the solution was observed to be more than 10 and hence the cationic complexes were formed.

Fractional attainment of equilibrium F.

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

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

TABLE 2 : 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	0.52	0.3160	0.76	0.9440
0.02	0.00036	0.27	0.0736	0.53	0.3320	0.77	0.9850
0.03	0.00076	0.28	0.0796	0.54	0.3480	0.78	1.0280
0.04	0.00141	0.29	0.0861	0.55	0.3650	0.79	1.0730
0.05	0.00229	0.30	0.0928	0.56	0.3800	0.80	1.1200
0.06	0.0032	0.31	0.0998	0.57	0.400	0.81	1.1710
0.07	0.0044	0.32	0.1070	0.58	0.4190	0.82	1.2240
0.08	0.0057	0.33	0.1147	0.59	0.4380	0.83	1.2800
0.09	0.0073	0.34	0.1226	0.60	0.4580	0.84	1.3400
0.10	0.0091	0.35	0.1308	0.61	0.4790	0.85	1.4040
0.11	0.0111	0.36	0.1391	0.62	0.5000	0.86	1.4680
0.12	0.0132	0.37	0.1485	0.63	0.5220	0.87	1.5430
0.13	0.0156	0.38	0.1577	0.64	0.5450	0.88	1.6230
0.14	0.0183	0.39	0.1670	0.65	0.5690	0.89	1.7100
0.15	0.0210	0.40	0.1770	0.66	0.5940	0.90	1.8000
0.16	0.0241	0.41	0.1880	0.67	0.6200	0.91	1.9100
0.17	0.0274	0.42	0.1990	0.68	0.6470	0.92	2.0300
0.18	0.0309	0.43	0.2100	0.69	0.6750	0.93	2.1600
0.19	0.0346	0.44	0.2220	0.70	0.7030	0.94	2.3200
0.20	0.0386	0.45	0.2340	0.71	0.7340	0.95	2.5000
0.21	0.0428	0.46	0.2460	0.72	0.7650	0.96	2.7000
0.22	0.0473	0.47	0.2590	0.73	0.7980	0.97	3.0100
0.23	0.0520	0.48	0.2730	0.74	0.8320	0.98	3.4100
0.24	0.0570	0.49	0.2870	0.75	0.8680	0.99	4.1100
0.25	0.0623	0.50	0.3010	0.75	0.9050	1.00	-

Dependence of fractional exchange (F) on percentage of acetone
 Table 2.2 Metal ion Cu (ii) 0.002 M
 Ammonium Tartrate 0.06 M

Time in	Time in (Min)	Fractional attainment of equilibrium (F)			
		Acetone percentage			
		0	30	50	70
1		2	3	4	5
	0	0	0	0	0
	30	0.200	0.240	0.280	0.310
	60	0.300	0.350	0.380	0.430
	120	0.550	0.640	0.660	0.680
	180	0.710	0.820	0.850	0.900
	240	0.850	0.950	0.980	0.990
	300	0.950	0.980	0.990	1.000
∞		1.000	1.000	1.000	1.000

Table No. 2.3 Metal Ion Cu (II) 0.004 M
Ammonium Tartrate 0.06 M

1	2	3	4	5
0.00	0.00	0.00	0.00	0.00
30	0.290	0.340	0.430	0.501
60	0.410	0.480	0.520	0.690
120	0.610	0.690	0.740	0.790
180	0.700	0.730	0.830	0.920
240	0.750	0.850	0.880	0.980
300	0.810	0.880	0.950	1.000
360	0.870	0.940	0.990	1.000
420	1.000	1.000	1.000	1.000
∞	1.000	1.000	1.000	1.000

Table 2.4 Metal Ion Cu (II) 0.006 M

Ammonium Tartrate 0.06 M

1	2	3	4	5
0.00	0.000	0.000	0.000	0.000
30.00	0.240	0.300	0.360	0.410
60.00	0.310	0.380	0.420	0.500
120.00	0.570	0.610	0.660	0.710
180.00	0.730	0.760	0.800	0.850
240.00	0.850	0.880	0.900	0.950
300.00	0.920	0.960	0.980	0.990
360.00	1.000	1.000	1.000	1.000
∞	1.000	1.000	1.000	1.000

Dependence of fractional exchange (F) on percentage of Acetone

Table 2.6 Metal ion Pb (II) 0.002 M

Ammonium Tartrate 0.06 M

Time in (Min.)	Fractional attainment of equilibrium (F)			
	Acetone percentage			
	0	30	50	70
1	2	3	[4	5
0.00	0.00	0.00	0.00	0.00
15	0.090	0.120	0.160	0.240
30	0.180	0.230	0.280	0.330
60	0.610	0.410	0.460	0.500
120	0.760	0.650	0.690	0.730
180	0.870	0.810	0.840	0.870
240	0.950	0.910	0.950	0.960
300	1.000	0.970	0.990	0.990
360	1.000	1.000	1.000	1.000

Table 2.7 Metal Ion Pb (II) 0.004 M

Ammonium Tartrate 0.06 M

1	2	3	4	5
0.00	0.00	0.00	0.00	0.00
15	0.110	0.170	0.240	0.300
30	0.220	0.280	0.340	0.400
60	0.400	0.460	0.500	0.550
120	0.570	0.620	0.700	0.750
180	0.790	0.840	0.860	0.900
240	0.910	0.960	0.970	0.990
300	1.000	1.000	1.000	1.000

Table 2.5 Metal Ion Cu (II) 0.008 M

Ammonium Tartrate 0.006 M

1	2	3	4	5
0.00	0.00	0.00	0.00	0.00
30	0.21	0.24	0.27	0.29
60	0.29	0.35	0.38	0.39
120	0.42	0.47	0.49	0.52
180	0.65	0.68	0.72	0.75
240	0.82	0.85	0.88	0.89
300	0.97	0.97	0.98	0.97
360	1.00	1.00	1.00	1.00
∞	1.00	1.00	1.00	1.00

Table 2.8 Metal Ion Pb (II) 0.006 M

Ammonium Tartrate 0.06 M

1	2	3	4	5
0.00	0.00	0.00	0.00	0.00
15	0.190	0.180	0.300	0.330
30	0.240	0.310	0.370	0.440
60	0.450	0.570	0.610	0.650
90	0.760	0.780	0.840	0.870
120	0.920	0.950	0.960	0.970
180	0.980	0.980	0.980	0.990
240	1.000	1.000	1.000	1.000
300	1.000	1.000	1.000	1.000

Table 2.9 Metal Ion Pb (II) 0.008 M

Ammonium Tartrate 0.06 M

1	2	3	4	5
0	0.000	0.000	0.000	0.000
15	0.140	0.170	0.200	0.230
30	0.200	0.250	0.280	0.320
60	0.350	0.380	0.420	0.450
120	0.570	0.600	0.630	0.660
180	0.850	0.760	0.880	0.820
240	0.950	0.870	0.910	0.940
300	0.990	0.970	0.980	0.990
360	1.000	0.990	0.990	0.990
420	1.000	1.000	1.000	1.000

Dependence of fractional exchange (F) on percentage of acetone

Table 2.10 Metal ion ~~Cu~~ (II) 0.002 M
Cu

Ammonium Tartrate 0.55 M
0.4 M

Time in (Min)	Fractional attainment of equilibrium (F)			
	Acetone percentage			
	0	30	50	70
I	2	3	4	5
0	0.000	0.000	0.000	0.000
10	0.170	0.250	0.290	0.340
30	0.201	0.292	0.330	0.370
60	0.420	0.480	0.520	0.550
120	0.630	0.660	0.698	0.720
180	0.780	0.840	0.850	0.890
240	0.890	0.960	0.980	0.790
300	1.000	1.000	1.000	1.000



Table 2.11 Metal ion Cu (II) 0.004 M

Ammonium Tartrate 0.4 M

1	2	3	4	5
0.000	0.000	0.000	0.000	0.000
30	0.220	0.300	0.400	0.450
60	0.400	0.470	0.540	0.590
120	0.570	0.640	0.680	0.760
180	0.700	0.750	0.850	0.880
240	0.850	0.892	0.950	0.997
300	0.910	0.960	0.980	1.000
360	1.000	0.1.000	1.000	1.000

Table 2.12 Metal ion Cu (II) 0.006 M

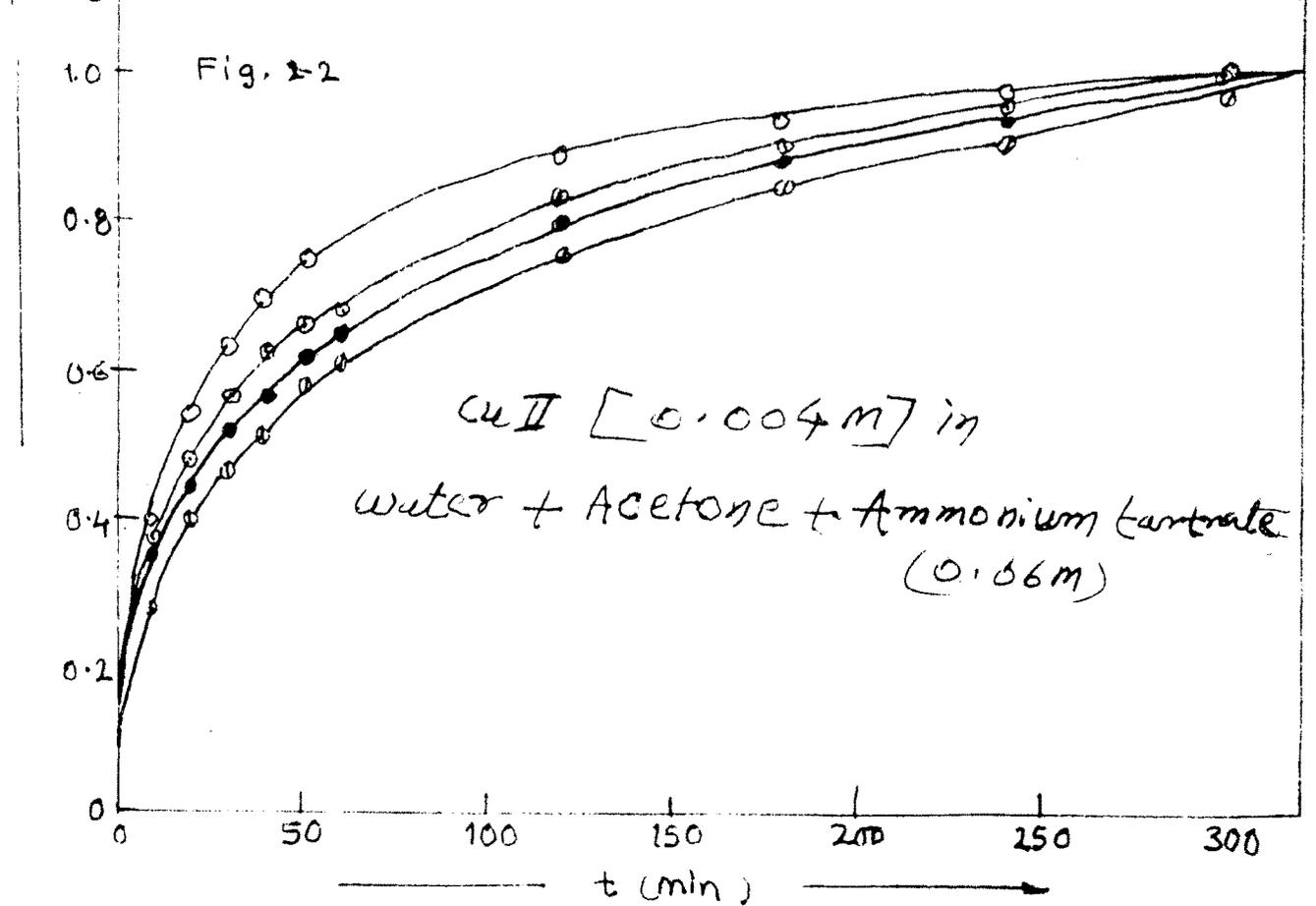
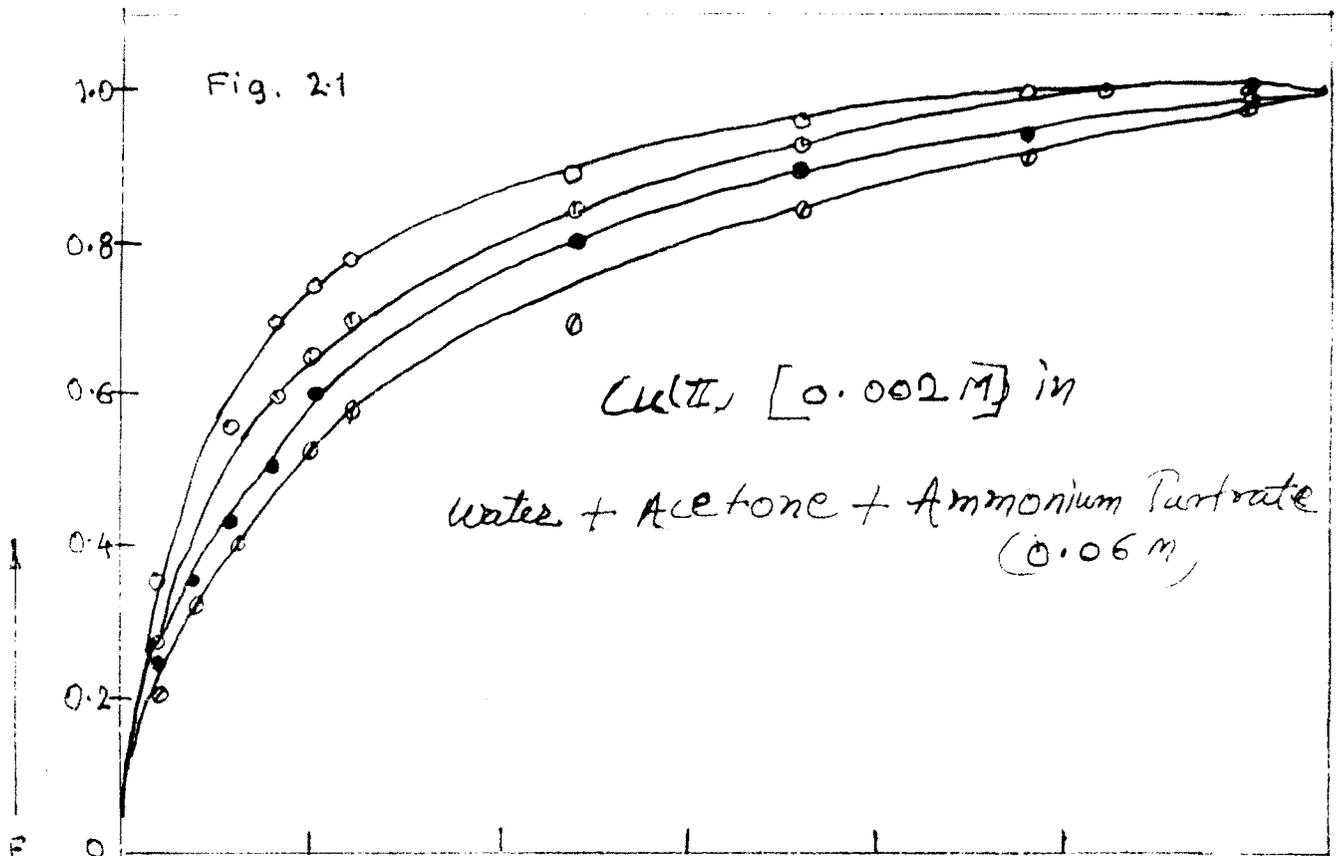
Ammonium Tartrate 0.4 M

1	2	3	4	5
0.00	0.00	0.00	0.00	0.00
30	0.120	0.148	0.180	0.220
60	0.200	0.240	0.272	0.310
120	0.333	0.380	0.410	0.440
180	0.400	0.450	0.540	0.570
240	0.570	0.620	0.650	0.680
300	0.660	0.700	0.743	0.802
360	0.750	0.820	0.850	0.870
420	0.880	0.900	0.930	0.950
480	1.000	1.000	1.000	1.000

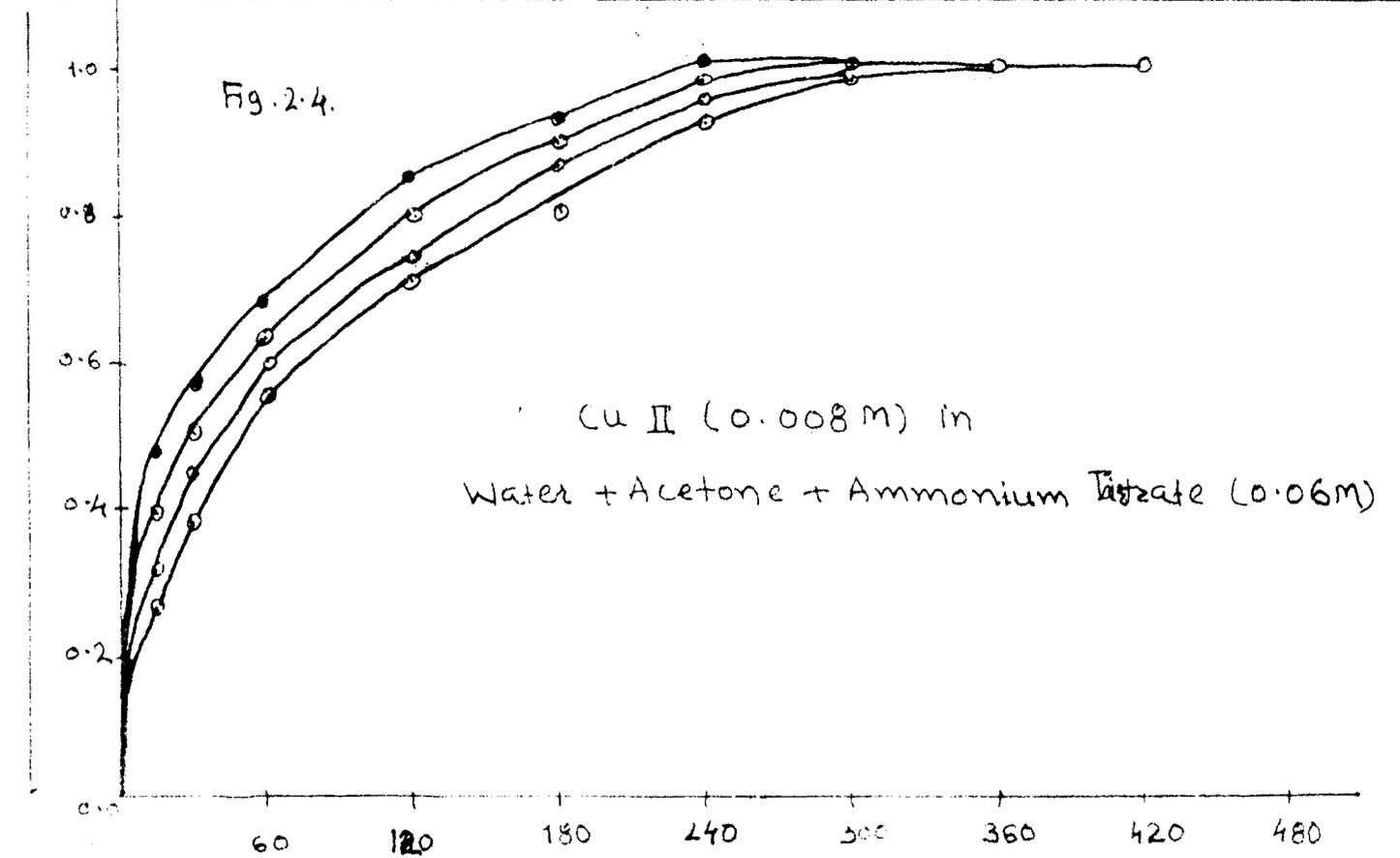
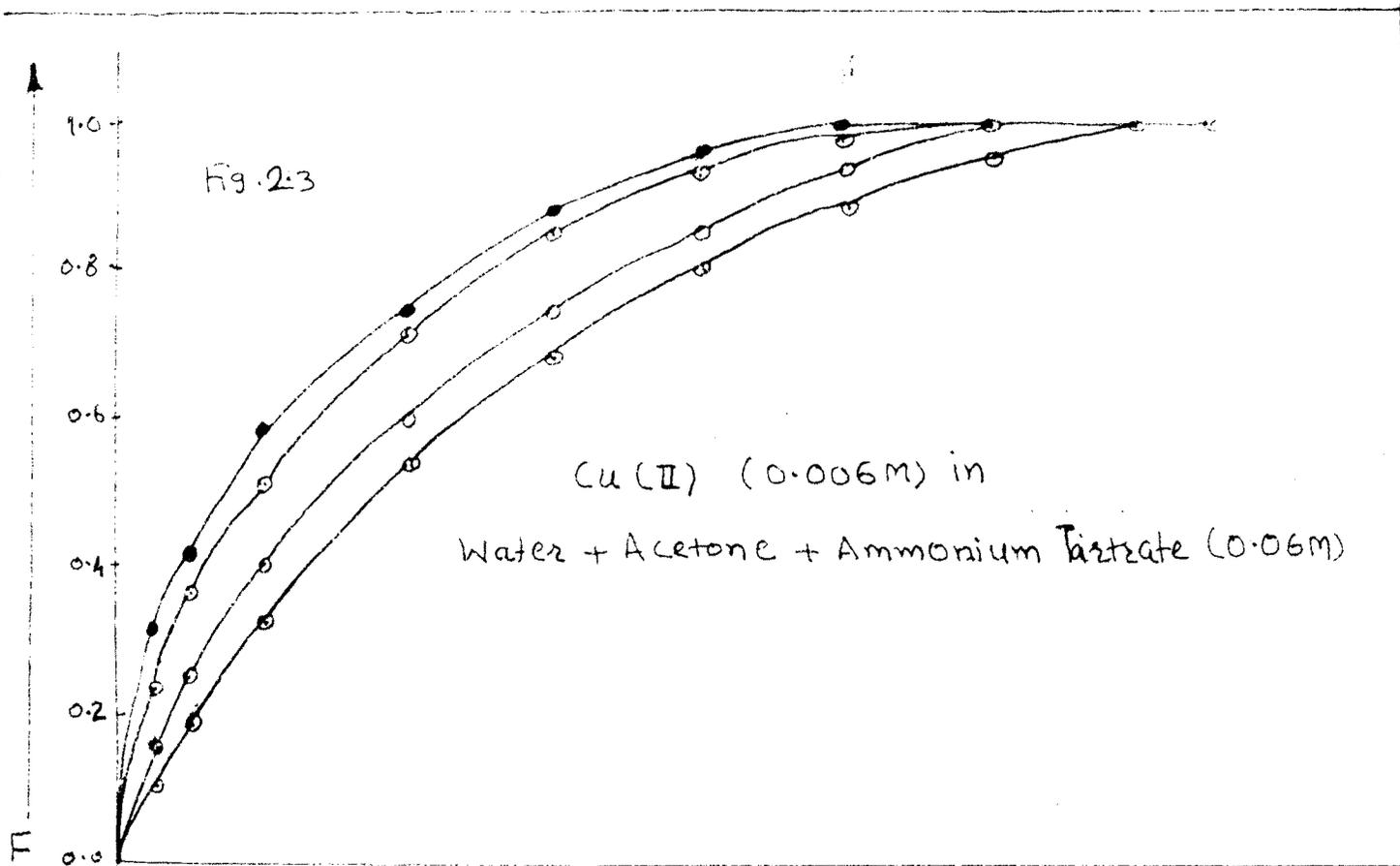
Table 2.13 Metal ion Cu (II) 0.008 M

Ammonium Tartrate 0.4 M

1	2	3	4	5
0.00	0.00	0.00	0.00	0.00
30.00	0.200	0.260	0.290	0.310
60	0.360	0.401	0.420	0.450
120	0.520	0.540	0.570	0.594
180	0.610	0.640	0.670	0.690
240	0.670	0.698	0.710	0.740
300	0.710	0.740	0.780	0.790
360	0.840	0.860	0.890	0.890
420	0.910	0.940	0.960	0.970
480	1.000	1.000	1.000	1.000

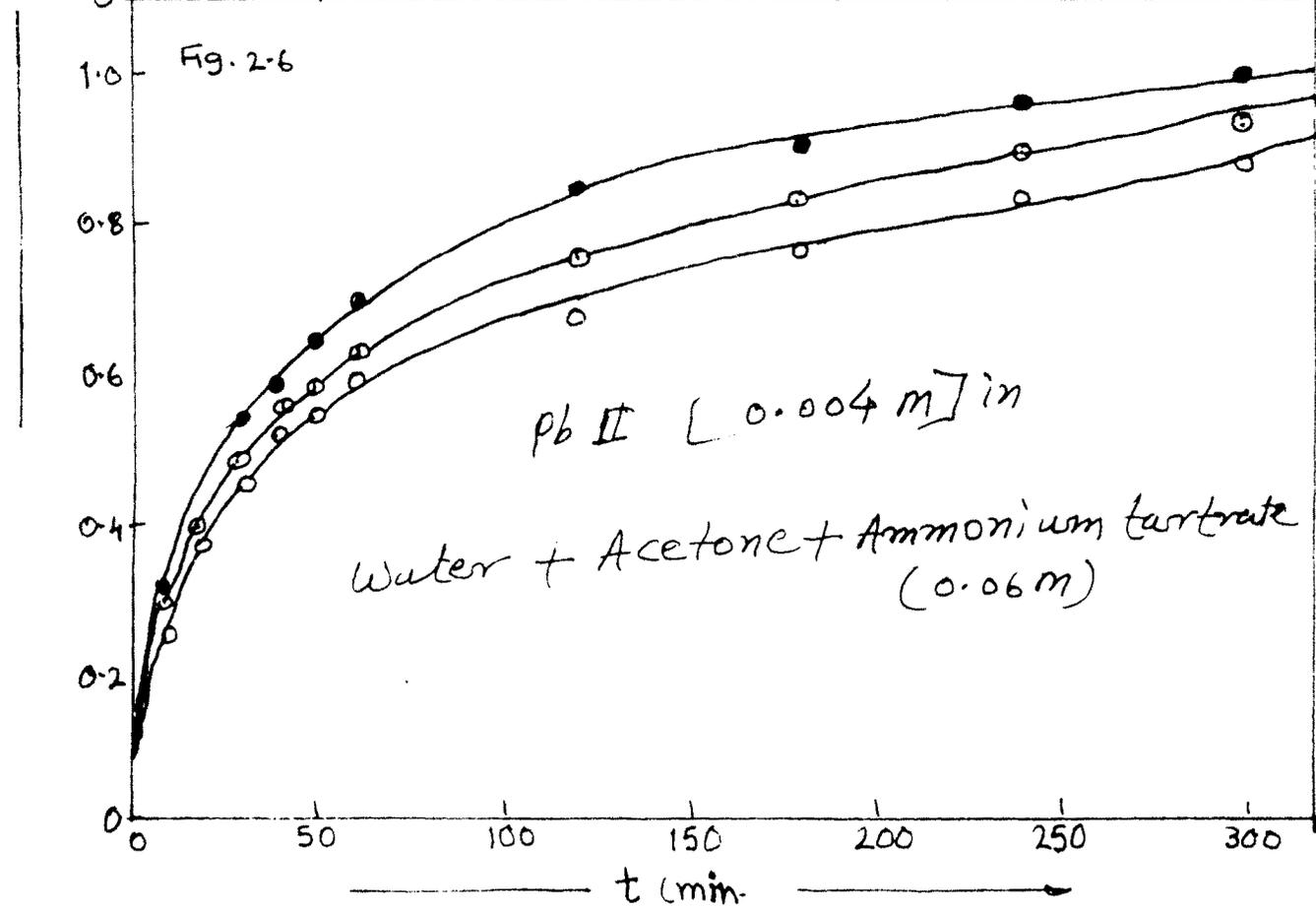
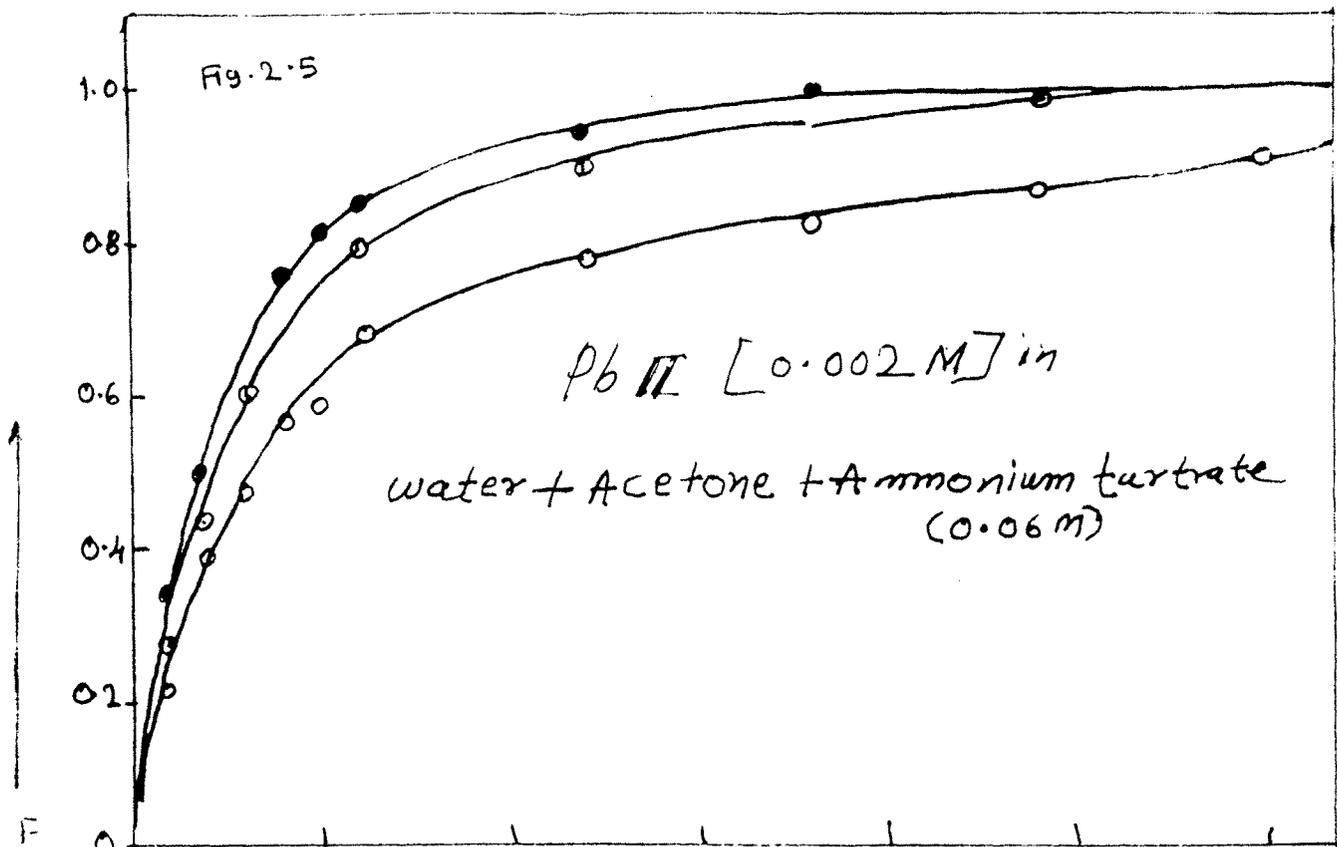


(○) 30% ; (●) 50% , (◐) 70% , (◑) 80% (Acetone %)

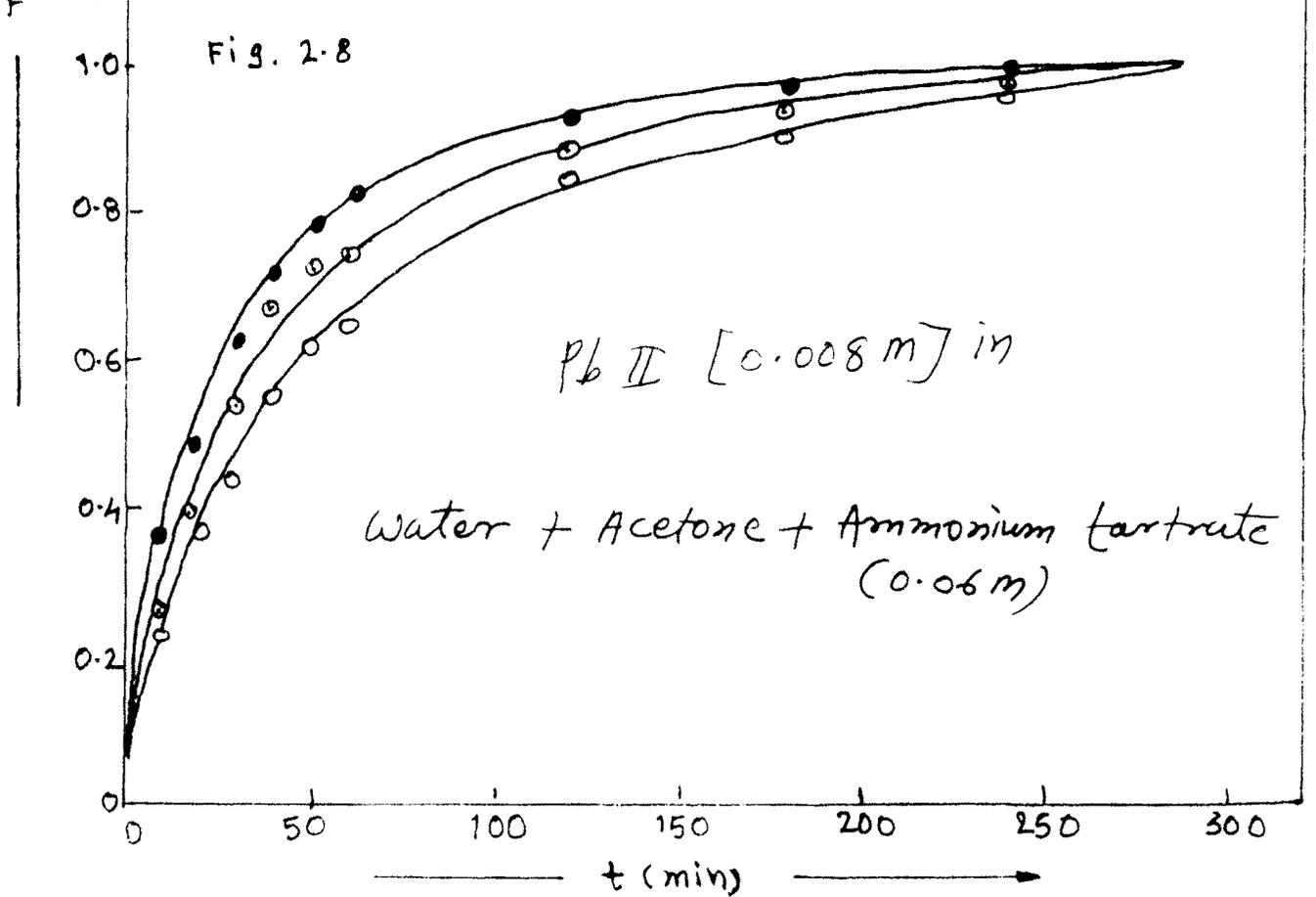
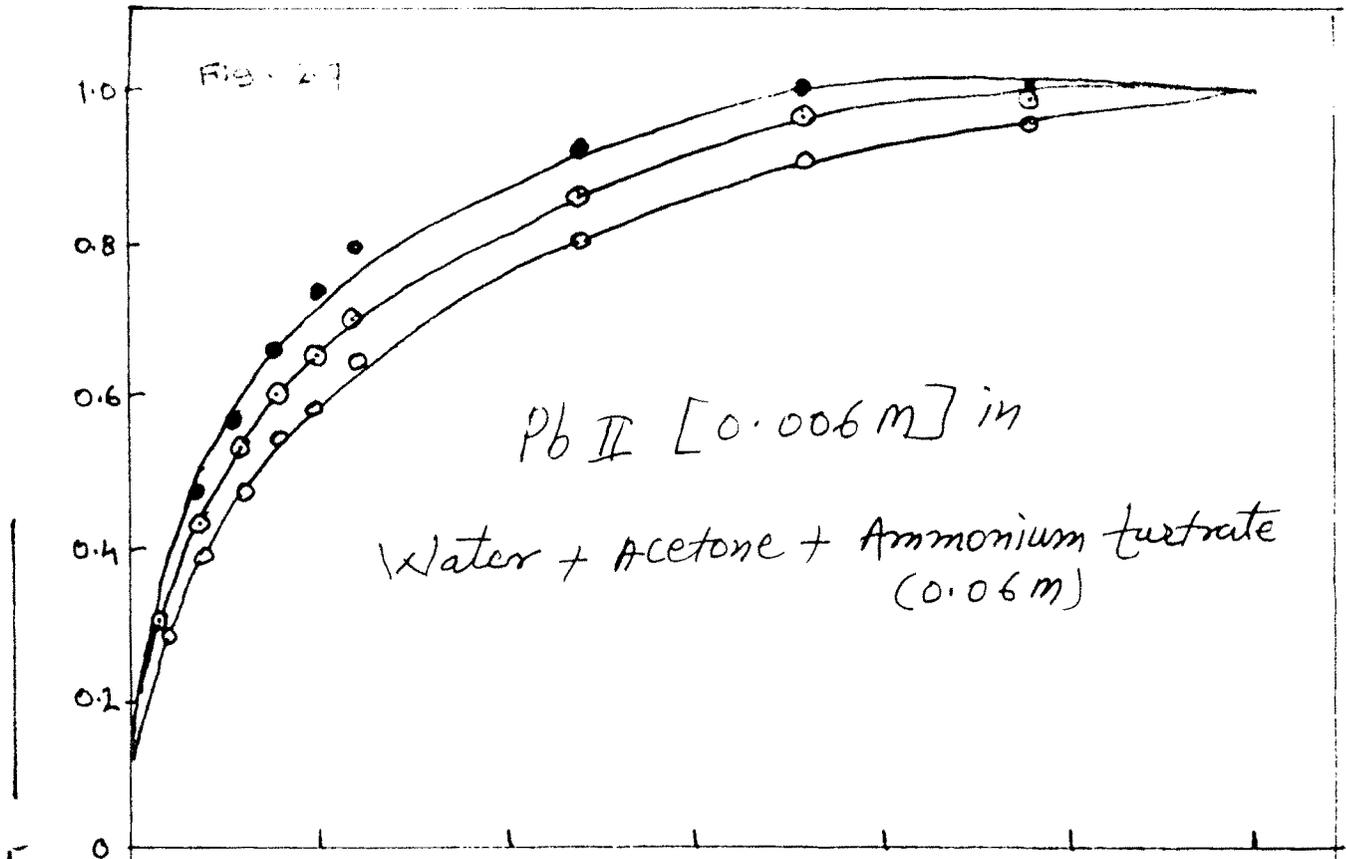


T (min)

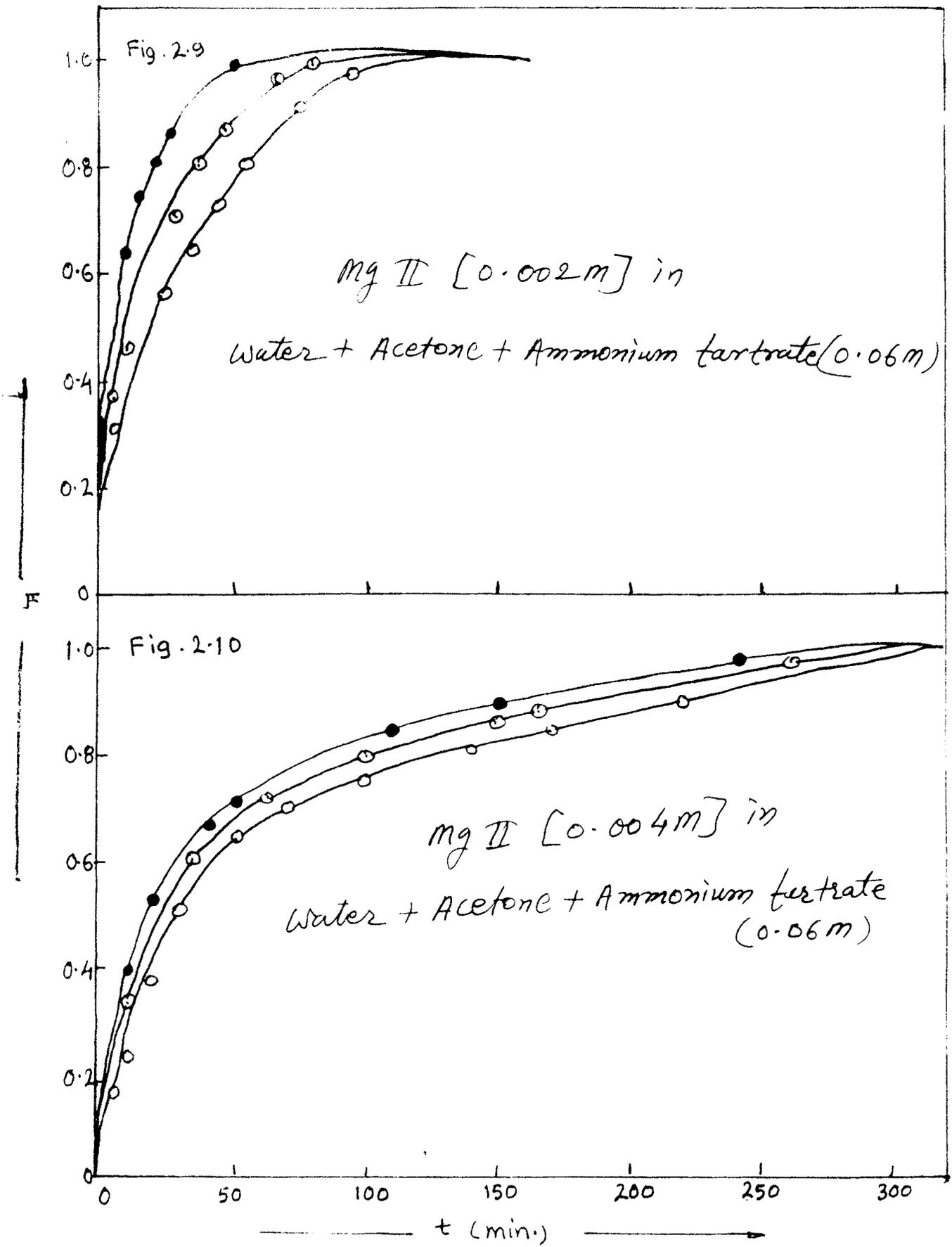
○ (0%), □ (30%), ● (50%), △ (70%) (Acetone %)



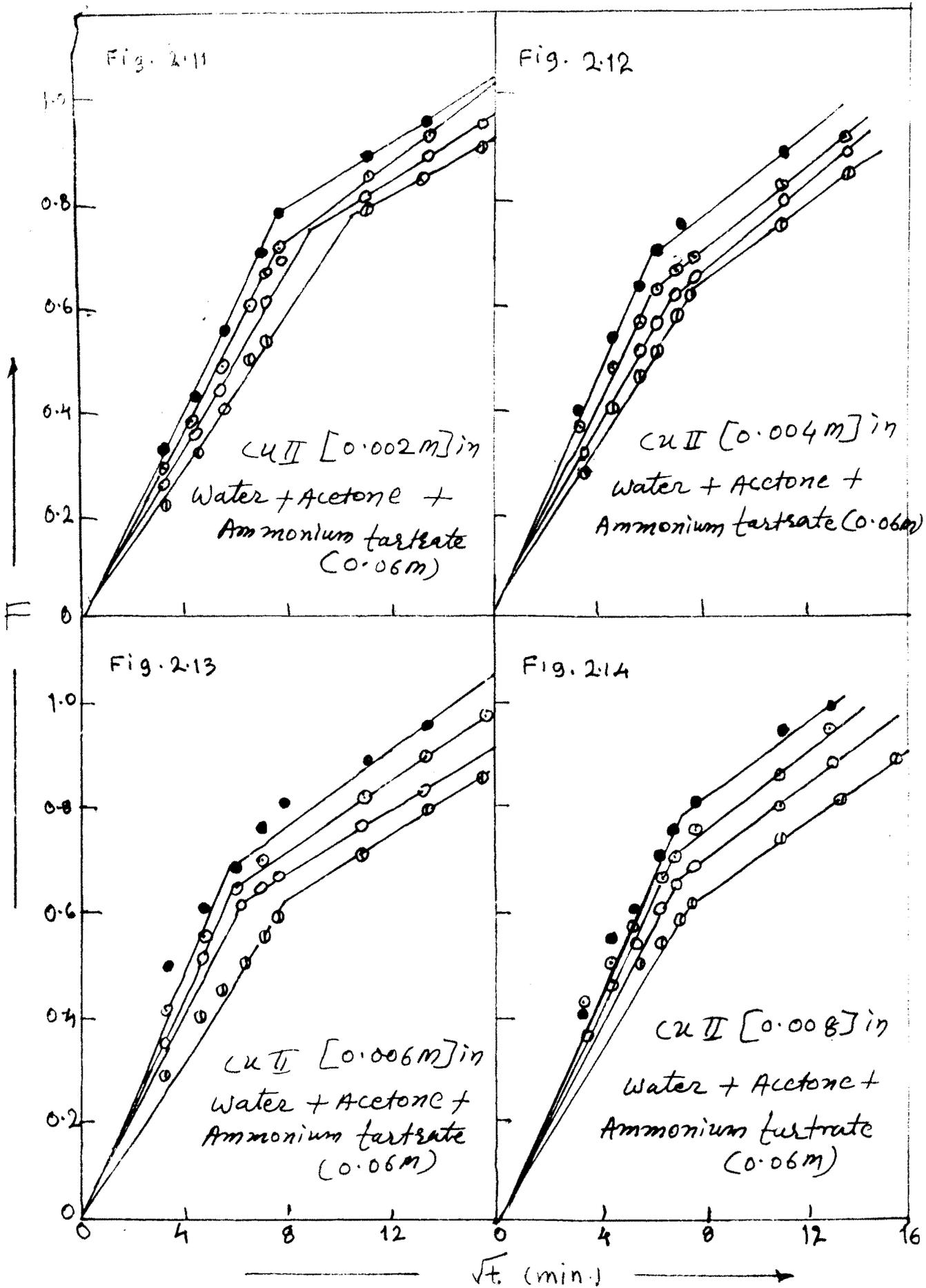
(---) 50% , (---) 70% , (---) 80% (Acetone %)



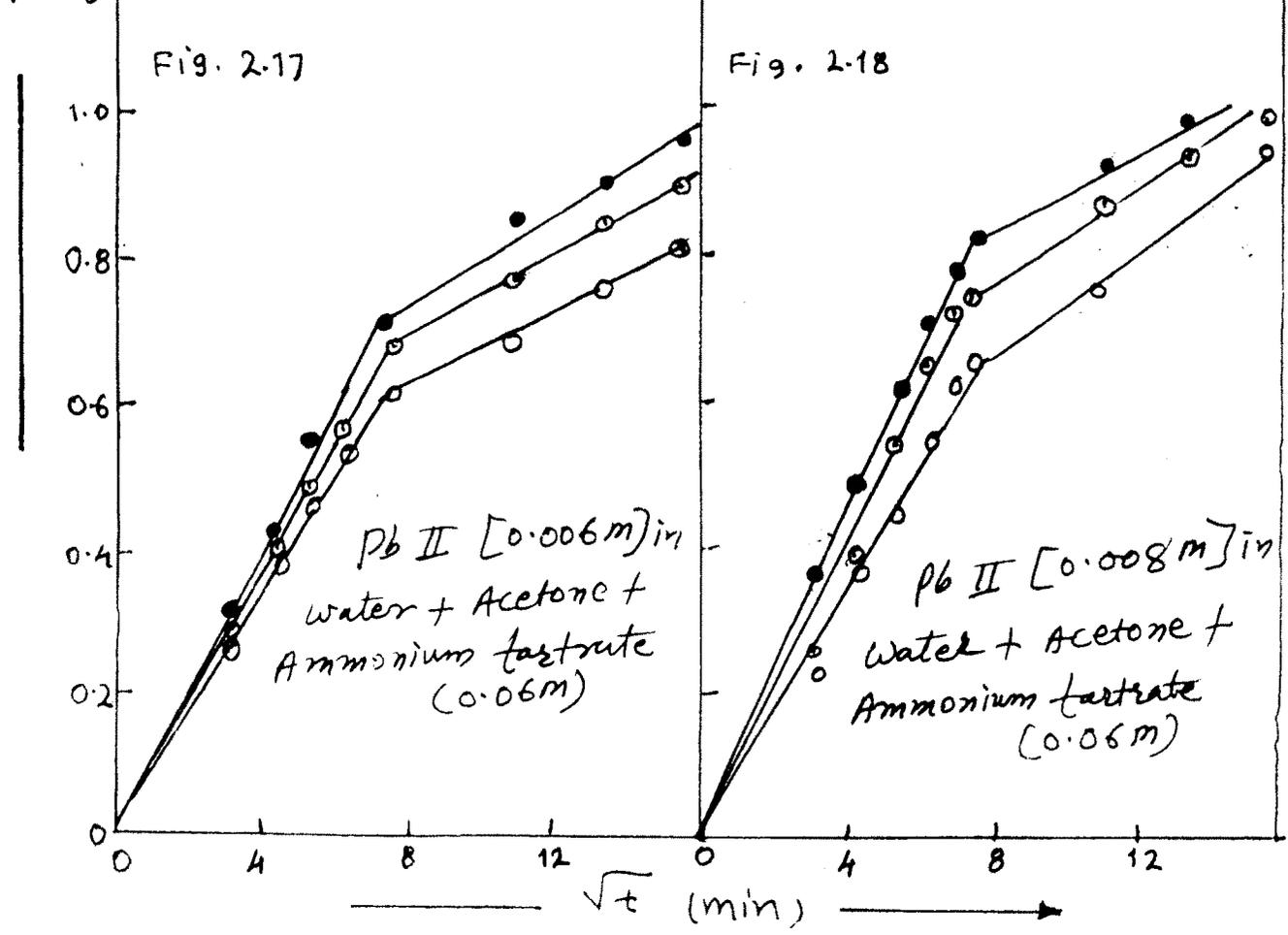
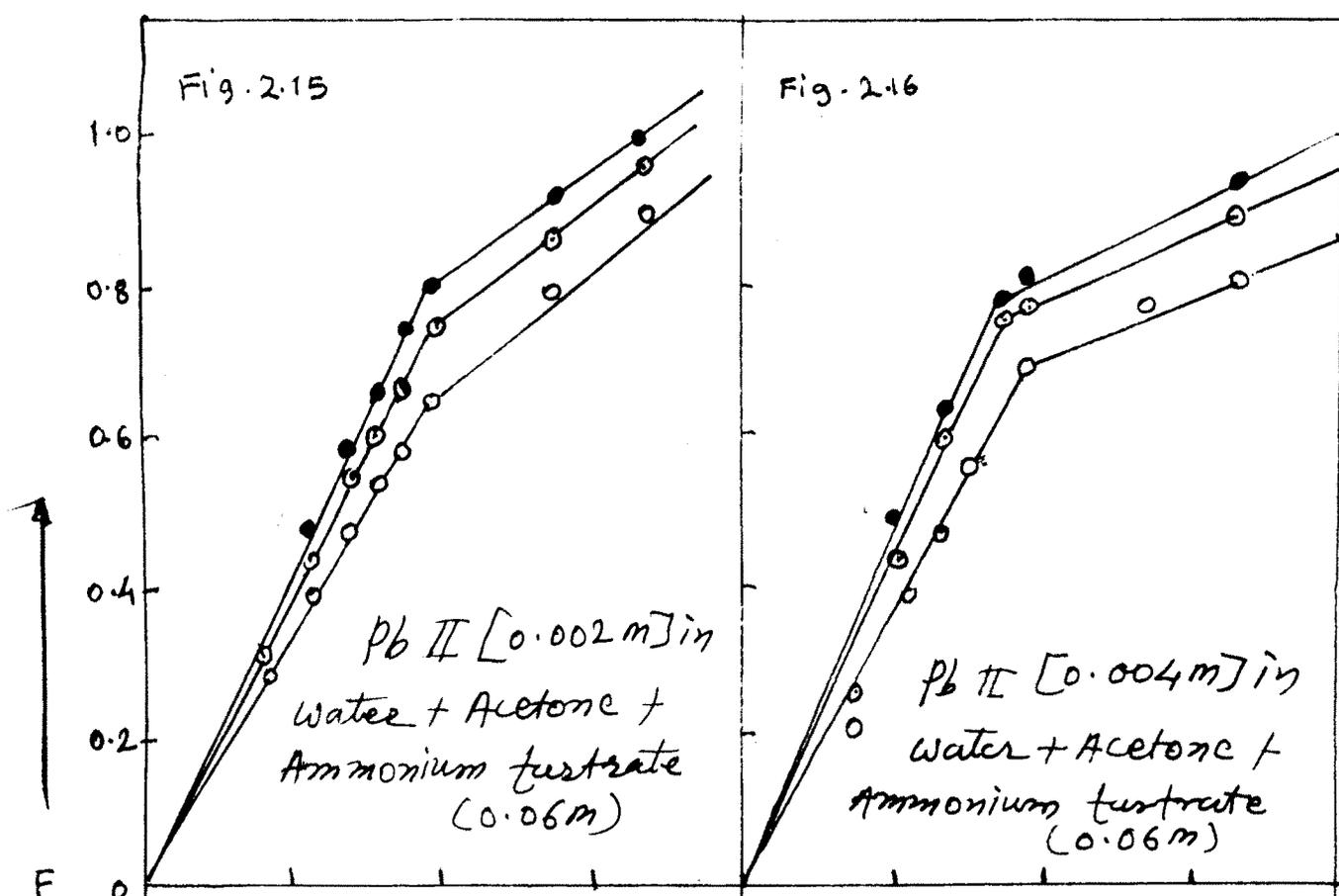
(○) 50%, (⊙) 70%, (●) 80% (Acetone %)



(-○-) 0% , (-○-) 10% , (-●-) 30% (Acetone %)



(\circ) 30%, (\ominus) 50%, (\odot) 70%, (\bullet) 80% (Acetone%)



(○) 50%, (◐) 70%, (●) 80% (Acetone %)

Table 2.12 Kinetic parameters calculated for the exchange of
 Cu (0.002, 0.004, 0.006, 0.008 M) on Amberlite MB-120
 (NH₄⁺) in aqueous acetone ammonium tartrate (0.06 M) at
 303°K

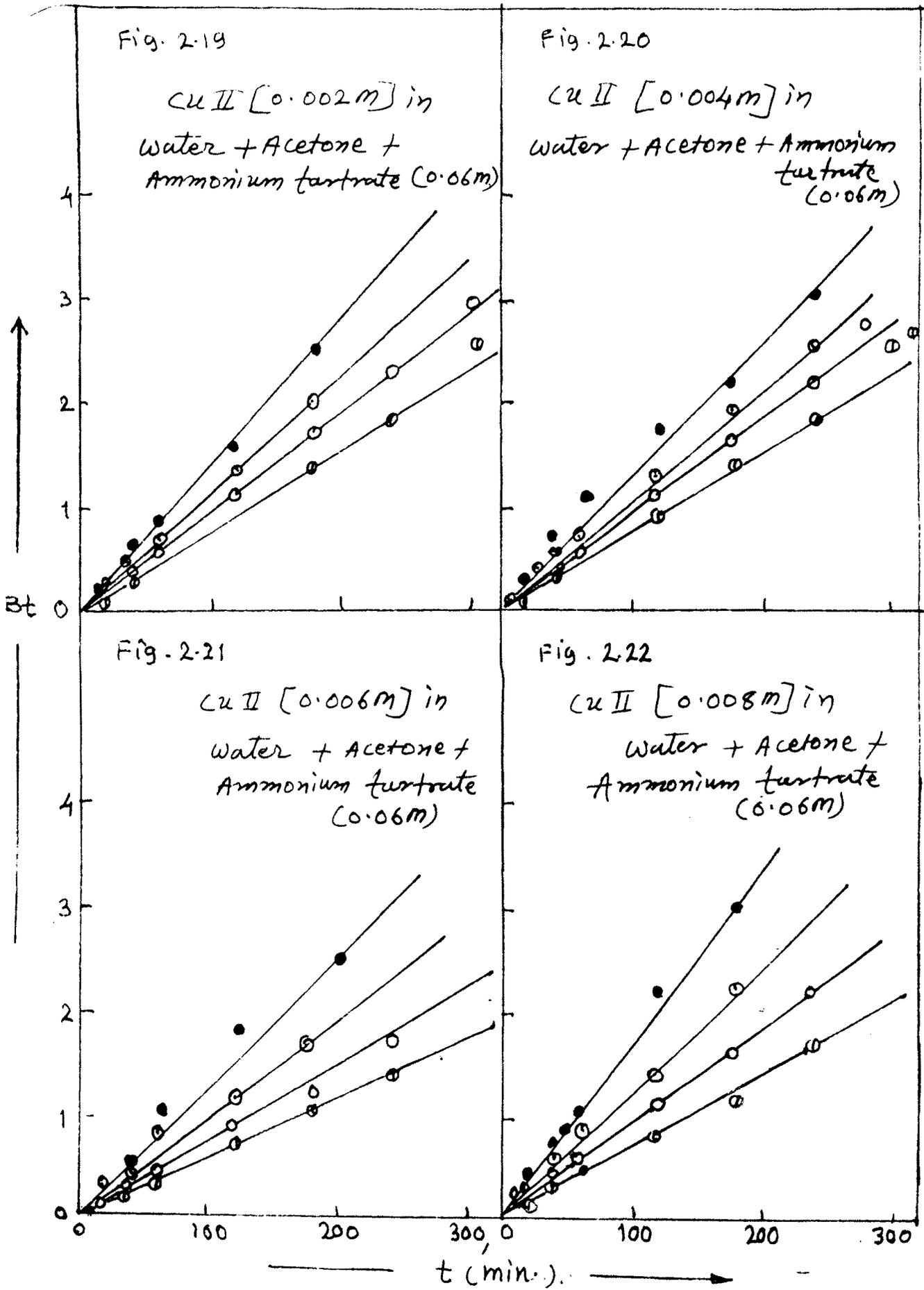
Acetone % v/v	$t^{1/2}$ min	$D \times 10^{10}$ m ² Sec ⁻¹	$B \times 10^2$ sec ⁻¹	Rate constant $k \times 10^2$ min ⁻¹	Parabolic diffusion constant K
Cu (0.002 M)					
50	34	0.79	1.00	0.89	0.096
70	24	1.12	1.60	1.15	0.109
80	20	1.25	2.30	2.56	0.112
Cu (0.004 M)					
50	38	0.71	0.60	0.89	0.085
70	32	0.84	0.75	1.05	0.085
80	24	1.13	1.05	1.28	0.093
Cu (0.006 M)					
50	36	0.75	1.00	0.79	0.091
70	30	0.90	1.20	1.15	0.090
80	24	1.13	1.65	1.44	0.110
Cu (0.008 M)					
50	36	0.75	0.90	1.10	0.088
70	26	1.04	1.12	1.44	0.100
80	20	1.38	1.90	1.77	0.106

Table 2.13 Kinetic parameters calculated for the exchange of
 Cu (0.002, 0.004, 0.006, 0.008 M) on Amberlite IR-120
 (NH₄⁺) in aqueous acetone Ammonium tartrate (0.06 M)
 at 303° K

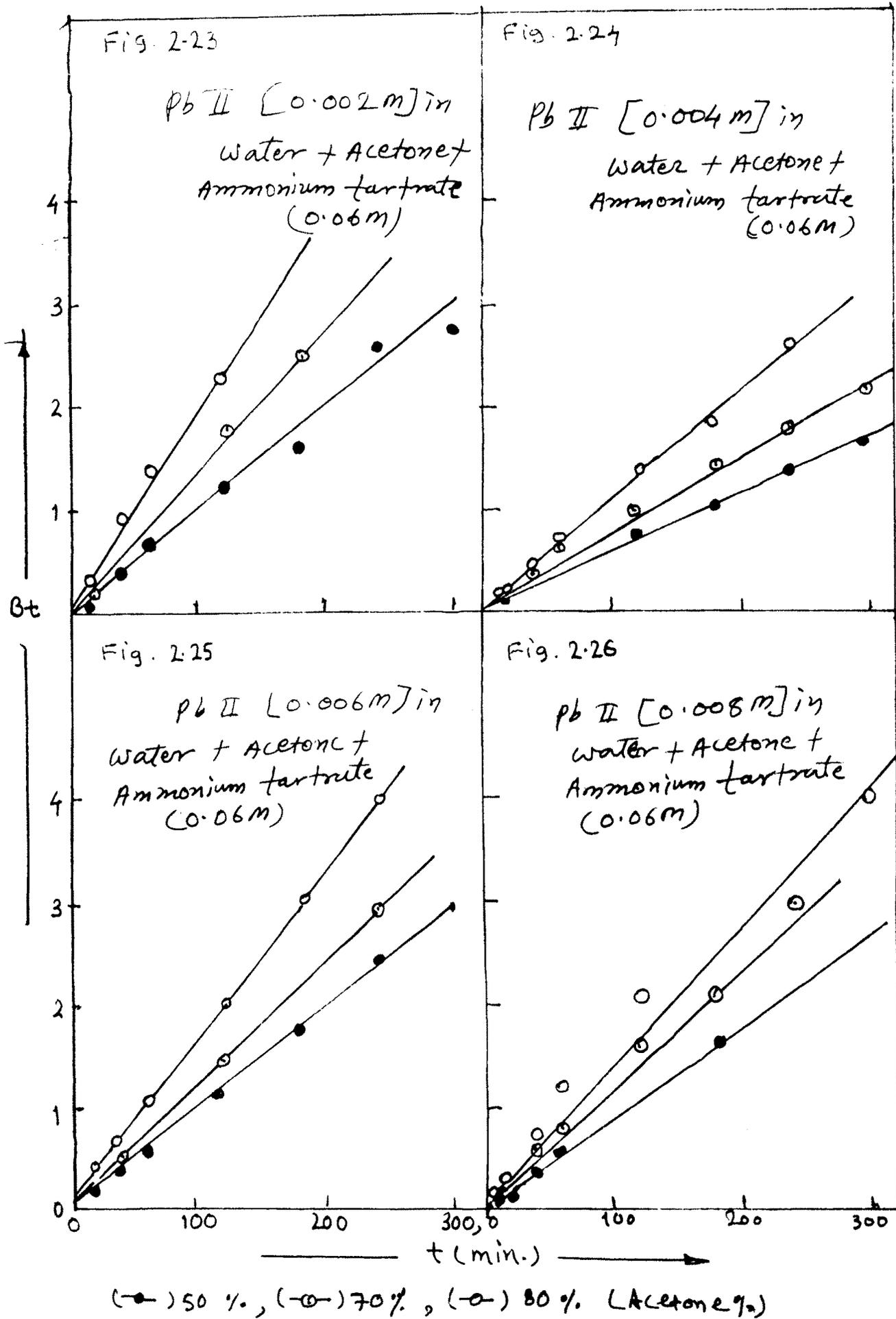
Acetone % v/v	t ^{1/2} min	D ₂ x 10 ¹⁰ m ² sec ⁻¹	B x 10 ² sec ⁻¹	Rate constant k x 10 ² min ⁻¹	Parabolic diffusion constant k
Cu (0.002 M)					
30	44	0.61	0.75	0.89	0.072
50	36	0.75	0.90	1.02	0.028
70	26	1.04	1.10	1.21	0.109
Cu (0.004 M)					
30	40	0.68	0.70	0.85	0.080
50	30	0.90	0.90	1.00	0.089
70	24	1.13	1.05	1.28	0.103
Cu (0.006 M)					
30	34	0.79	0.60	0.89	0.079
50	18	1.50	0.75	1.15	0.100
70	12	2.25	1.00	0.40	0.109
Cu (0.008 M)					
30	30	0.90	0.70	1.07	0.083
50	24	1.13	0.95	1.28	0.088
70	16	1.68	1.25	1.54	0.106

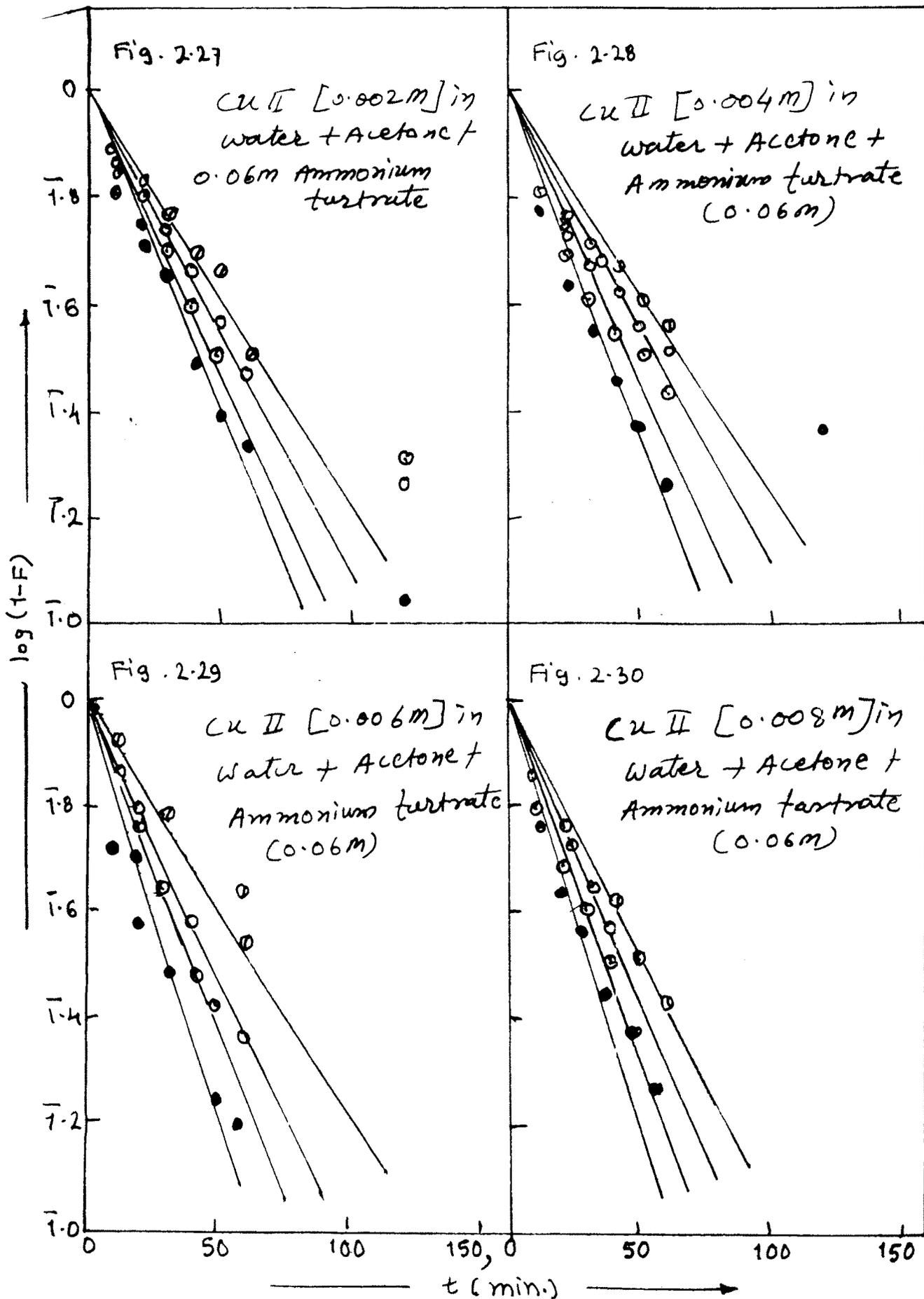
Table 2.14 Kinetic parameters calculated for the exchange of Cu (0.002, 0.004 M) on Amberlite IR-120 (NH₄⁺) in aqueous acetone AMMONIUM TARTRATE (0.06 M) at 303°K

Acetone % V/V	$t^{1/2}$ min	$D \times 10^{10}$ m ² sec ⁻¹	$B \times 10^2$ sec ⁻¹	Rate constant $K \times 10^2$ min ⁻¹	parabolic diffusion constant K
Cu (0.002 M)					
0	18	1.50	2.00	3.22	0.105
10	8	3.37	4.00	4.60	0.123
30	4	6.75	5.00	7.67	0.172
Cu (0.004M)					
Cu					
0	30	0.90	0.85	2.01	0.093
10	20	1.35	1.05	2.55	0.100
30	14	1.92	1.20	3.53	0.113

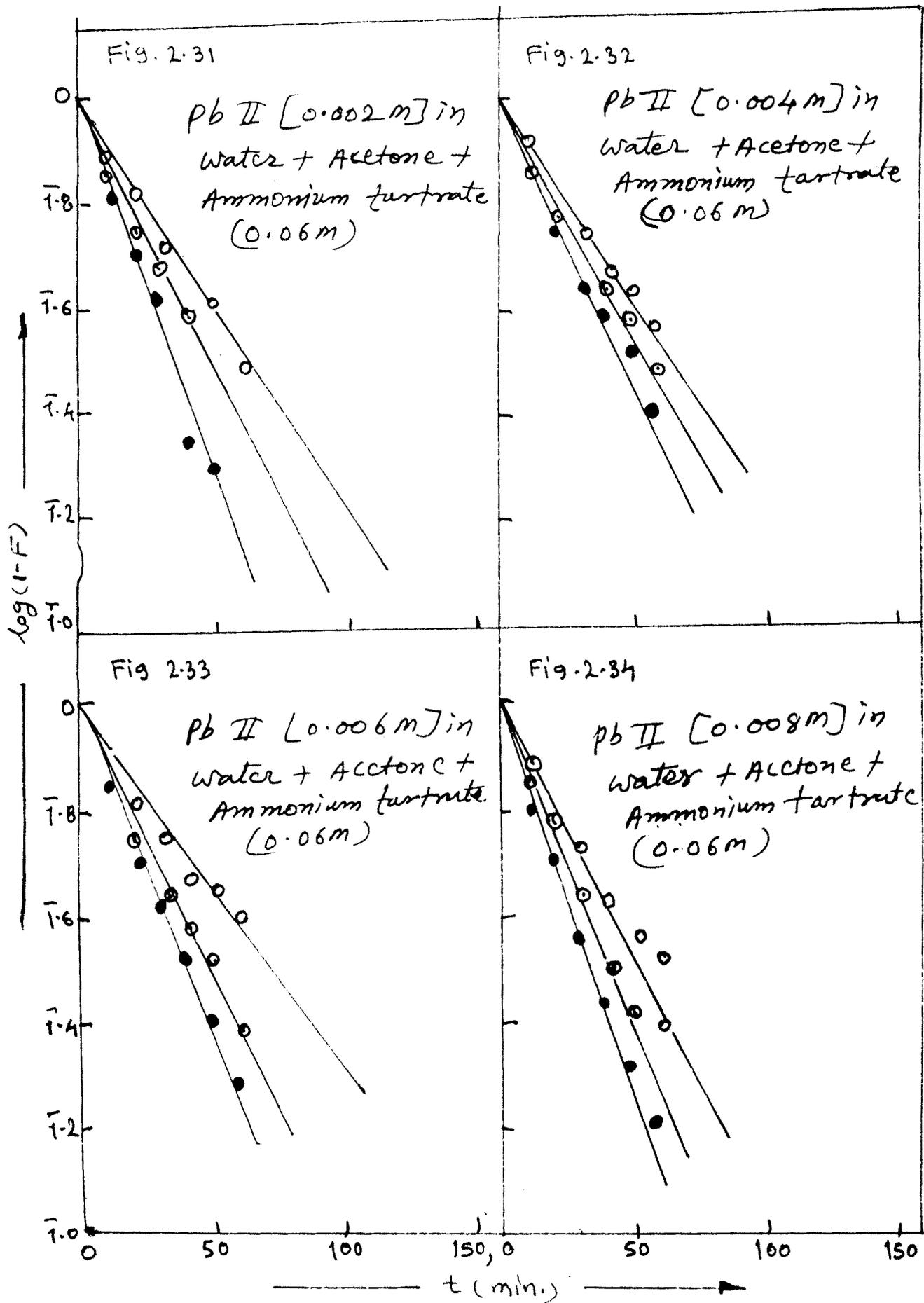


(○) 30%, (◐) 50%, (◑) 70%, (●) 80% (Acetone%)





(○) 30%, (◐) 50%, (◑) 70%, (●) 80% (Acetone%)



(○) 50 %, (○●) 70 %, (●) 80 % (Acetone %)

Table 2.15 Dependence of fractional exchange (F) on temperature

Metal ion Cu (II) 0.004 M

T	Time in (Min)	Fractional attainment of equilibrium (F)					
		Temperature in °K					
		308		313		318	
	a	b	a	b	a	b	
	0	0.0	0.0	0.0	0.0	0.0	0.0
	10	0.265	0.270	0.354	0.360	0.458	0.468
	20	0.472	0.370	0.555	0.572	0.612	0.631
	21	0.606	0.448	0.655	0.682	0.715	0.726
	40	0.662	0.592	0.710	0.785	0.785	0.792
	50	0.740	0.652	0.762	0.842	0.811	0.855
	60	0.785	0.760	0.770	0.770	0.956	0.829
	120	0.890	0.855	0.825	0.979	0.959	0.948
	180	0.909	0.902	0.921	1.000	0.988	0.992
	240	0.930	0.925	0.958	1.000	1.000	1.000
	300	0.985	0.979	0.968	1.000	1.000	1.000
	∞	1.000	1.000	1.000	1.000	1.000	1.000

WHERE a = 50% Acetone + 0.06 M Ammonium tartrate

b = 70% Acetone + 0.06 M Ammonium tartrate

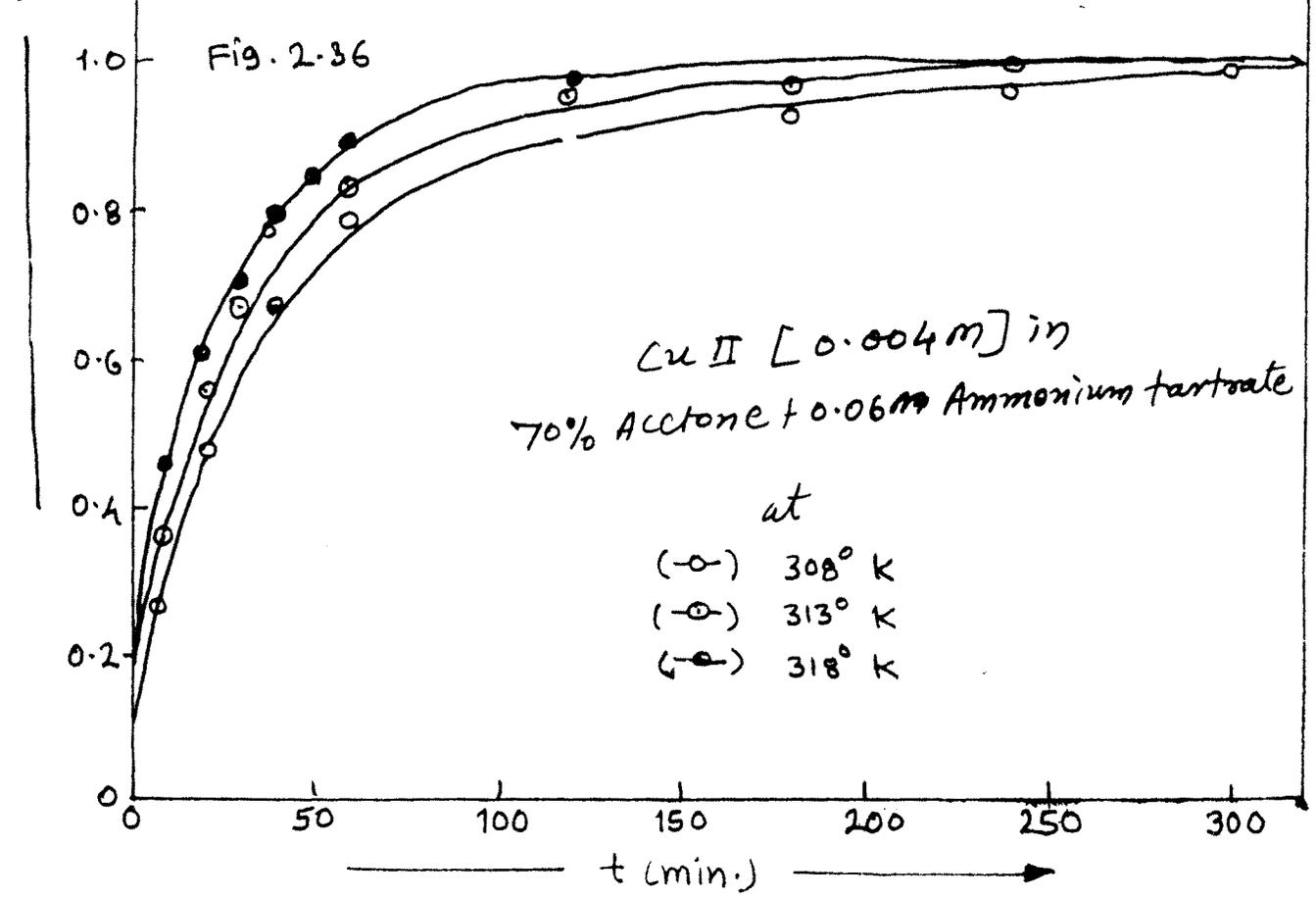
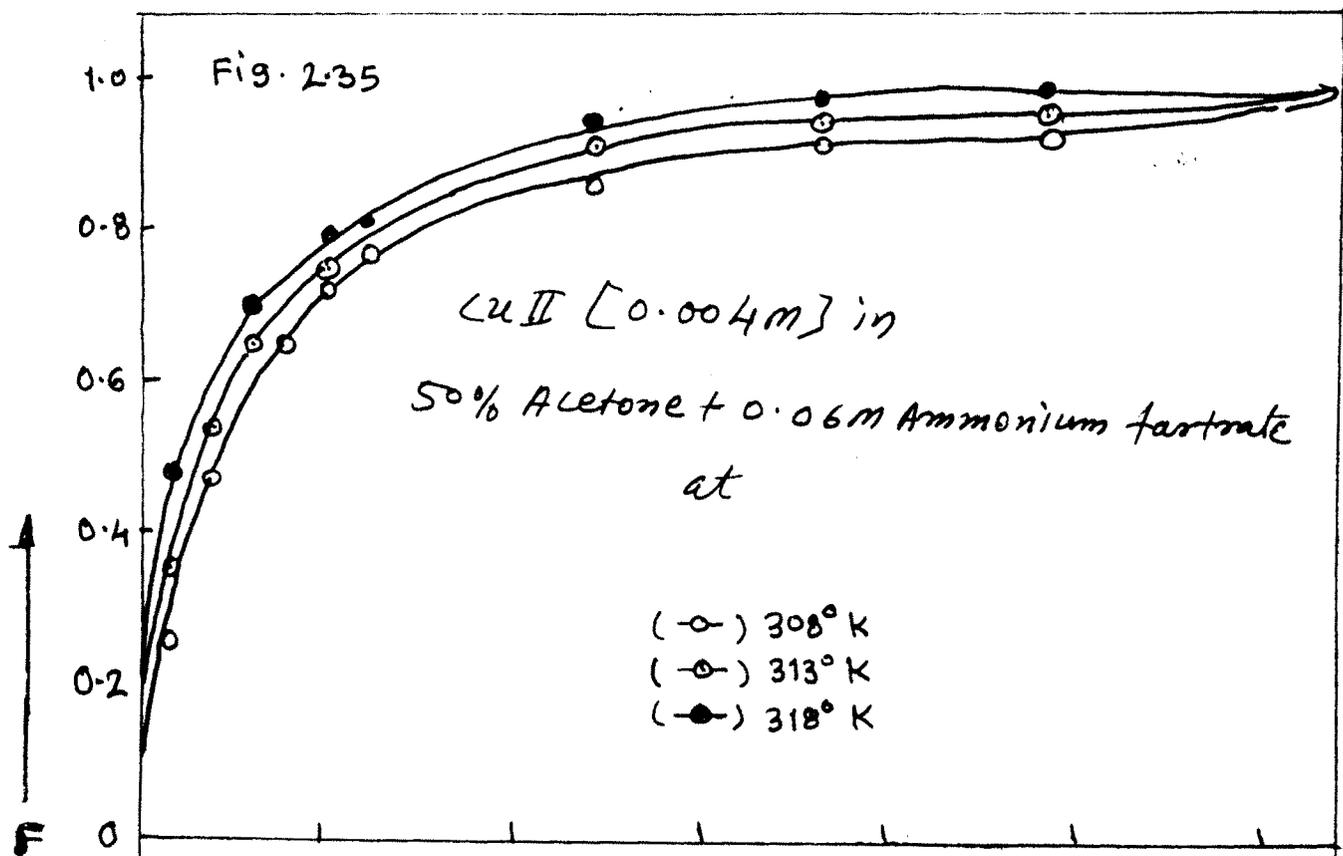
TABLE 2.16 Dependence of fractional exchange (F) on temperature

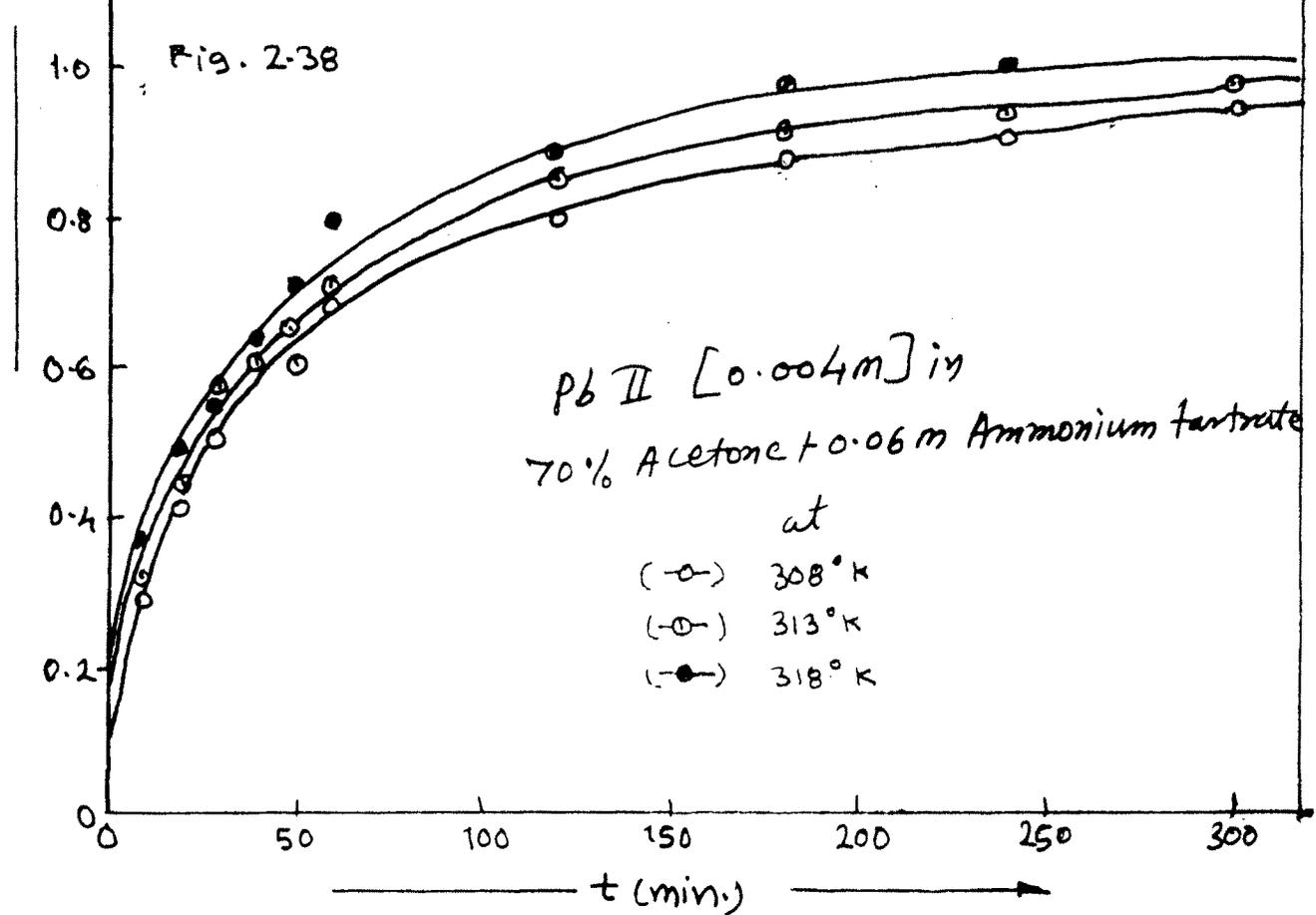
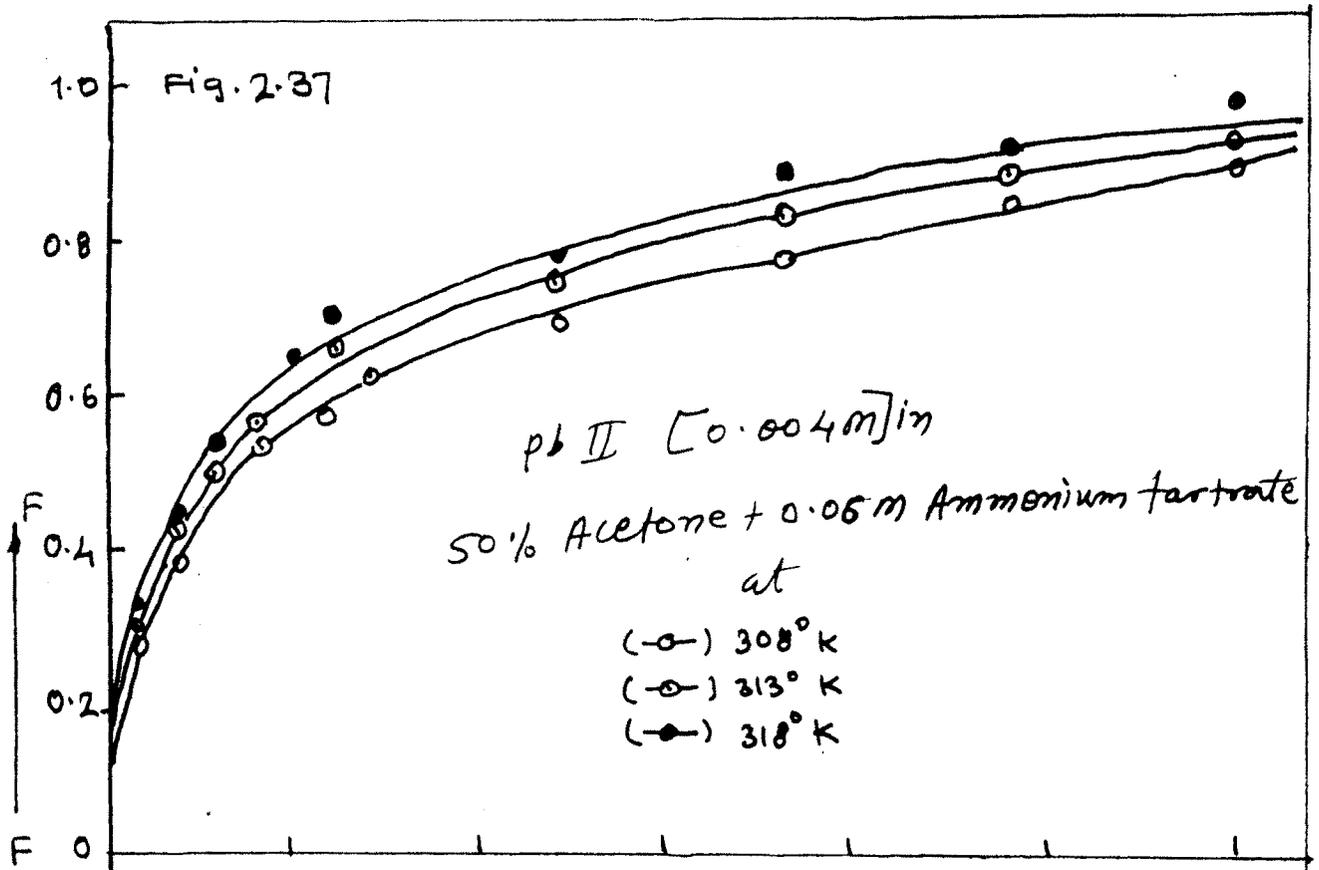
Metal ion Mg (II) 0.004 M

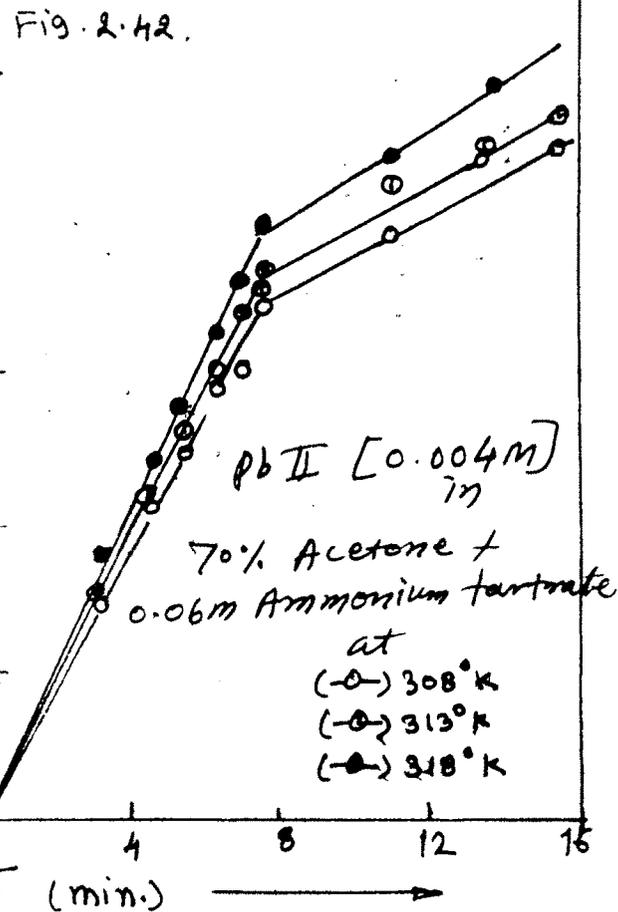
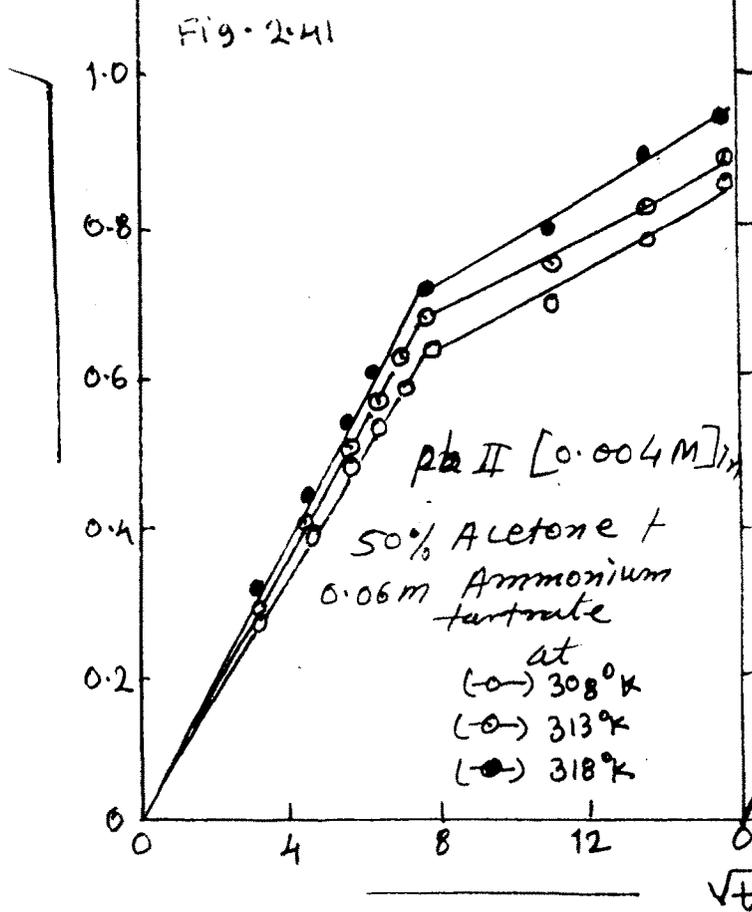
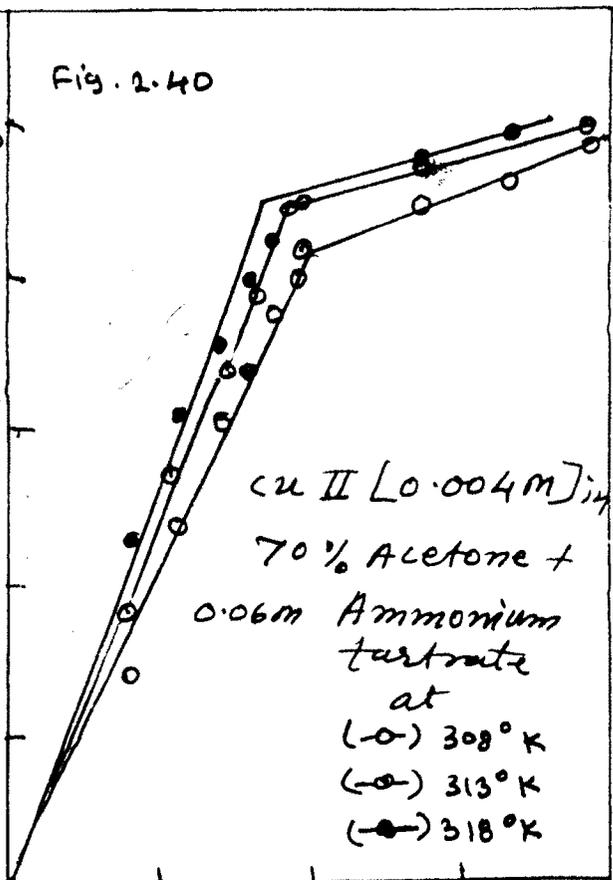
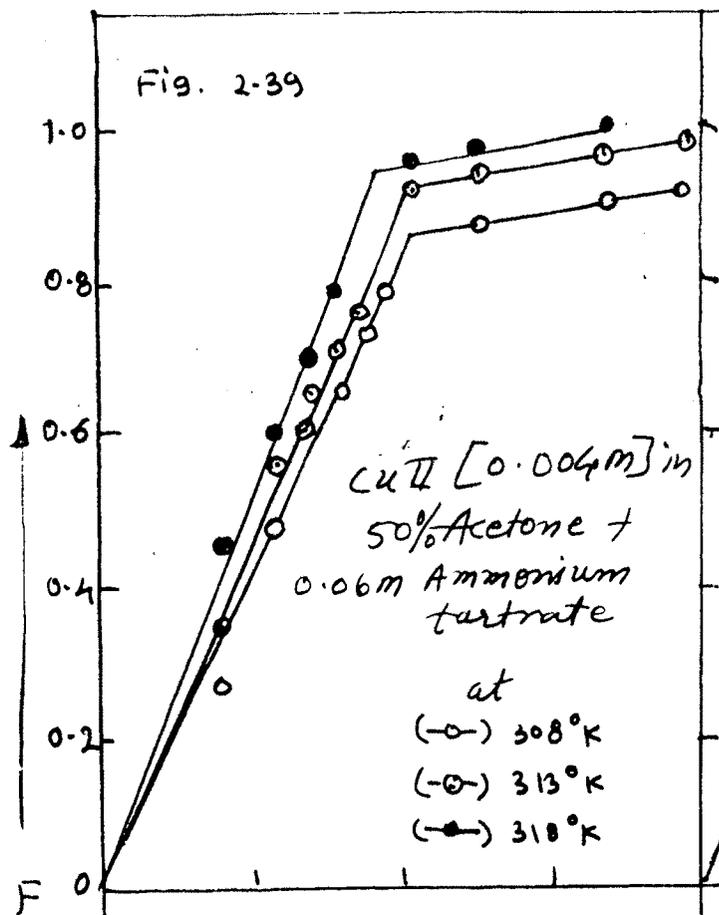
Time in (Min)	Fractional attainment of equilibrium (F)					
	Temperature in °K					
	308		313		318	
	a	b	a	b	a	b
0	0	0	0	0	0	0
10	0.242	0.251	0.263	0.271	0.282	0.291
20	0.312	0.324	0.334	0.345	0.356	0.362
30	0.382	0.395	0.406	0.426	0.442	0.468
40	0.481	0.495	0.496	0.528	0.545	0.550
50	0.582	0.621	0.525	0.622	0.681	0.672
60	0.632	0.678	0.621	0.681	0.696	0.698
120	0.693	0.790	0.742	0.853	0.790	0.880
180	0.780	0.882	0.821	0.909	0.916	0.989
240	0.862	0.911	0.892	0.938	0.942	0.998
300	0.969	0.979	0.961	0.981	0.968	1.000
∞	1.000	1.000	1.000	1.000	1.000	1.000

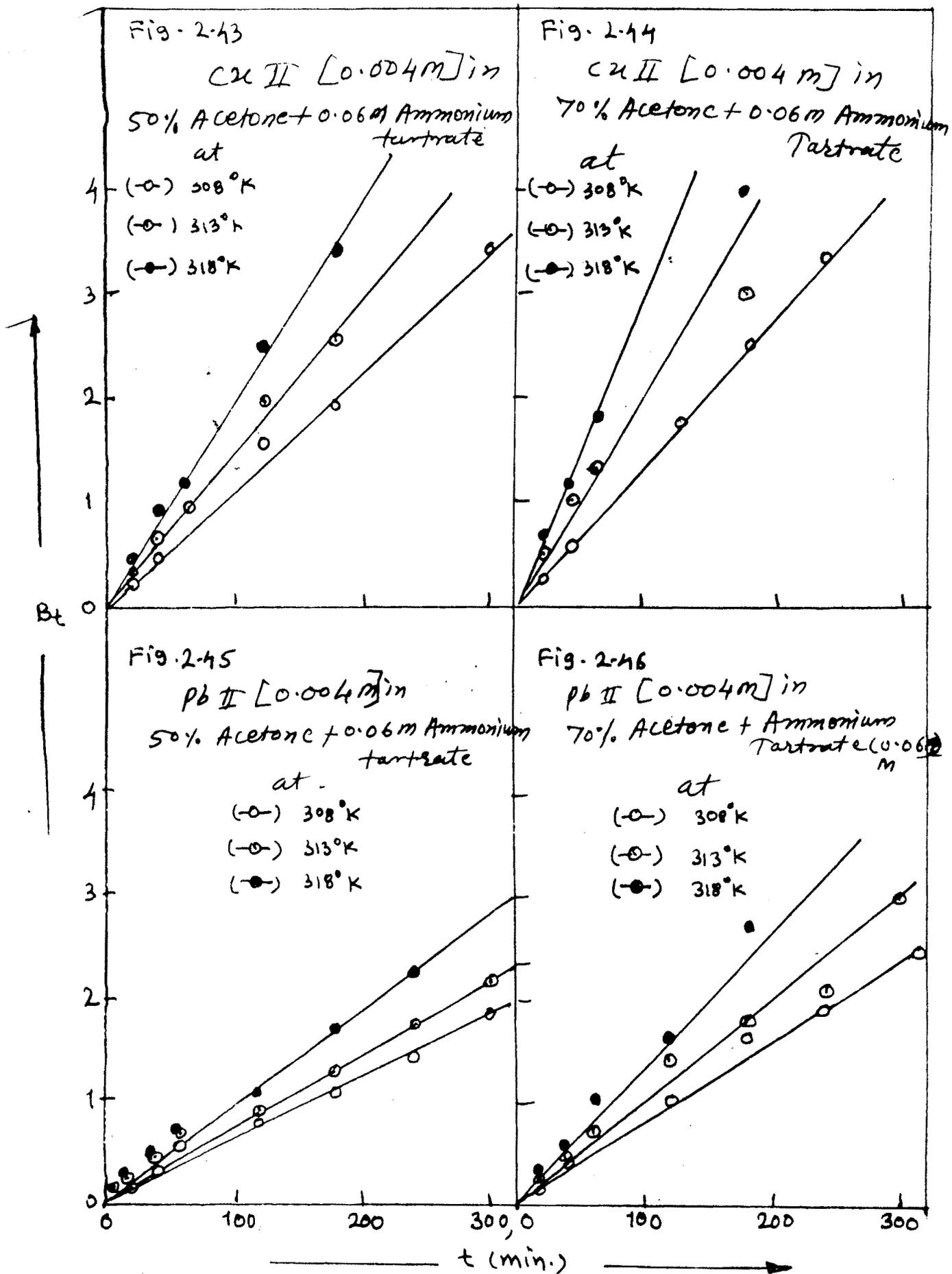
WHERE a = 50% Acetone + 0.006 M. Ammonium Tartrate

b = 70% Acetone + 0.06 M. Ammonium Tartrate.









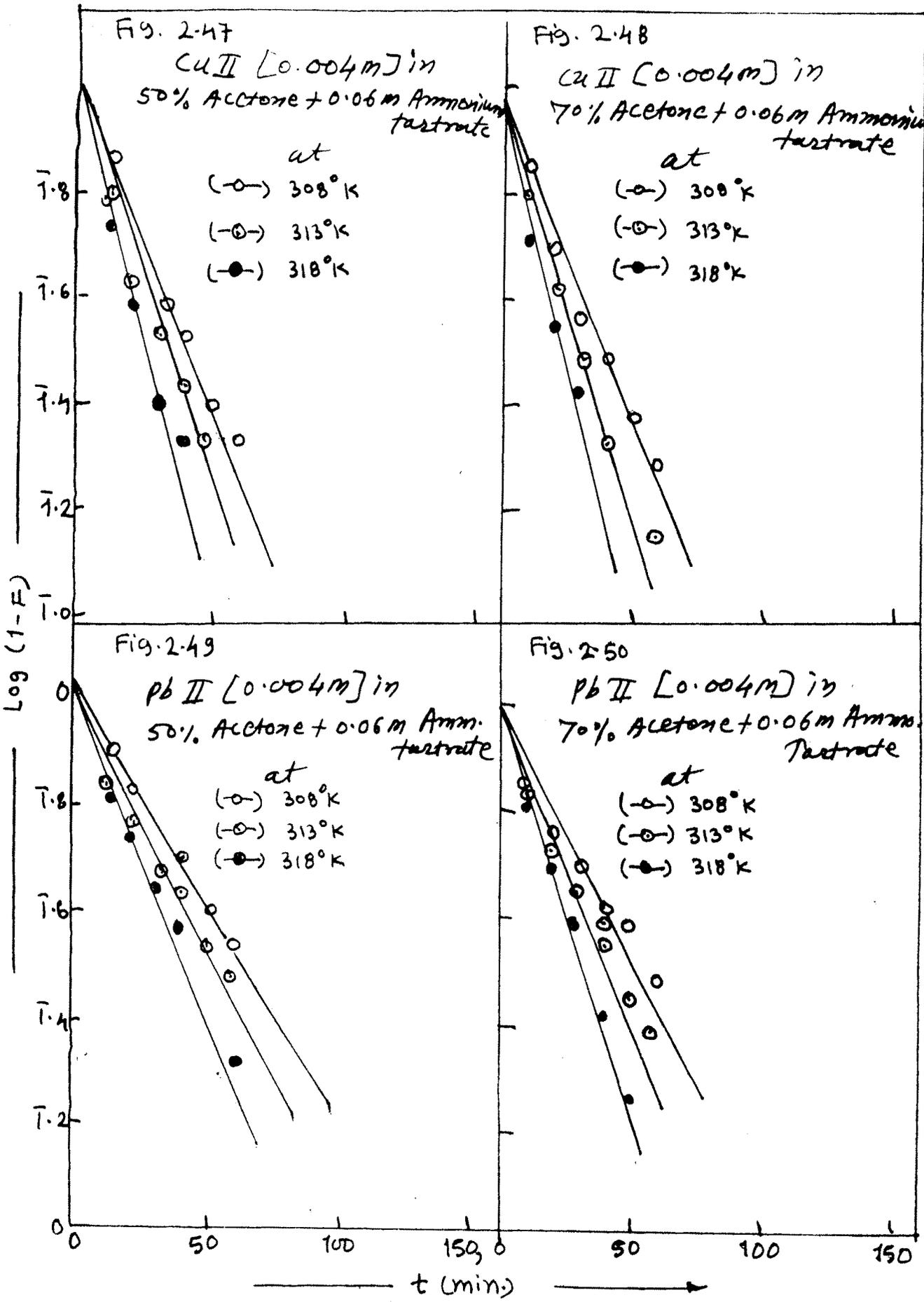
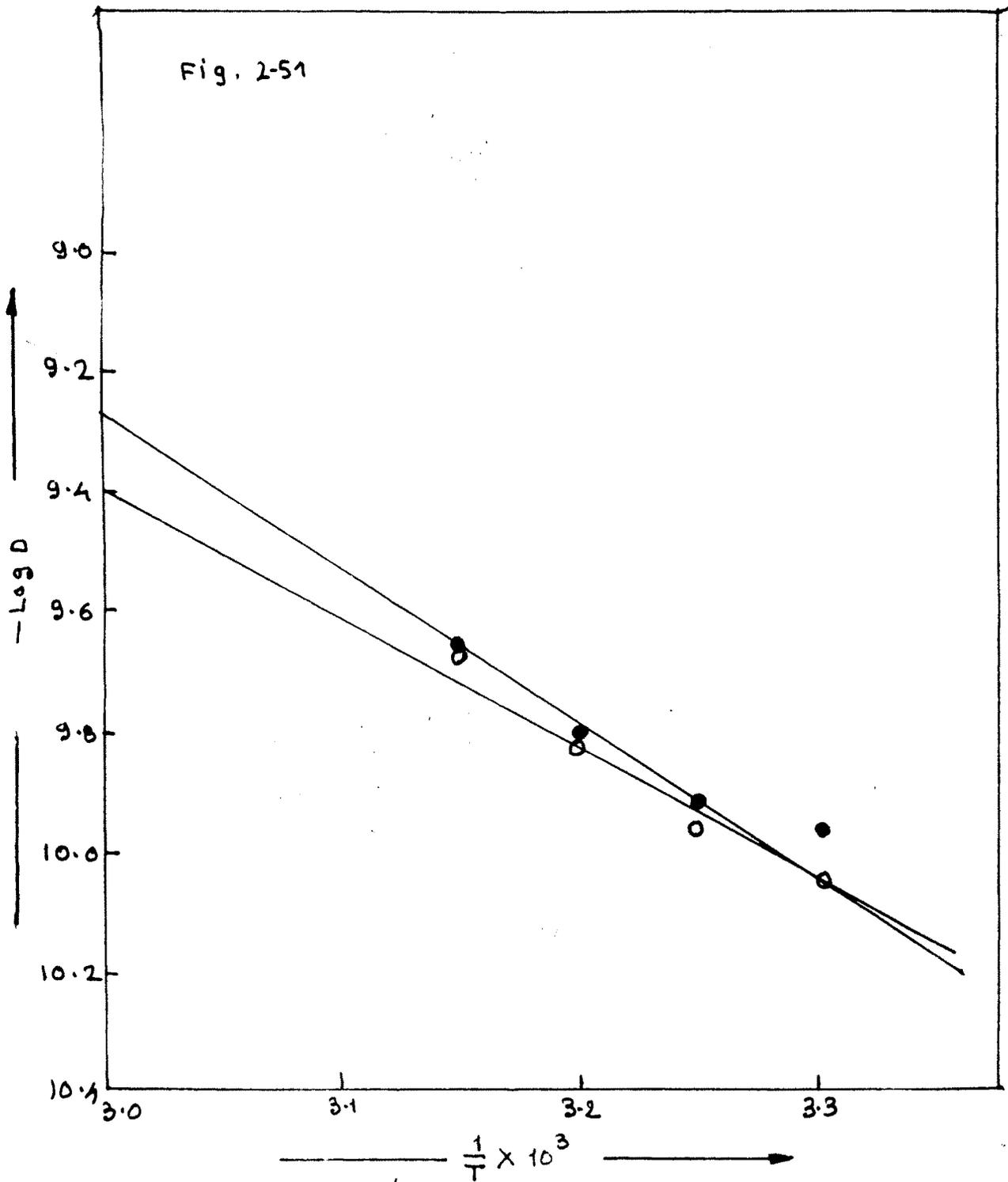
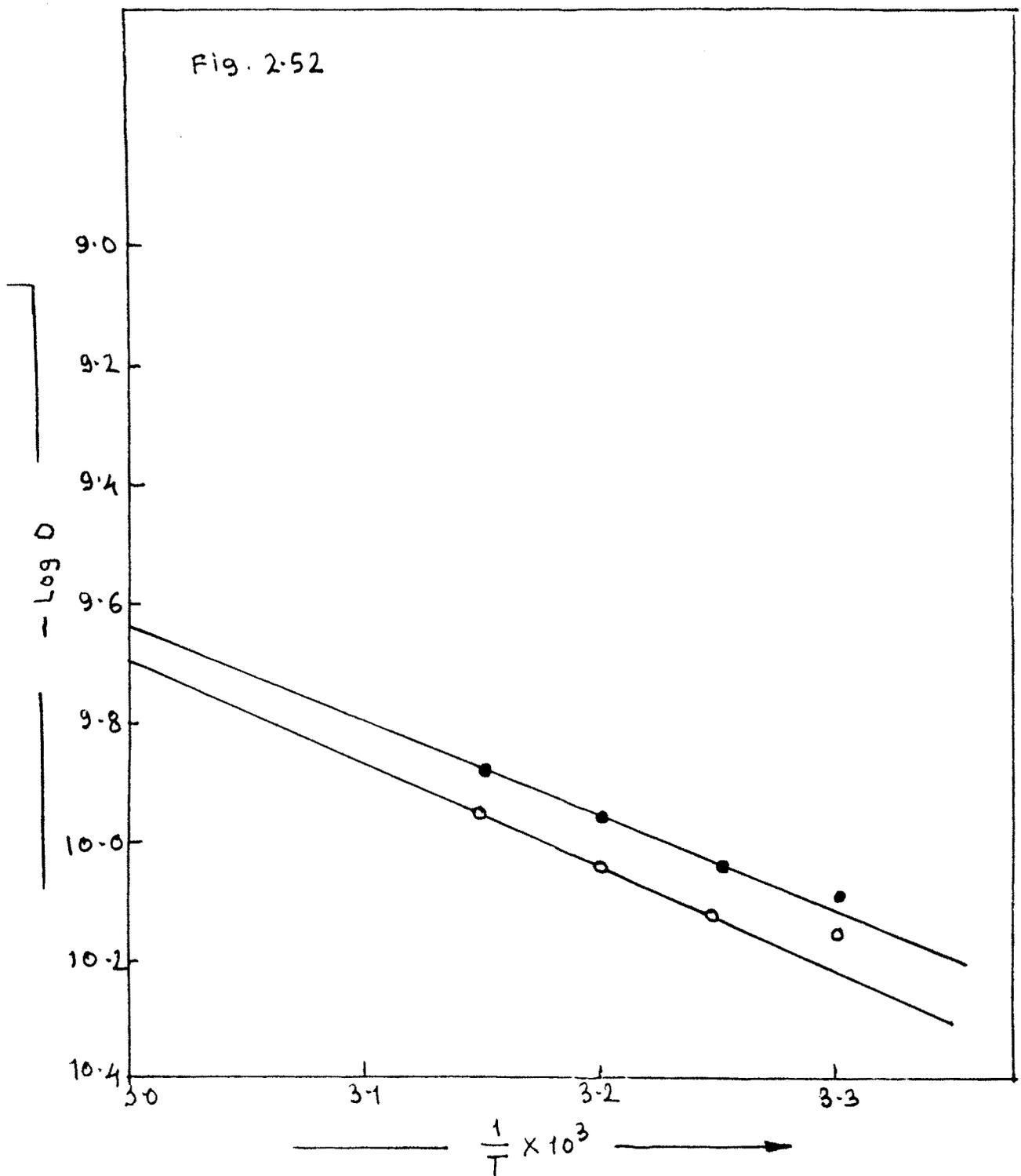


Table 2.17 Kinetic parameters calculated for the exchange of Cu and Mn (0.004 M) on Amberlite IR-120 NH_4^+ in aqueous acetone Ammonium Tartrate 0.06 M at various temperatures.

Temp. °K	$t^{1/2}$ min.	$D \times 10^{10}$ $\text{m}^2 \text{sec}^{-1}$	$B \times 10^2$ sec^{-1}	Rate constant $k \times 10^2$ min^{-1}	Parabolic diffusion constant K
Cu (0.004 M) Acetone 50% , v/v					
303	38	0.71	0.60	0.86	0.085
308	36	0.75	0.60	0.92	0.083
313	30	0.90	0.70	1.90	0.089
318	24	2.13	0.95	1.35	0.098
ACETONE 70% , v/v					
303	32	0.84	0.75	1.05	0.085
308	30	0.90	0.80	1.09	0.096
313	24	1.13	1.05	1.40	1.104
318	20	1.35	1.40	1.77	0.107
Mg (0.004 M) Acetone 50%, v/v					
303	30	0.90	0.90	1.02	0.089
308	24	1.13	1.15	1.40	0.100
313	18	1.50	1.50	1.65	0.100
318	12	2.25	1.95	2.30	0.115
Acetone 70%, v/v					
303	24	1.13	1.08	1.29	0.103
308	22	1.23	1.40	1.40	0.105
313	16	1.68	2.80	1.85	0.096
318	11	2.25	2.95	2.55	0.115



Plots of $\text{Log } D$ vs $\frac{1}{T}$ for kinetics of $\text{Cu} [0.004 \text{ M}]$ on Amberlite IR-120 in aqueous acetone-ammonium tartrate $[0.06 \text{ M}]$ medium. Acetone % v/v \rightarrow (○) 50%, (●) 70%.



Plot of $\text{Log } D$ vs $\frac{1}{T}$ for kinetics of Pb [0.004M] on Amberlite IR-120 NH_4^+ in Aqueous Acetone-Ammonium tartrate medium. Acetone % v/v \rightarrow (o) 50% (\bullet) 70%.

Table 2.18 Values of energy of activation (E_a), pre-exponential constant (D_0) and entropy of activation (ΔS) for Cu(II) and Mg (II) (0.004 M)(0.06 M Ammonium tartrate)

Metal ion	Acetone	$D_0 \times 10^{10}$ $\text{m}^2 \text{Sec}^{-1}$	E_a KJ mol^{-1}	ΔS $\text{J mol}^{-1} \text{deg}^{-1}$
Cu	50	3.981	32.82	- 33.25
	70	5.248	49.01	- 32.82
Zn Mg	50	1.995	32.83	- 34.31
	70	2.239	29.35	- 34.13

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 metal ion in exchanger phase, and \bar{V} is the volume of 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,¹⁴ Nelfferien¹⁵ and Blichenstaff^{15,16} in their studies. Hence,

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \cdot e^{-9nt^2} \quad (1)$$

where

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

r = radius of the fully swollen resin bead,

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 of F are presented in Tables 2.2 to 2.11 and the behaviour of F with time t is presented by Figs. 2.1 to 2.10. Values of Bt where $B = \frac{\pi^2 D}{r^2}$, were obtained corresponding to various F values using Reichenberg table R. The Bt versus t plots are shown by Figs. 2.19, 2.26 and the values of B are obtained from the slopes of these plots. The values of B are given in Table 2.12 to 2.14 and 2.17.

Effect of concentration of Acetone :

The values of F , fractional attainment of equilibrium

presented in Tables 2.2 to 2.11 and the graphs of F versus t give an idea of the exchange process concerned. It is observed that the half exchange time $t_{1/2}$ decreases as the percentage of acetone increases. It indicates that the process of exchange becomes faster in presence of acetone. As per equation

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

$t_{1/2}$ is inversely proportional to D and hence the values of D increases with the rise in concentration of acetone. It is noted that the equilibrium period decreases with the rise in percentage of acetone. The nature of graph, F vs t, indicates the sudden rise in earlier part and becomes parallel to time axis leading towards saturation. The greater adsorption tendencies of these metal ions on Amberlite IR-120 (NH_4^+) are in agreement with the high values of distribution coefficients present in Tables, 3.1 to 3.4 in Chapter III.

The various factors contributing to this observation are,

- i) The swelling and solvent fractionation behaviour of NH_4^+ as well as metal forms of Amberlite IR-120 (NH_4^+) in mixed media.
- ii) the solvated 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 sizes of the ions under study are governed by overall solvation of the ions in 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 shall depends upon the ability of the organic solvent to solvate the cation. In this extent, a study by Zipp¹⁷ shows that alkali metal cations are solvated almost euqly 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 shall consisting of water molecules and, more or less, the some number of organic solvent molecules, depending upon the composition of the mixed solvent.

In the mixed systems, ionic selectivities of the resins have also been considered as a factor influencing the rates¹⁸.

The rate determining step in ion exchange is, as a rule, interdiffusion of the counter ions either in the resin itself or across the adherent liquid film. The slower of these processes controls the overall rate. In systems with organic solvents, the mobilities of the counter ions in the resin are usually lower than in aqueous systems because swelling is less pronounced and electrostatic interactions wit fixed charges are stronger. Particle diffusion thus is relatively slow and usually is the rate controlling mechanism.¹⁹

The problem of diffusion in porous media is usually approached with the use of either of two rather different types

of models. In the first type, the medium is considered as consisting of two phases, namely the solid frame work and the interstitial pore phase. Diffusion is viewed on taking place in the pores only. In such models, diffusion is necessarily slower than in the corresponding homogenous systems having the same composition as the pore phase. In the second type of models, 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 chloride has been as analogous organic electrolytes.

Parabolic diffusion constant (K)

The rate determining process for most cation exchange resins is primarily the diffusion rates of the ions throughout the gel structure, and are therefore dependent on particle size, concentration, temperature degree of saturation of exchange capacity, and resin hydration. Fractional attainment of equilibrium F is related with time t by parabolic diffusion law namely²⁰.

$$F = K \sqrt{t}$$

where K is a constant that varies linearly with the reciprocal of the particle diameter. The values of K were obtained from slope of curves F versus \sqrt{t} presented by Figs. 2.11 to 2.18.

It is observed that the values of K are constant at a particular concentration of a metal ion and is independent on the percentage of acetone. The values of K for Cu are greater than the corresponding values of Pb in aqueous acetone 0.06 M Ammonium Tartrate media. The values of K for the exchange of Mg are found to be greater than those of Cu and Pb. This indicates that the selectivity of the resin is in the order of $Cu > Pb > Mg$. The same trend is observed in the studies of distribution

coefficients in Chapter III.

The diffusion mechanism may be decided by Bt versus t graphs. The graphs are presented by Figs. 2.19 to 2.26. It is observed that these plots are linear passing through the origin. The values of B are presented in Tables 2.12, 2.13 and 2.14. It is observed that the values of B increase with the increase in percentage of acetone, indicating that the rate of adsorption is increased at higher concentrations of acetone. These results support our results on distribution coefficients that the distribution coefficients increase at higher concentrations of acetone. The values of B follow the sequence that $B_{Cu} > B_{Pb} > B_{Mg}$. This sequence supports our findings of selectivity of metal ions towards the resin.

For the systems studied at various percentages of acetone, the linear nature of Bt versus t plots, passing through the origin, suggests that the rate of diffusion is controlled by particle diffusion. Some of the curves show slight deviation, at later stages, indicating that the final stage of exchange is not controlled by particle diffusion alone.

Effect of temperature

The exchange of Cu (0.004 M) and Mg (0.004 M) on ~~Resin~~ Amberlite IR -120 (NH_4^+) form in aqueous acetone ammonium tartrate media was studied at 308, 313 and 318° K. The effect of temp. on fractional attainment of equilibrium (F), half exchange time ($t^{1/2}$), interdiffusion coefficient (D), parabolic diffusion (K)

and B values is seen from the values presented in Table 2.15 to 2.17

The variation of F versus t at 308, 313 and 318° K in 50% and 70% acetone (0.05 M) of Ammonium tartrate are presented in Figs. 2.35 to 2.38. It is observed that the uptake of Cu and Mg (0.004 M) ions is increased at higher temperatures. The amount of adsorption of Cu and Mg at 308, 313 is nearly doubled at 318° K upto 40 minutes. The comparative rates of uptake becomes slower upto 3 hrs and the rates are nearly the same after 5 hrs. It is also observed that the rate of adsorption of Cu and Mg at 70% acetone is greater than that at 50% acetone.

The values of half exchange time $t^{1/2}$ decrease and those of interdiffusion coefficients increase with rise in temperature. It is concluded that the rate of exchange is enhanced by the temp. The energies of activation (E_a) were calculated from log D versus $1/T$ plots (Figs. 2.51 and 2.52) and the values are presented in Table 2.18, suggest that the rates of metal ions are activated by the energy supplied by temperature.

The values of energy of activation for $\text{Cu}(\text{NH}_4^+) \text{ tart.}$ exchanges are 32.82 and 49.01 K J mol⁻¹ at 50 and 70 percentages of acetone respectively and for $\text{Mg}(\text{NH}_4^+) \text{ tart.}$ exchanges the values are 32.83 and 29.35 K J mol⁻¹ at 50,70 percentages of acetone. The values of K_a for particle diffusion mechanism in standard ion exchange resins were found^{21,22} to be 25.1 to 41.84 K J mol⁻¹. The values of E_a for the systems under study are in good agreement with the above values indicating that the exchange are mostly governed by particle diffusion mechanism.

The pre exponential constant, D_0 is related with the entropy of activation ΔS^* as follows.

$$D_0 = 2.72 (K T_0^2/h) \exp (\Delta S^*/R)$$

Where k_B = Boltzmann constant, $T = 303^{\circ}\text{K}$, d = ionic jump (distance between two successive position of ion in the process of diffusion) taken as equal to $5 \times 10^{-10}\text{m}$, h = Planck's constant and R = gas constant.

The values of entropy are found to be negative and are not measurably affected by acetone. According to Frank and Evans ionisation of neutral molecules into charged species. The negative values of entropy were also observed by the behaviour of the dissociation of acetic acid in methanol²³. The negative values of entropy are indeed what one would expect in reactions involving ionization of neutral molecules.²⁴ Since the transformation of the outer to the inner complex involves ionization it is likely that the activated complex is also similar to ion pair, and will therefore be stabilized by solvation to a greater extent than the initial state.²⁵ The negative entropy indicates that the activated complex is less favourable²⁶.

Rate constants

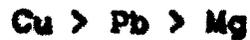
Log $(1-F)$ versus time (t) for the exchange systems are plotted, and are presented in Figs 2.27 to 2.34. The plots are linear showing that the exchange systems follow the first order kinetic equation.

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

Where K represents the exchange rate constant. The K values for the exchange processes have been computed from the slopes of these linear plots and recorded in Table 2.12 to 2.14. The values of rate constants (K) are in agreement with the following overall relations.

a) The rate constant 'K' increases as the percentage of acetone increases.

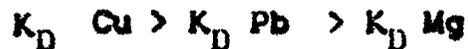
b) The values of K for the metal ions in aqueous acetone citric acid are in the following sequence



c) The rate constant increases as the concentration of metal ions is increased from 0.002 to 0.0008 M solutions.

d) The rate of ion exchange increases with the increase in temperature from 303° to 318° K (Table 2.17), suggesting that the mobility of the ion increases with increasing temperature. The uptake increases with time.

These findings are similar to the findings of the distribution coefficients (chapter III) of the metal ions in these media. The distribution coefficients increase with the rise in percentage of acetone. The distribution coefficients of the metal ions showed the following order.



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