CHAPTER- TWO

Kinetics of Ion Exchange of
Hg, Sr and Pb
ON
DOWEX-21 K (Cl^-)
IN
Aqueous Acetone - Tartaric Acid Medium

CHAPTER - II

INTRODUCTION :

Many investigators have studied ion exchange phenomena and approached the subject from various directions. A large number of papers come from the soil chemist and, consequently, deal largely with ionic distribution in soils. Other investigators have described industrial uses and applications. Data on ionic equilibria between exchanger and solution have been collected. However little information can be gathered if one wants to learn something about the rates of reaction taking place between the ions in the solution and in the ion exchange material. One encounters qualitative statements that the reaction proceeds rapidly at first[1,2] and then slows down as the equilibrium is approached.

DuDomaine, Swain and Hougen[3] focussed their attention on cation exchange softening rates. Their technique consisted in passing hard water through thin layers of exchange material. The small dimension of the bed permitted disregarding concentration gradients and Nachod and Wood[4] arrived at differential rate equations. Certain limitations of the procedure are stated by them and no rate constants were given nor was the order of the reaction determined by these experiments. The data obtained by these authors are of value only for a particular cation exchange and a particular water composition. No net reaction rate could be obtained by their procedure. Beaton and Furnas[5] obtained transfer coefficients by considering base exchange to be analogous to heat transfer. Their data on the hydrogen-copper exchange show again that the reaction is very rapid and about 90 % of it is completed in thirty minutes.

The difference between a good and a bad exchanger was shown graphically by Austerweil[6]. His experiments show that the exchange reaction is extremely rapid and completed after approximately fifteen minutes.

Nachod and Wood[7] endeavored to measure the rate of reaction of ion exchange, The ion exchange materials which were studied comprise two clanes. In the first class are siliceous materials of natural origin, e.g., the glauconite or greensand type exchangers as well as synthetic siliceous gel type exchangers which all are cation exchangers.

The organic materials which form the second class embrace cation exchangers, characterized by the functional groups $-SO_3H$, $-COOH$, and $-OH$, may be either of the sulphonated Coal[8] or of the synthetic resin[9] category. The symbol H represents the exchangeable ion which in thin case is H. The anion exchange materials are all resins which contain functional amino groups, i.e. RNH_2, R_2NH and R_3N.

The reaction rate could be determined by following the rate with which ions from solution are removed by the solid ion exchanger or conversely the rate with which exchangeable ions are released from the exchange material into the solution. Both procedures were used and gave satisfactory results. The solid ion exchange material containing exchangeable ion was brought into contact with the solution containing the other type of exchangeable ion in considerable 4-5 fold excess, and the system was vigorously agitated. Due to the rotation of the reaction vessel the solid granules fall at random through the solution and concentration gradients in the liquid phase are minimized.

Kinetics of exchange reactions in aqueous media has been studied by many workers, 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[10]. However, later workers could not varify this conclusion[11,12].

Matsuzuru and Wadachi have reported that the rate determining steps for the sorption of Co(II) and Ce(III) on anion exchanger Dowex A1 were particle diffusion and chemical reaction respectively[13].

The difference 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. The kinetics of ion exchange system between a solution $Fe(SO_4)_2^-$ and a strong base anion exchanger in the SO_4^{2-} from was examined by Zaki[14]. This study was carried out statically under the condition that the concentrated iron complex anion exists in decinormal H_2SO_4. The ion exchange process $Fe(SO_4)_2^- / SO_4^{2-}$ was found to follow particle diffusion mechanism. Zaki[15] calculated the interdiffusion coefficients as well as the first order rate constants for $BiCl_5^{2-}/Cl^-$ exchange on Wofatit SBW resin (8% DVB). The observed values of half time (t ½) for ion exchange process have been evaluated under conditions favouring the particle diffusion mechanism. The ion exchange process under study was found to be first order; controlled by the slow particle diffusion mechanism.

In most ion exchange separations water has been used as a solvent because of its high dielectric constant. Recently, interest in the field is directed towards the use of non aqueous and mixed solvents having equally high dielectric constants. The potentiality of ion exchange technique is further enhanced by the use of radiosotope tracers. Radiotracers were first applied by Boyd et al.[16] to deduce diffusion coefficients of ions using both anion and cation exchange resins. Mehta and Bhatnagar[17] studied the kinetics of anion exchange between labelled[18] SO_4^{2-} ions (10^{-6} M anilinium sulphate solution) and Cl^- ions on strongly basic anion exchanger Dowex 1X4 with trimethyl benzyl ammonium as functional group (4% DVB), using different compositions of dimethyl sulphoxide water mixed solvents. The exchange was observed to obey first order kinetic equation and the film diffusion was found to be the rate controlling step.

The kinetics of exchange of SO_4^{2-} and Cl^- on the strongly basic anion exchanger Dowex 1 X 8 of different particle diameters was studied by Abdel-Rassoul et al.[19] The diffusion coefficients are calculated by two methods, discussed in relation to processes governing the exchange reaction. They were controlled by the particle diffusion. The distribution of SO_4^{2-}, SO_3^{2-} , $S_2O_3^{2-}$ and S^{2-} between aqueous KCl solutions of different concentrations was studied by using different forms of resins. The dataare explained by different interactions between both aqueous and resinous phases. The effect of alkali metal chloride materials in the aqueous phase (LiCl, NaCl and KCl) on exchange of different S^{--} anion was also investigated. The results were interpreted in relation to water-water interaction and the competition for hydration between alkali metals Cations and the exchanged sulphide anions. Kinetics of ion exchange of a negatively charged chloride complexes of

Cadmium[20] and Zinc[21] were studied by Kulkarni and Soman. The mechanism of the rate controlling process was suggested as the slow particle diffusion.

Present Work :

The kinetics behaviour of exchange reactions of Hg, Sr and Pb ions with Cl^- ions of Dowex 21K resin has been investigated in aqueous acetone tartaric acid media. The kinetic parameters such as interdiffusion coefficient (D), half exchange time ($t_{1/2}$), parabolic diffusion constant (k) were computed. The effect of concentration of acetone, tartaric acid and metal ions on these kinetic parameters are reported in this chapter. The plots of Bt versus t indicate the probable mechanism of diffusion. The effect of concentration of acetone and of metal ions on the rate constant (k) was studied. The values of energy of activation (Ea), The pre-exponential constant (D_o) and entropy of activation ($\triangle S$) were obtained by the studied of kinetics of exchange reactions at different temperatures.

EXPERIMENTAL

Solutions :

1. Chloride solutions of Strontium(II) = 0.05 and 0.5M
2. Lead (II) nitrate solution = 0.05 M and 0.5 M
3. Mercury nitrate = 0.05 M and 0.5 M
4. Tartaric Acid = 0.05 M and 0.5, 0.1 M
5. Acetone % - 0, 10, 30, 50, 70.

Procedure :

Exactly 1 g of air dried resin Dowex 21-K (Cl^-) from [illegible] was taken in an erlynmeyer flask. 50 ml of mixture containing acetone water tartaric acid was added. Appropriate quantity of metal ions solution was added into it at noted time so that the overall metal concentration would be 0.002, 0.004, 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 Hg^{2+} , Sr^{2+} and Pb^{2+} ions on Dowex 21 K (Cl^-) resin in aqueous acetone tartaric acid media was studied. The studies represent the mechanism of $[M(Tart)_2]^{2-}/Cl^-$ where M=Hg, Sr and Pb. The formation of anionic complex such as $[Cd(Tart)_2]^{2-}$ was suggested by M.Singh[R1] [R2] Hence the exchange is supposed to take place between $[Hg(Tart)_2]^{2-}$, $[Sr(Tart)_2]^{2-}$, $[Pb(Tart)_2]^{2-}$ and Cl^- of the resin Dowex 21 K.

Table 3.1 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	0.0796	0.53	0.3480	0.78	1.0280
0.04	0.00141	0.29	0.0861	0.54	0.3650	0.79	1.0730
0.05	0.00219	0.30	0.0928	0.55	0.3800	0.80	1.1200
0.06	0.0032	0.31	0.0998	0.56	0.400	0.81	1.1710
0.07	0.0044	0.32	0.1070	0.57	0.4190	0.82	1.2240
0.08	0.0057	0.33	0.1147	0.58	0.4380	0.83	1.2800
0.09	0.0073	0.34	0.1226	0.59	0.4580	0.84	1.3400
0.10	0.0091	0.35	0.1308	0.60	0.4790	0.85	1.4040
0.11	0.0111	0.36	0.1391	0.61	0.5000	0.86	1.4680
0.12	0.0132	0.37	0.1485	0.62	0.5220	0.87	1.5430
0.13	0.0156	0.38	0.1577	0.63	0.5450	0.88	1.6230
0.14	0.0183	0.39	0.1670	0.64	0.5690	0.89	1.7100
0.15	0.0210	0.40	0.1770	0.65	0.5940	0.90	1.8000
0.16	0.0241	0.41	0.1880	0.66	0.6200	0.91	1.9100
0.17	0.0274	0.42	0.1990	0.67	0.6470	0.92	2.0300
0.18	0.0309	0.43	0.2100	0.68	0.6750	0.93	2.1600
0.19	0.0346	0.44	0.2220	0.69	0.7030	0.94	2.3200
0.20	0.0386	0.45	0.2340	0.70	0.7340	0.95	2.5000
0.21	0.0428	0.46	0.2460	0.71	0.7650	0.96	2.7000
0.22	0.0473	0.47	0.2590	0.72	0.7980	0.97	3.0100
0.23	0.0320	0.48	0.2730	0.73	0.8320	0.98	3.4100
0.24	0.0570	0.49	0.2870	0.74	0.8680	0.99	4.1100
0.25	0.0623	0.50	0.3010	0.75	0.9050	1.00	-

Table 2.2 : Dependence of fractional exchange (F) on percentage of acetone

Metal ion Hg (II) 0.002 M

Tartaric Acid 0.05 M

Time in (min)	Fractional attainment of equilibrium (F)			
	Acetone percentage (v/v)			
	0	10	30	50
1	2	3	4	5
0	0.000	0.000	0.000	0.0000
5	0.0588	0.0529	0.763	0.8241
10	0.1176	0.275	0.913	0.9890
20	0.5882	0.584	0.913	1.000
30	0.6470	0.682	0.967	1.000
40	0.764	0.780	1.000	1.000
50	0.764	0.805	1.000	1.000
60	0.882	0.850	1.000	1.000
120	0.895	0.948	1.000	1.000
180	0.948	1.000	1.000	1.000
240	1.000	1.000		
300	1.000	1.000		
360	1.000	1.000		
∞	1.000	1.000		

Table 2.3 : Dependence of fractional exchange (F) on percentage of acetone

Metal ion Hg (II) 0.004 M

Tartaric Acid 0.05 M

Time in (min.)	Fractional attainment of equilibrium(F)			
	Acetone percentage (v/v)			
1	2	3	4	5
0	0.000	0.000	0.000	0.000
5	0.1102	0.153	0.775	0.850
10	0.153	0.358	0.925	0.975
20	0.256	0.512	0.975	1.000
30	0.435	0.589	1.000	1.000
40	0.435	0.615	1.000	1.000
50	0.6410	0.820	1.000	1.000
60	0.846	0.948	1.000	1.000
120	0.892	0.948	1.000	
180	0.948	0.988	1.000	
240	1.000	1.000		
300	1.000	1.000		
360	1.000	1.000		
∞	1.000	1.000		

Table 2.4 : Dependence of fractional exchange (F) on percentage of acetone

Metal ion Hg (II) 0.006 M
Tartaric Acid 0.05 M

Time in (min)	Fractional attainment of equilibrium (F)			
	Acetone percentage (v/v)			
1	2	3	4	5
0	0.00	0.000	0.000	0.000
5	0.129	0.166	0.833	0.945
10	0.148	0.277	0.981	0.988
20	0.185	0.333	1.000	1.000
30	0.333	0.574	1.000	1.000
40	0.444	0.629	1.000	1.000
50	0.444	0.722	1.000	
60	0.481	0.818		
120	0.907	0.851		
180	0.962	0.962		
240	1.000	1.000		
300	1.000	1.000		
360	1.000	1.000		
∞	1.000	1.000		

Table 2.5 : Dependence of fractional exchange (F) on percentage of acetone

Metal ion Hg (II) 0.008 M

Tartaric Acid 0.05 M

Time in (min)	Fractional attainment of equilibrium (F)			
	Acetone percentage (v/v)			
1	2	3	4	5
0	0.00	0.000	0.000	0.00
5	0.0735	0.955	0.897	0.942
10	0.0735	0.970	0.955	0.985
20	0.2500	1.000	1.000	1.000
30	0.338	1.000	1.000	1.000
40	0.352	1.000	1.000	1.000
50	0.573	1.000		
60	0.735			
120	0.735			
180	0.911			
240	0.970			
300	1.000			
360	1.000			
∞	1.000			

Table 2.6 : Dependence of fractional exchange (F) on percentage of acetone

Metal ion Sr (II) 0.002 M

Tartaric Acid 0.05 M

Time in (min)	Fractional attainment of equilibrium(F)			
	Acetone percentage (v/v)			
1	2	3	4	5
0	0.000	0.000	0.000	0.000
5	0.250	0.363	0.453	0.643
10	0.423	0.685	0.688	0.750
20	0.552	0.771	0.774	0.801
30	0.705	0.828	0.882	0.855
40	0.793	0.880	0.925	0.942
50	0.882	0.914	0.971	1.000
60	0.915	0.930	1.000	1.000
120	0.9444	0.950	1.000	1.000
180	0.976	0.971	1.000	1.000
240	1.000	1.000	1.000	1.000
300	1.000	1.000	1.000	1.000
360	1.000	1.000	1.000	1.000
∞	1.000	1.000	1.000	1.000

Table 2.7 : Dependence of fractional exchange (F) on percentage of acetone

Metal ion Sr(II) 0.004 M

Tartaric Acid 0.05 M

Time in (min)	Fractional attainment of equilibrium (F)			
	Acetone percentage (v/v)			
1	2	3	4	5
0	0.000	0.000	0.000	0.000
5	0.000	0.000	0.263	0.263
10	0.470	0.588	0.558	0.789
20	0.588	0.705	0.732	0.805
30	0.651	0.725	0.750	0.813
40	0.764	0.777	0.850	0.910
50	0.818	0.853	0.949	0.971
60	0.935	0.880	0.960	1.000
120	0.980	0.960	1.000	1.000
180	0.986	0.985	1.000	1.000
240	1.000	1.000	1.000	1.000
300	1.000	1.000	1.000	
360	1.000	1.000	1.000	
∞	1.000	1.000	1.000	

Table 2.8 : Dependence of fractional exchange (F) on percentage of acetone

Metal ion Sr(II) 0.006 M

Tartaric Acid 0.05 M

Time in (min)	Fractional attainment of equilibrium (F)			
	Acetone percentage (v/v)			
1	2	3	4	5
0	0.000	0.000	0.000	0.000
5	0.000	0.000	0.000	0.000
10	0.203	0.412	0.610	0.833
20	0.397	0.694	0.717	0.907
30	0.481	0.750	0.785	1.000
40	0.537	0.781	0.856	1.000
50	0.613	0.809	0.856	1.000
60	0.687	0.818	0.932	1.000
120	0.812	0.875	0.960	
180	0.905	0.959	0.980	
240	0.931	0.988	1.000	
300	0.981	1.000	1.000	
360	1.000	1.000	1.000	
∞	1.000	1.000	1.000	

Table 2.9 : Dependence of fractional exchange (F) on percentage of acetone

Metal ion Pb(II)   0.002 M

Tartaric Acid   0.05 M

Time in (min)	Fractional attainment of equilibrium (F)			
	Acetone percentage (v/v)			
1	2	3	4	5
0	0.00	0.00	0.000	0.000
5	0.210	0.460	0.500	0.654
10	0.263	0.650	0.650	0.783
20	0.315	0.750	0.810	0.900
30	0.360	0.802	0.846	0.956
40	0.421	0.890	0.930	0.960
50	0.450	0.910	0.957	0.980
60	0.526	0.925	0.957	0.980
120	0.726	0.950	0.977	1.000
180	0.789	0.980	0.990	1.000
240	0.947	1.000	1.000	1.000
300	1.000	1.000	1.000	1.000
360	1.000	1.000	1.000	1.000
∞	1.000	1.000	1.000	1.000

Table 2.10 : Dependence of fractional exchange (F) on percentage of acetone

Metal ion Pb(II) 0.004 M

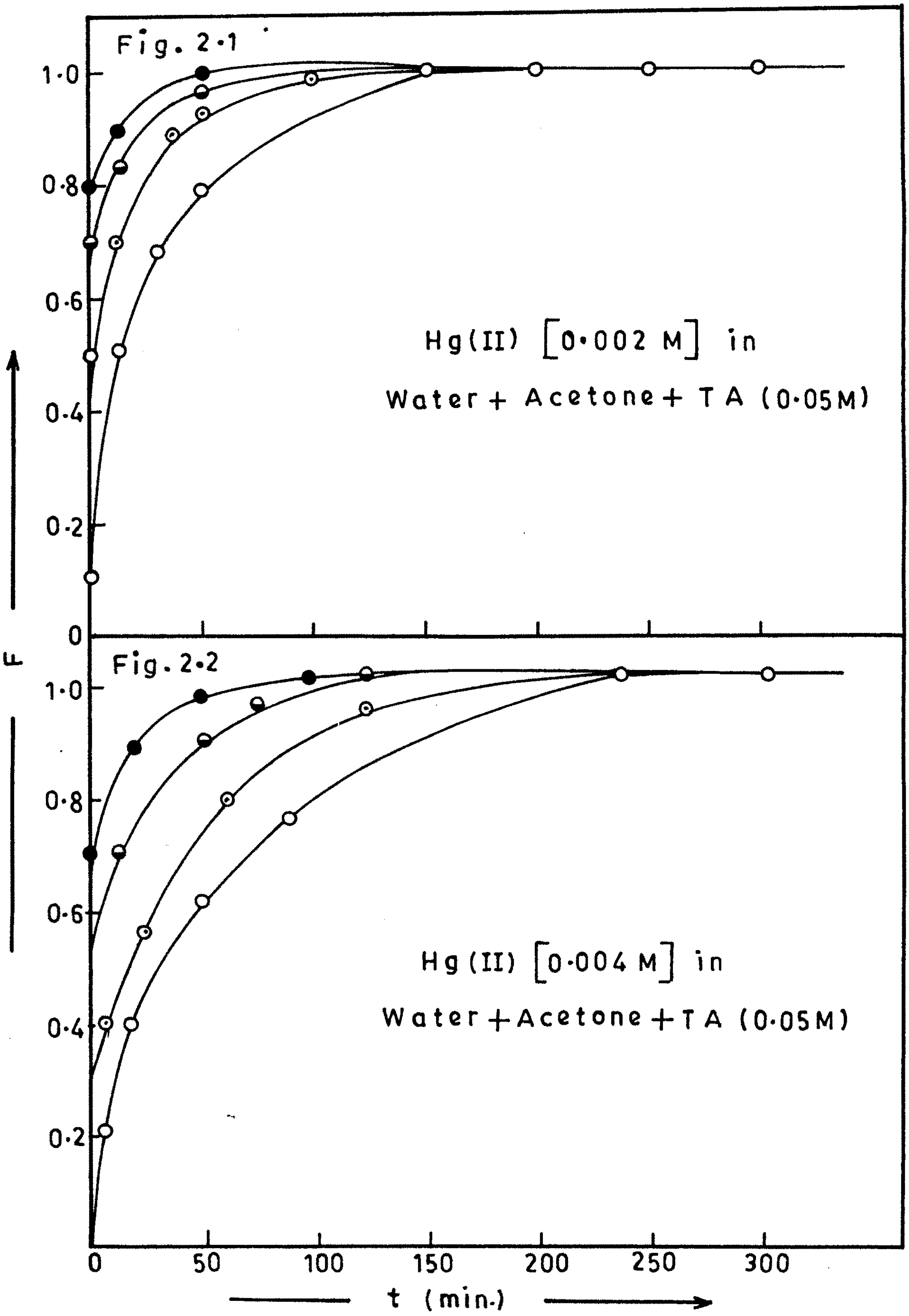
Tartaric Acid 0.05 M

Time in (min)	Fractional attainment of equilibrium(F)			
	Acetone percentage (v/v)			
0	0.000	0.000	0.000	0.000
5	0.267	0.269	0.290	0.302
10	0.385	0.400	0.425	0.457
20	0.460	0.502	0.526	0.556
30	0.510	0.600	0.583	0.583
40	0.556	0.653	0.683	0.652
50	0.615	0.653	0.683	0.750
60	0.673	0.750	0.766	0.846
120	0.793	0.815	0.853	0.904
180	0.846	0.860	0.959	0.978
240	0.945	0.956	0.990	1.000
300	1.000	1.000	1.000	1.000
360	1.000	1.000	1.000	1.000
∞	1.000	1.000	1.000	1.000

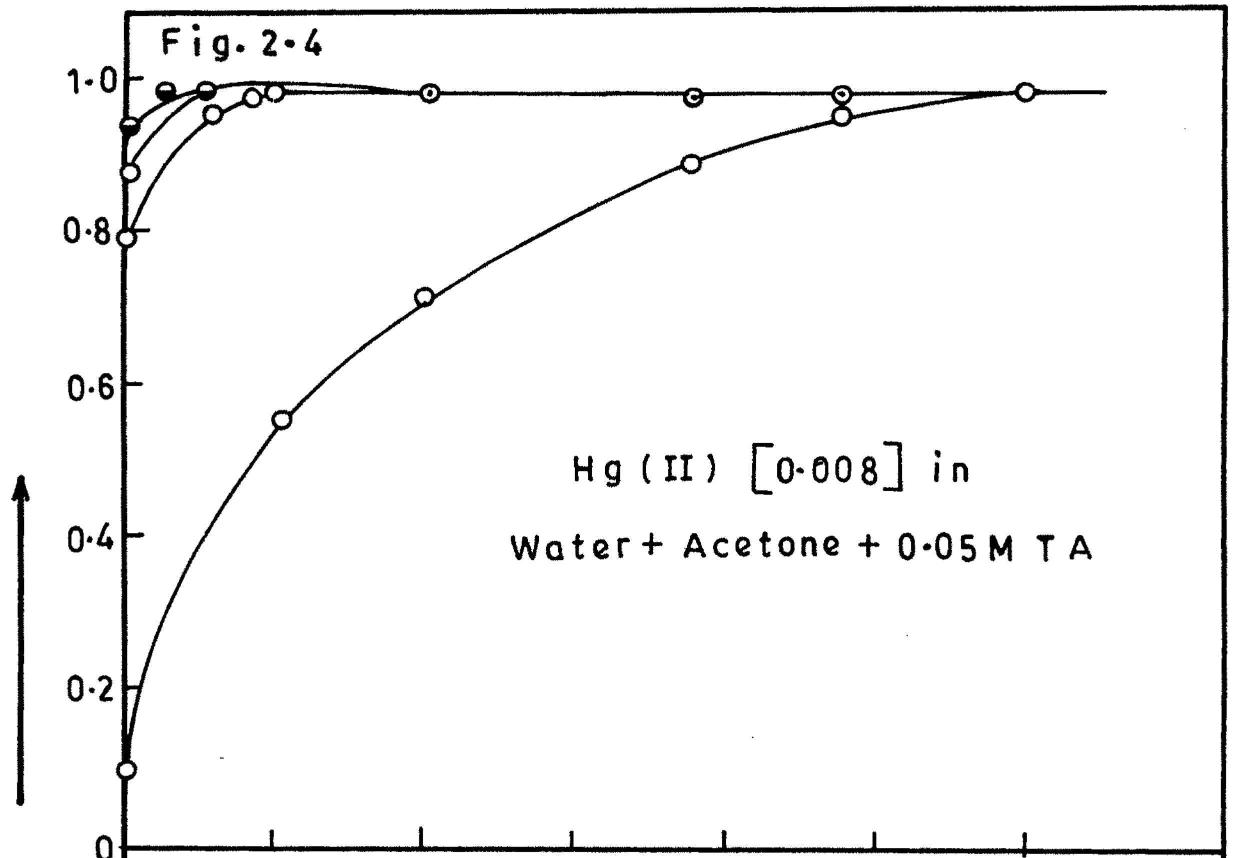
Table 2.11 : Dependence of fractional exchange (F) on percentage of acetone

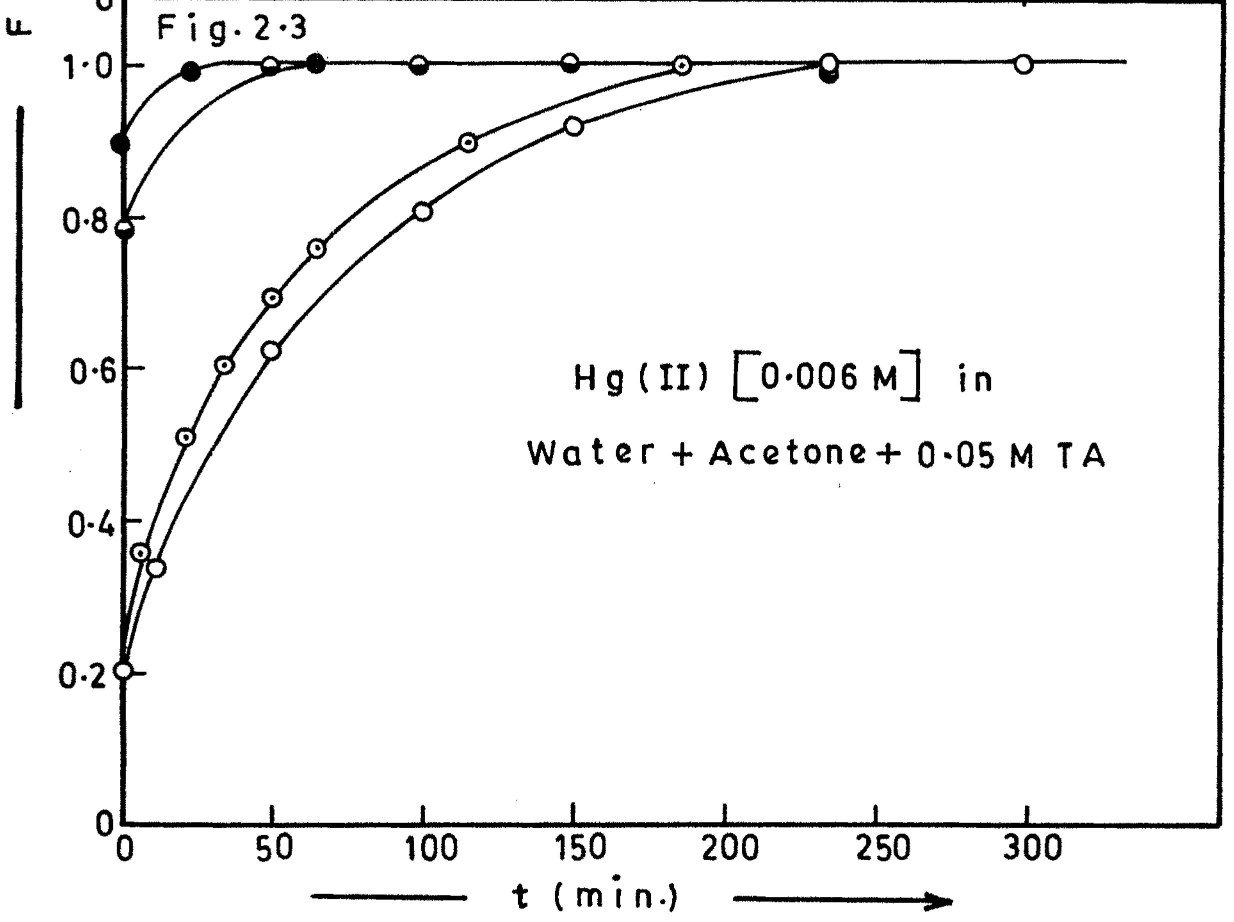
Metal ion Pb(II) 0.006 M
Tartaric Acid 0.05 M

Time in (min)	Fractional attainment of equilibrium (F)			
	Acetone percentage (v/v)			
1	2	3	4	5
0	0.000	0.000	0.000	0.000
5	0.265	0.315	0.418	0.555
10	0.387	0.426	0.537	0.619
20	0.460	0.467	0.550	0.722
30	0.510	0.526	0.569	0.722
40	0.555	0.590	0.624	0.835
50	0.610	0.750	0.763	0.865
60	0.679	0.786	0.858	0.926
120	0.770	0.790	0.954	0.956
180	0.848	0.913	0.962	0.980
240	0.957	0.925	1.000	0.981
300	1.000	0.988	1.000	1.000
360	1.000	1.000	1.000	1.000



(Acetone%)(-○-) 0 %, (-⊙-) 10 %, (-⊖-) 30 %, (-●-) 50 %.





Acetone%(-○-) 0 %, (-⊙-) 10 %, (-◒-) 30 %, (-●-) 50 %.

Fig. 2·5

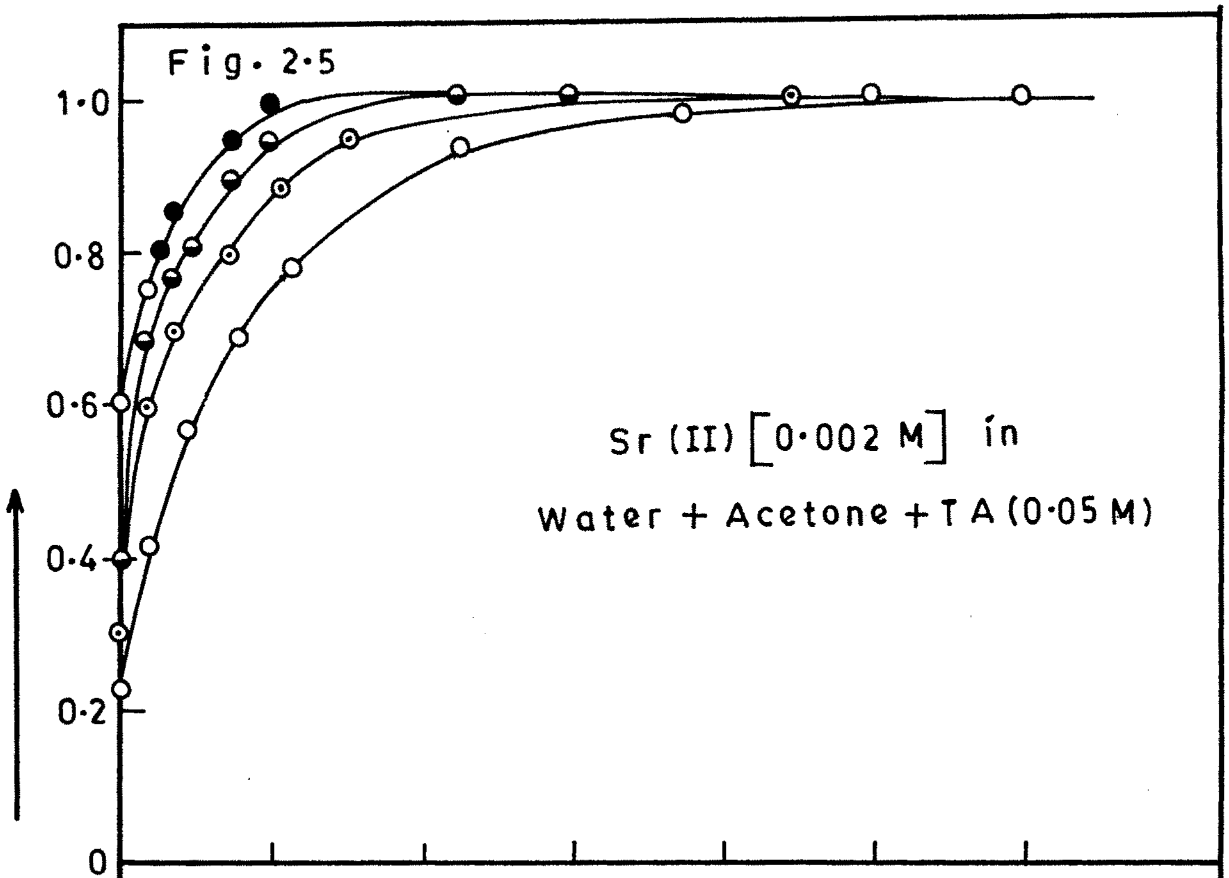
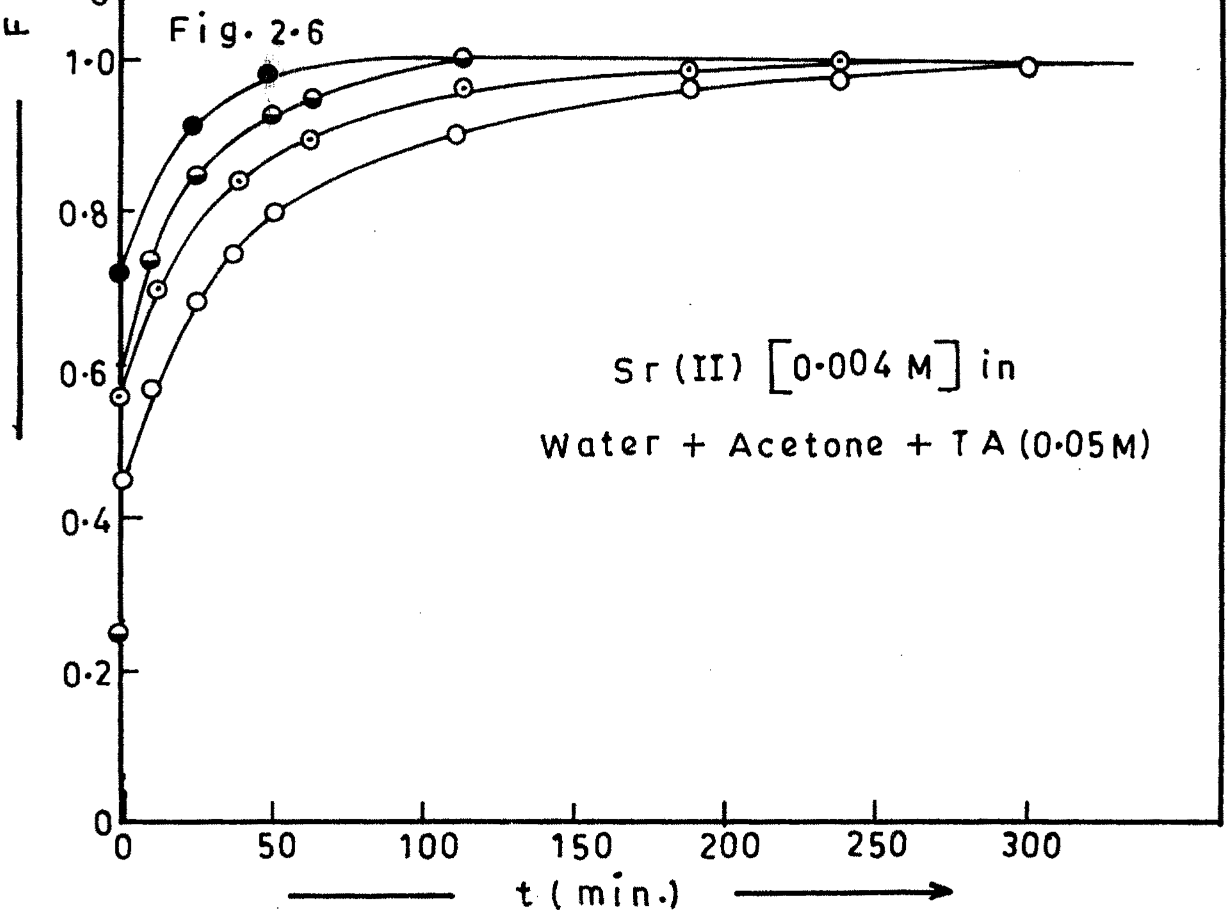


Fig. 2·6



(Acetone%) (-○-) 0 %, (-⊙-) 10 %, (-◐-) 30 %, (-●-) 50 %.

Fig. 2·7

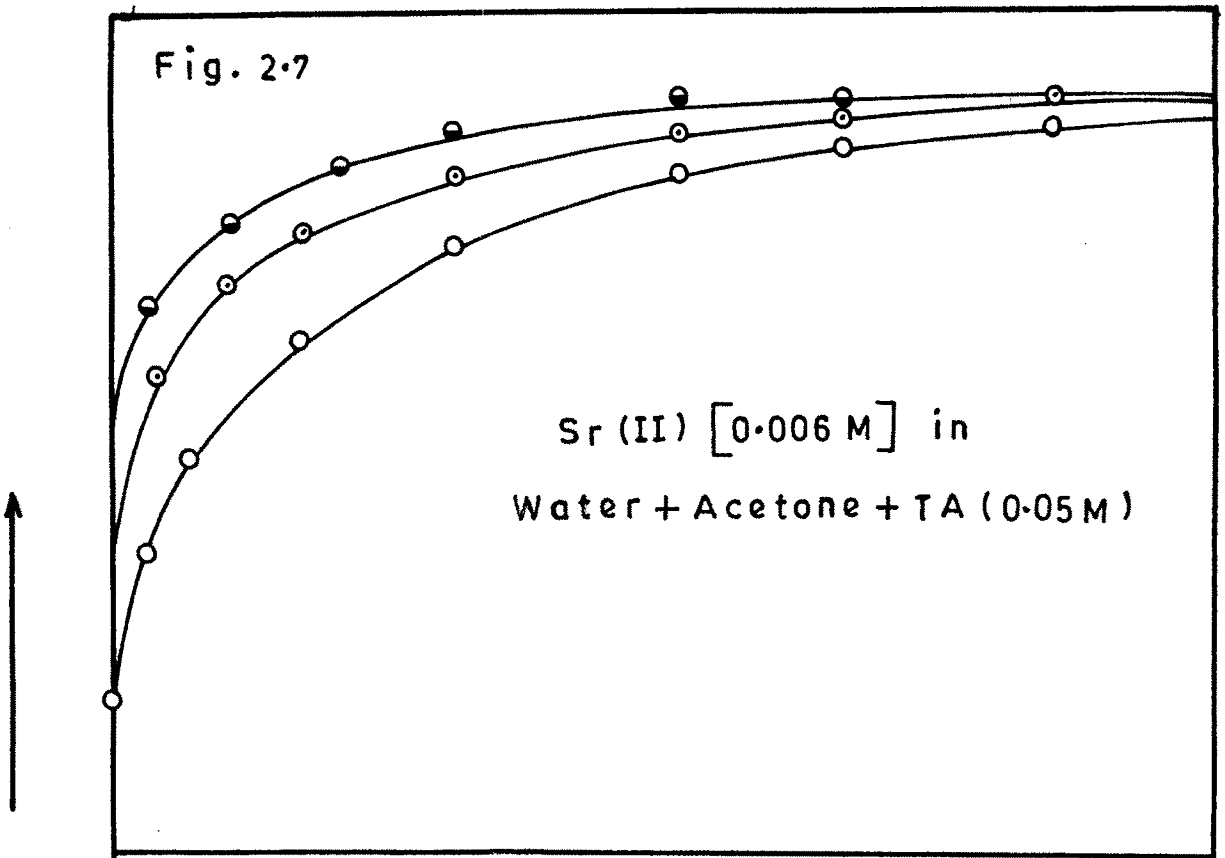
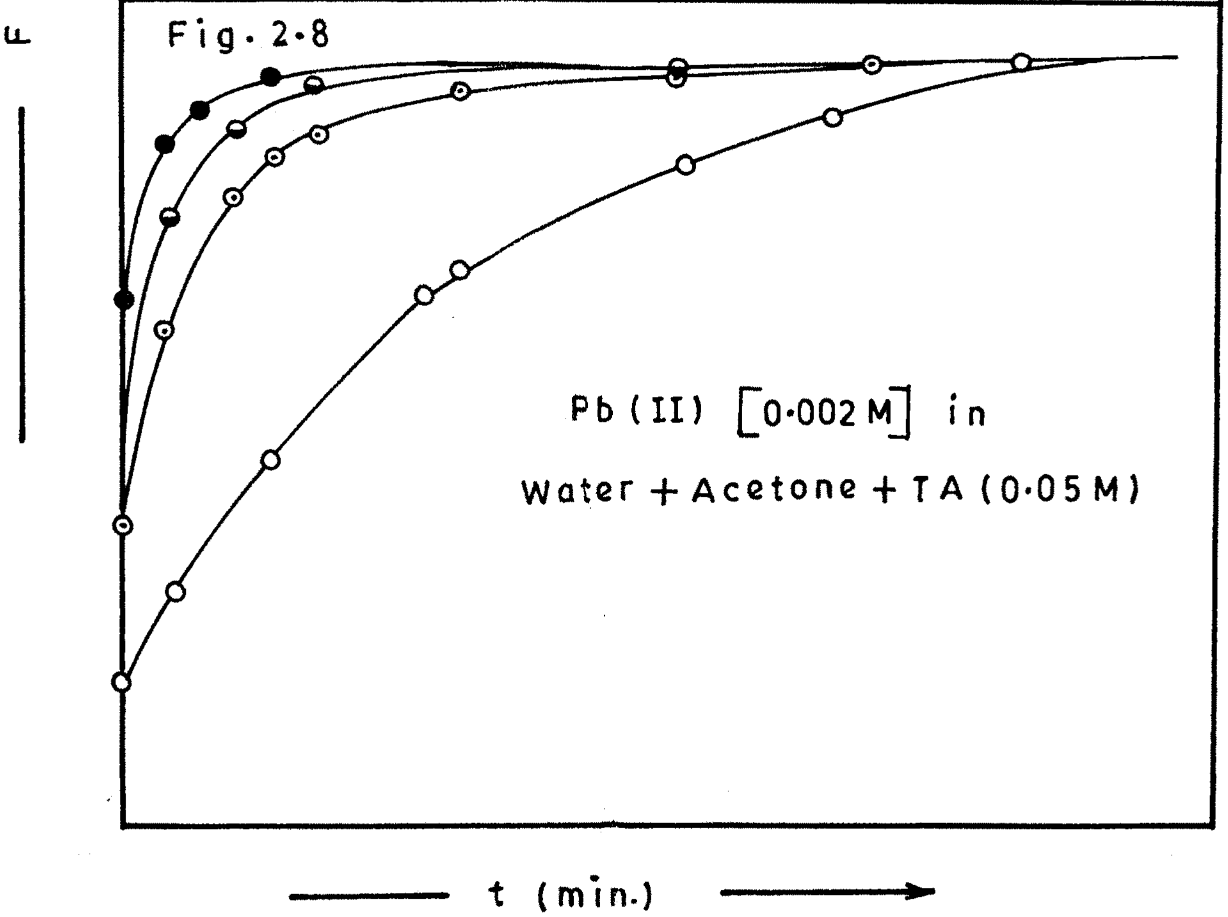


Fig. 2·8



(Acetone %) (-○-) 0 %, (-⊙-) 10%, (-⊖-) 30 %, (-●-) 50 %.

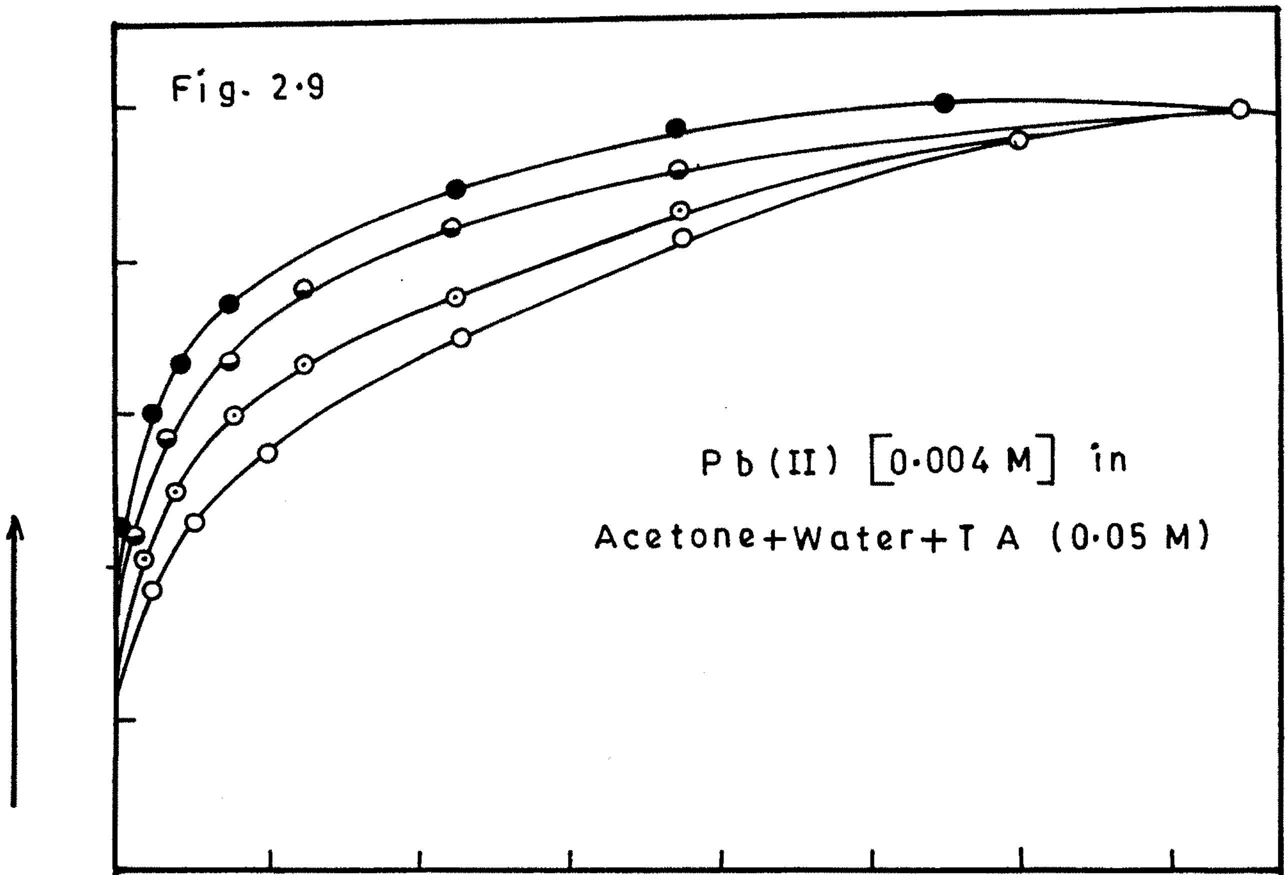


Fig. 2·9

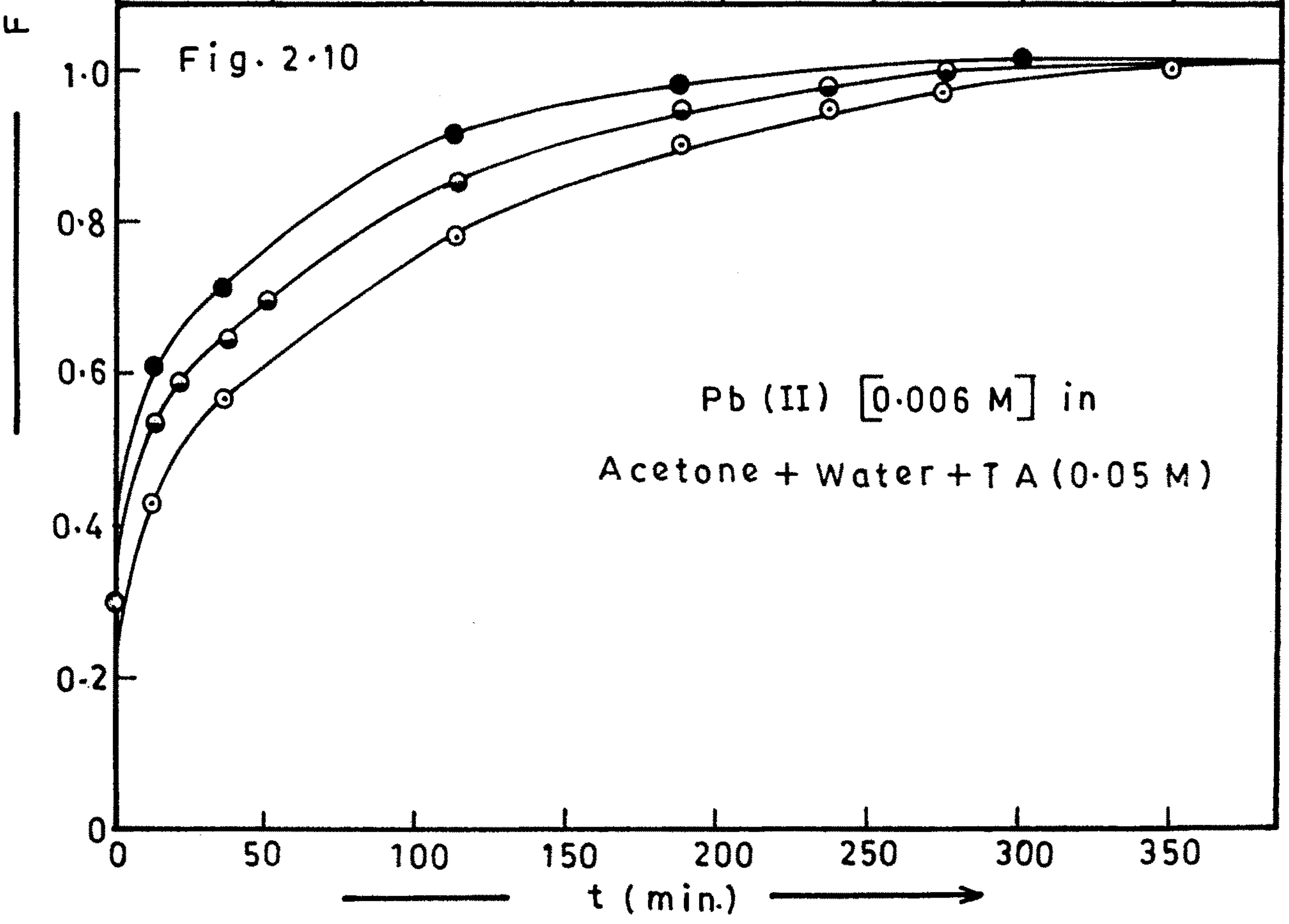
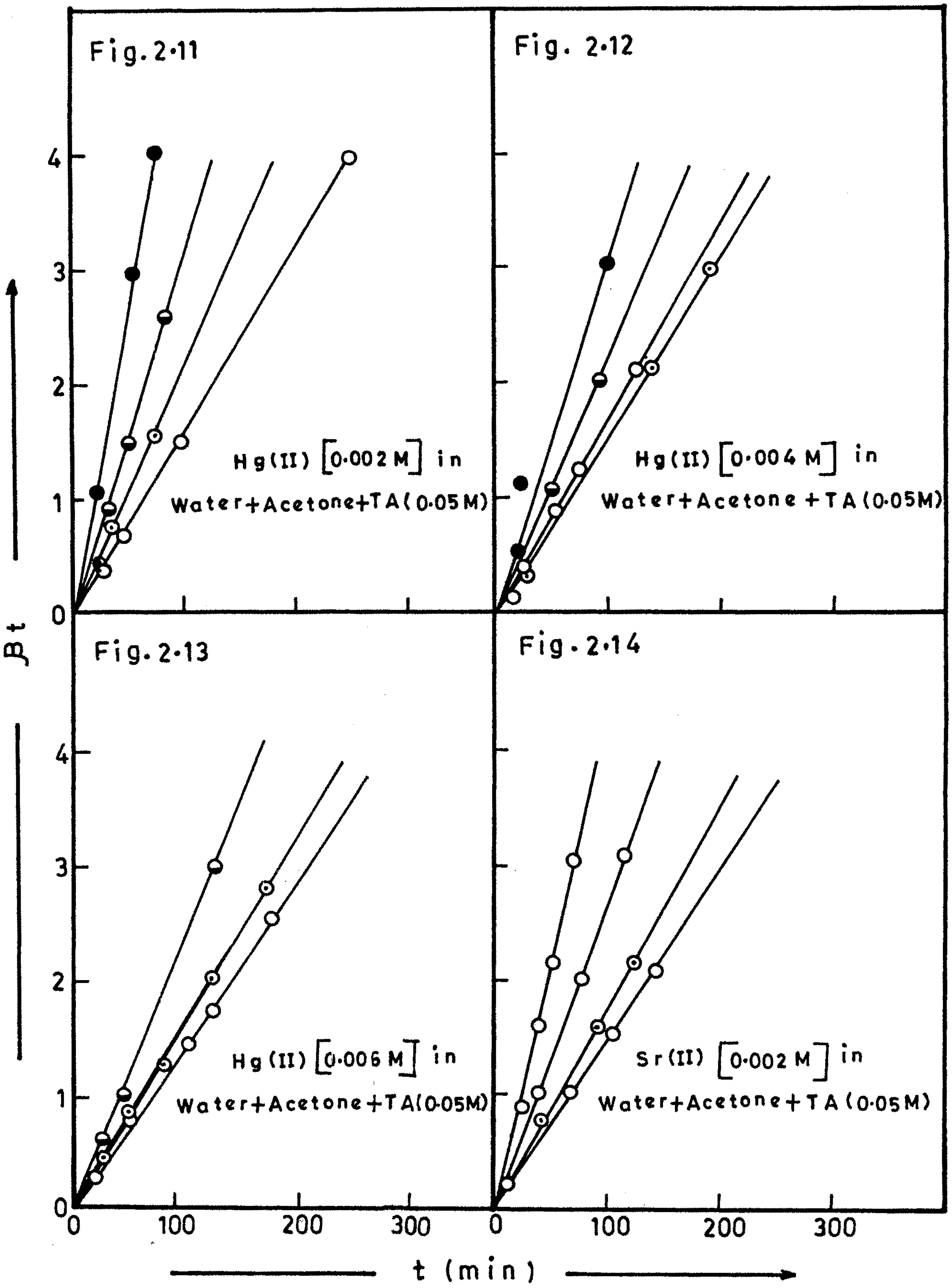


Fig. 2·10

(Acetone %) (-○-) 10 %, (-⊙-) 30 %, (-⊖-) 50 %, (-●-) 70 %.



Acetone %, (-○-) 0 %, (-⊙-) 10 %, (-⊖-) 30 %, (-●-) 50 % .

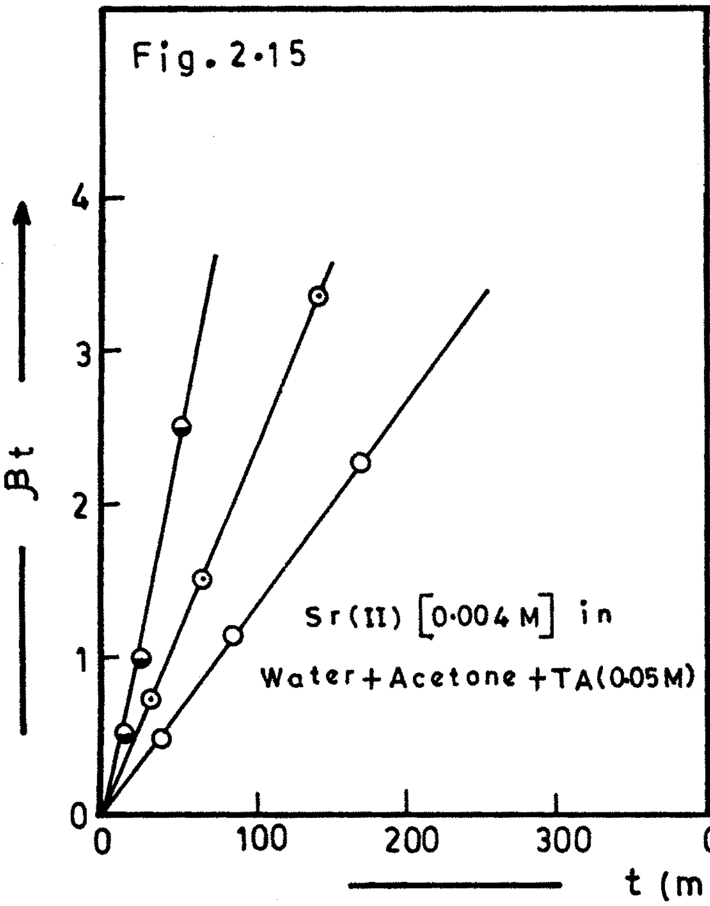


Fig. 2.15

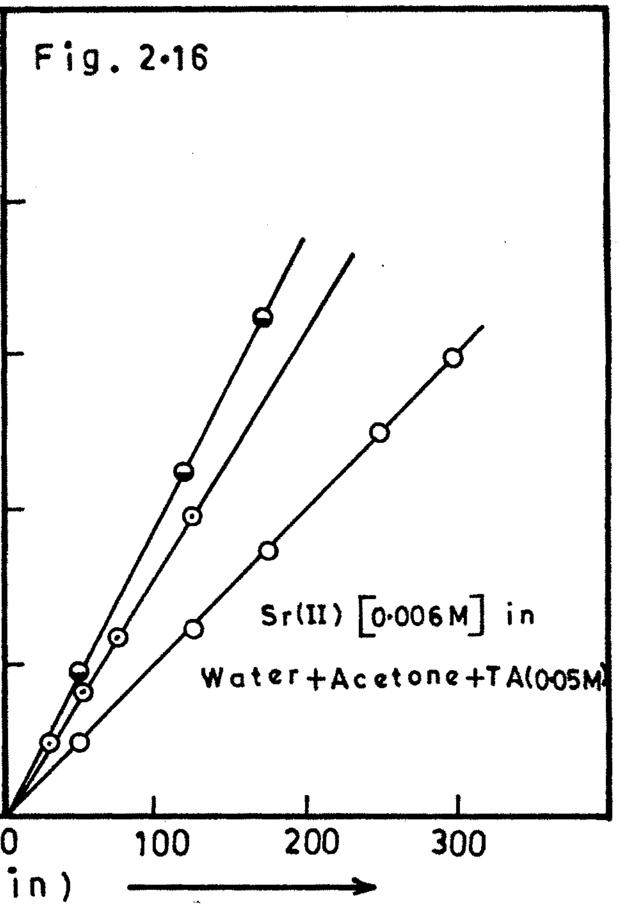


Fig. 2.16

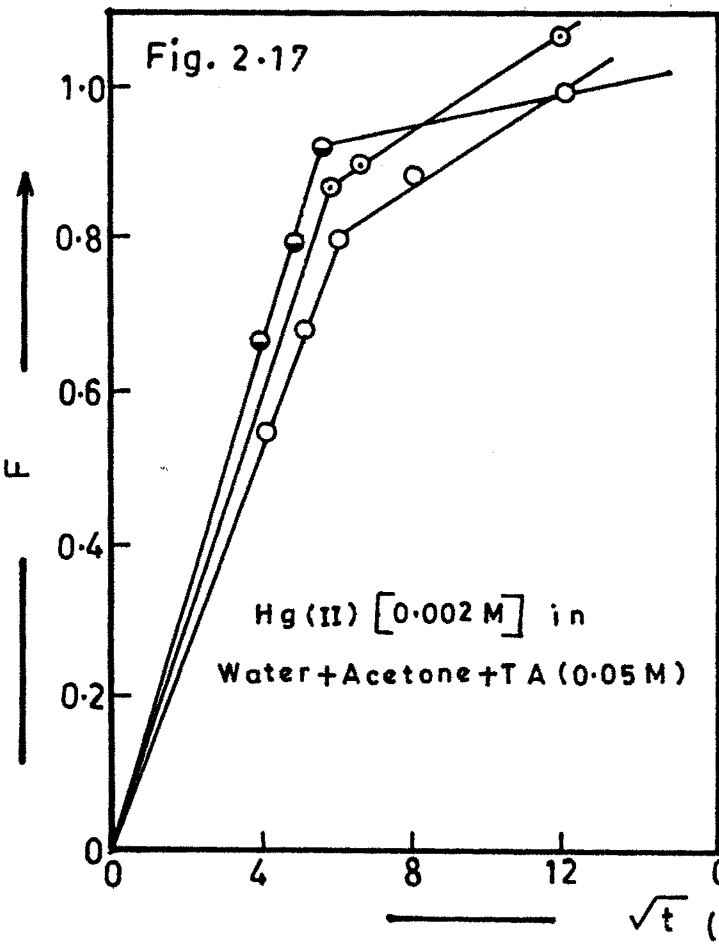


Fig. 2.17

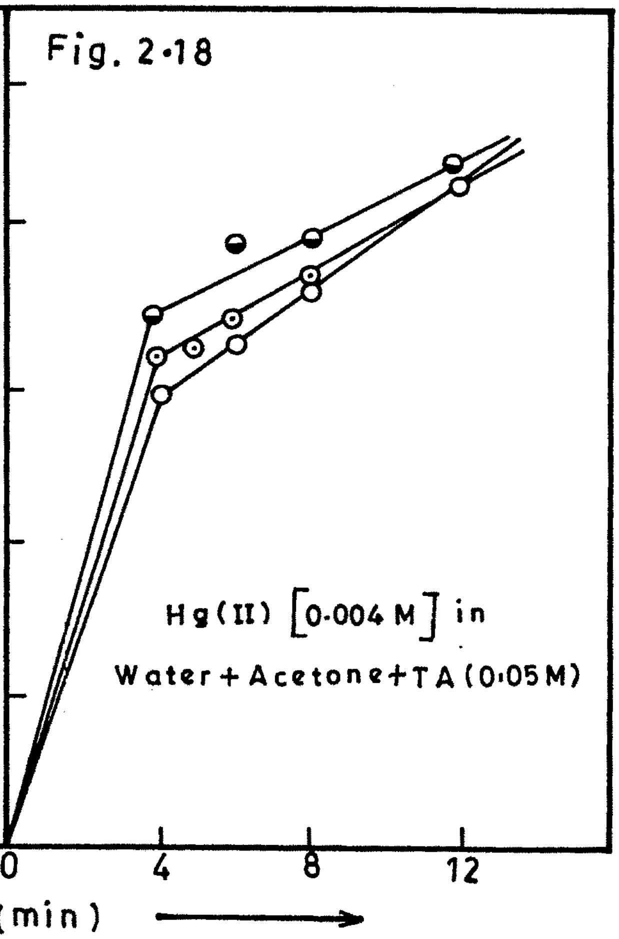


Fig. 2.18

Acetone % – (–○–) 0 %, (–⊙–) 10 %, (–◒–) 30 %, (–●–) 50 %.

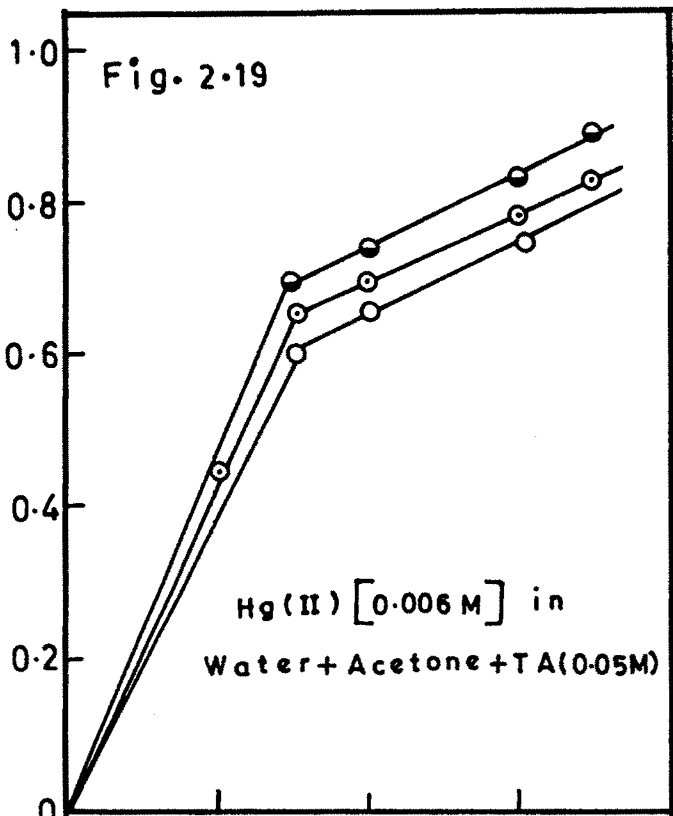


Fig. 2·19

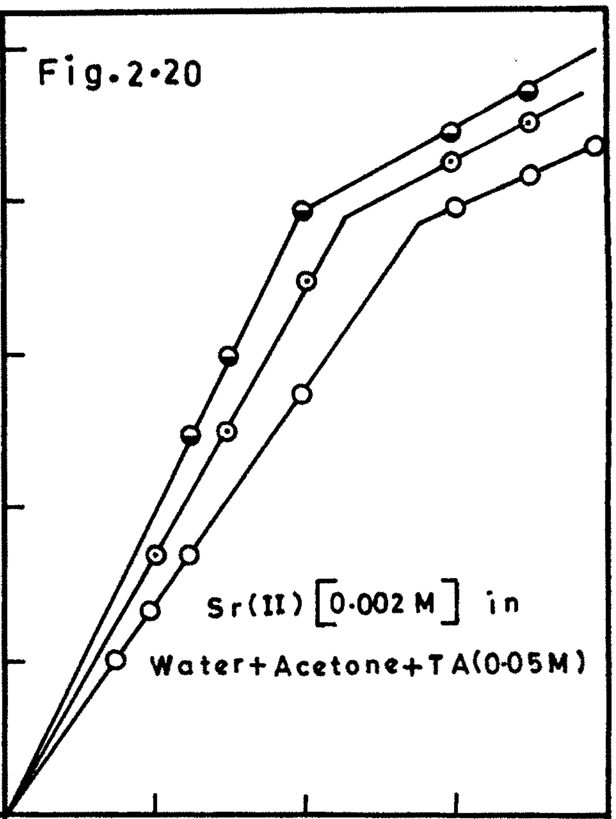


Fig. 2·20

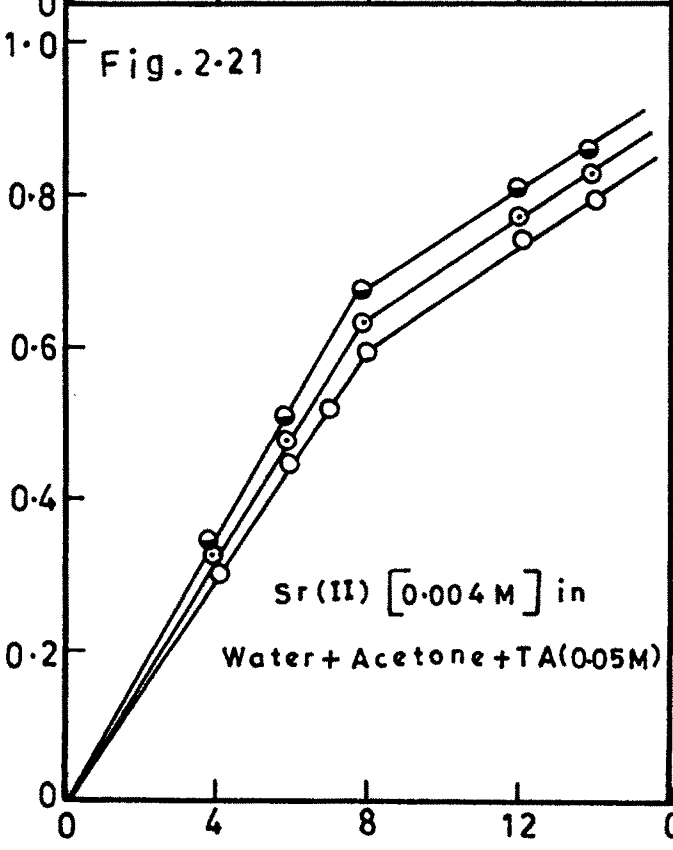


Fig. 2·21

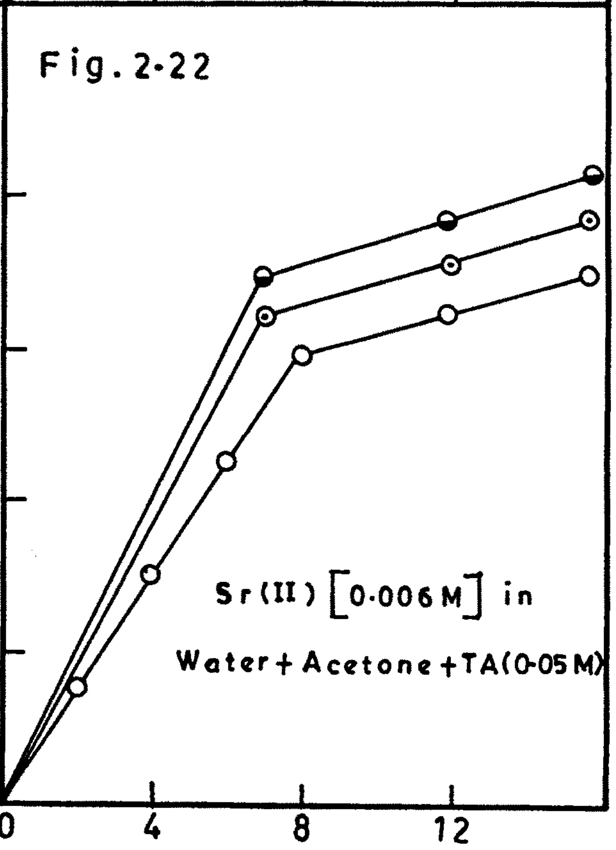


Fig. 2·22

F

$\sqrt{t}$ (min)

Acetone % — (-○-) 0 %, (-⊙-) 10 %, (-●-) 30 %.

Table 2.12 :Kinetic parameters calculated for the exchange of Hg,Sr (0.002, 0.004, 0.006 M)on Dowex 21-K(Cl$^-$)in aqueous acetone tartaric acid (0.05M) at 303^{o}K

Acetone of V/v	t ½ min	D x 10^{10} m^2Sec^{-1}	B x 10^2 Sec^{-1}	Rate constant K x 10^2 min^{-1}	Parabolic diffusion constant K
1	2	3	4	5	6
		Hg (0.002 M)			
0	18	1.35	1.35	1.32	0.116
10	10	2.70	1.25	1.77	0.118
30	5	5.75	5.00	2.54	0.236
		Hg (0.004 M)			
0	45	0.61	0.75	0.89	0.072
10	25	1.14	1.05	1.28	0.103
30	5	5.70	4.35	2.32	0.216
		Hg (0.006 M)			
0	62	0.50	0.70	0.85	0.080
10	30	0.90	0.85	0.70	0.107
30	5	5.40	4.75	2.50	0.235

1	2	3	4	5	6
		Sr (0.002 M)			
0	20	1.35	1.35	1.32	0.116
10	10	2.70	1.25	1.77	0.118
30	5	5.75	5.00	2.54	0.236
		Sr (0.004 M)			
0	20	1.35	1.35	1.32	0.116
10	12	2.25	1.00	1.40	0.109
30	4	6.25	5.00	7.67	0.172
		Sr (0.006 M)			
0	40	0.68	0.70	0.85	0.080
10	18	1.50	0.75	0.89	0.072
30	10	2.70	1.25	1.54	0.117

Table 2.13 Kinetic parameters calculated for the exchange of Pb(0.002, 0.004, 006 M) on Dowex 21-K (Cl^-) in aqueous acetone - tartaric acid (0.05M) at 303^oK

Acetone % V/v	t ½ min	D $\times 10^{10}$ m^2 Sec^{-1}	B $\times 10^2$ Sec^{-1}	Rate constant K x 10^2 min^{-1}	Parabolic diffusion constant K
		Pb(0.002 M)			
0	55	0.62	0.68	0.77	0.078
10	7	3.40	4.00	4.60	0.123
30	5	6.85	5.00	4.70	0.175
		Pb(0.004 M)			
0	30	0.90	1.20	1.15	0.100
10	20	1.35	1.35	1.32	0.116
30	15	1.60	1.25	1.77	0.118
		Pb(0.006 M)			
0	30	0.90	1.20	1.15	0.100
10	28	1.040	1.10	1.21	0.109
30	10	2.70	1.25	1.77	0.118

Fractional attainment of Equilibrium(F)

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

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

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, althrough 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[22] Helfferich[23] and Blickenstaff[24] in their studies, Hence,

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

Where,

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

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 interger having any value from 1 to ∞

The values of F are presented in +Tables 2.2 to 2.1 and behaviour of with time t is presented by figs. 2.3 to 2.10 values of Bt where $B = \frac{\pi}{r^2}$, where obtained corresponding to various F values using Riechenberg table R. The Bt versus t plots are shown by Figs 2.1 to 2.10 and the values of B are obtained from the slopes of these plots. The values of B are given in Tables 2.12 to 2.14.

Interdiffusion Coefficient (D):

From the second Ficks law Barrer[22] developed an expression for the mathematical description of the particle diffusion mechanism

$$F = \frac{6}{\gamma}\sqrt{\frac{Dt}{\pi}} \qquad F < 0.3 \qquad \ldots. \quad 2$$

For $F > 70.8$ the terms of higher than first order in equation (1) can be disregarded. Less accurate than equation (1), but more convenient for practical use is vermeulen's approximation, which fits the whole range $0 \leqslant F \leqslant 1$:

$$F \cong \left[1 - \exp \left(- \frac{Dt\,\pi^2}{r_o^2} \right) \right]^{\frac{1}{2}} \qquad \ldots.\ 3$$

The half exchange time $t_{\frac{1}{2}}$ is related with D by an equation.

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

The values of half exchange time ($t_{\frac{1}{2}}$) were found out from the graphs of F versus t. The interdiffusion coefficients (D) were calculated by equation (4) and are presented in tables

<u>Effect of Concentration of Acetone:</u>

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 $t_{\frac{1}{2}}$ decreases as the percentage of acetone increases. It indicates that the process of exchange become faster in presence of acetone. As per equation

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

$t_{1/2}$ is inversely proprotional to D and hence the value 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. This change is observed at low concentrations (0.002, 0.004, 0.006 M and 0-10 percentages acetone for Hg, 0.002, 0.004, 0.006 M and 0, 10, 30, 50 percentage[5] acetone for Pb of metal ions. The equilibrium is attained very quickly at 50 percent acetone for Hg and Sr. It indicates that $[Hg\ (Tart)_2]^{2-}$ and $[Sr(Tart)_2]^{2-}$ —Cl^- exchanges are more favourable than $[Pb(Tart)_2]^{2-}/Cl^-$ exchange. The equilibrium period for exchanges in lower percentages of acetone (0,10) is 3-5 hrs for all metal ions. The equilibrium period at high percentages of acetone (30,50) is 1 hr, 20 min for Hg, 2.1 hr for Sr and 4,3 hrs for Pb. The uptake of these metal ions is fast in earlier stages and become slower at later stage. The nacture 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 Dowex 21 K (Cl^-) are in agreement with the high values of distribution coefficient present in Tables 3.1 to 3.4 in Chapter-III.

The ~~values~~ various factors contributing to this observation are ,

I) the selling and solvent fractionation behaviour of Cl^- as well as metal forms of Dowex 21-K 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 concentration 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 shell depends upon the ability of the organic solvent to solvate the cation. In this extent, a study by Zipp[26] 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, and more or less, the same number of organic solvent molecules, depending upon the composition of the mixed solvent.

In the mixed system, ionic selectivities of the resins have also been considered as a factor influencing the rates[27].

The rate determing step in ion exchange is, as a rule, interdiffusion of the counter ion either in the resin itself or across the adherent liquid film. The slower of these processes controls the overall rates. In systems with organic solvents, the mobilities of the counter ions in the resin are usually lower than in aqueous system because swelling in less prononced and electrostatic interactions with fixed charges are stronger. Particle diffusion this is relatively slow and usually is the rate controlling mechanism[28].

The problem of diffusion in porous media is usually approached with the use of either of two rather different types of modes, in 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 pore only. In such models, diffusion is necessarly slower than in the corresponding homogeneous 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 resin, is assumed to be no different from that in solution of analogous organic electrolytes. Benzyltrimethyl ammonium chloride has been used as a model electrolyte for Dowex 1 anion exchanger in Cl^- form[29].

Parabolic diffusion Constant (K)

The rate determining process for most anion 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 namely[30].

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

where K is a constant that varies linearly with the reciprocal the diameter. The values of K were obtained from slope of Curves F versus $\sqrt{t}$ presented by Figs. 2.17 to 2.24

It is observed that the values of parabolic diffusion constant (K) increases with the rise in percentages of acetone for metal ions studied. The values of K are slightely afected at 0 to 10 percentage of acetone but considerably affected at 30 percentage of acetone. It indicates that the mode of exchange fast at high concentrations of acetone. No prominent changes are observed in values of K in Hg and Sr. The values of K of Pb are less than those of Hg and Sr. This indicates that the selectivity of the resin is in the order of Hg $>$ Sr $>$ Pb. The sametrend is observed in the studies of distribution coefficients in Chapter-III.

Effect of Concentration of Ions :

It is observed that the values of $t_{1/2}$ decreases and those of D increase with the rise in concentration of metal ions. The rate of diffusion becomes faster at higher metal ion concentration.

From eq (2), It is observed that F in the reaction controlled by particle diffusion is proportional to the square root of the time, and inversely to the particle radius. The results of F Vs $\sqrt{t}$ are plotted in Figs. A linear relationship is obtained for Hg, Sr and Pb. At lower concentration of the metal ions (0.002, 0.004, 0.006M) and (0-10 % acetone) the exchange is fast in the begining and becomes slower and slower and hence two linear segments were observed. At higher percentages of acetone the exchange is fast maintaining linearity. When the results are plotted in the form of log (1-F) Vs t, straight lines passing through origin are obtained. The rate of exchange increases with increasing ionic strength. The rate of exchange controlled by particle diffusion should also increase alongwith ionic strength provided that the resin volume remains unchanged. Accordingly to Nikalaevls loose quasi-crystal model[31,32] freely moving ions, cation genenions present in the resin phase distort and diminish the depth of the potential well. The rate of diffusion of the ion which oscillates in a potential well a near the functional group, thus increases with an increase in ionic strength.

The rate determining step of exchanges changes from film to particle diffusion with ionic strength. This may be explained as follows. In a range of lower ionic strength, the rate of diffusion through film is retarded by Donnan exclusion becoming significently slow as compared with that of particle diffusion with increasing ionic strength the Donnan potential and the film thickness might be sufficiently reduced to make the rate of diffusion through film by far greater than that of particle diffusion. The rates of exchange for Ag^+ and Zn^{2+} on chelating resin ~~were~~ on Dowex A1 Were found to govern by film diffusion at a low ionic strength and by particle diffusion at a high ionic strength[33].

Table 2.14 :Dependence of Fractional exchange (F) on Temperature
Metal ion Hg (II) 0.004 M

Time in (min)	Fractional attainment of equilibrium (F)								
	Temperature in ^{o}K								
	303				308			313	
	a	b	c	d	a	b	c	a	b
0	0.00	0.00	0.00	0.00	0.00	0.00	0.000	0.000	0.000
5	0.11025	0.153	0.775	0.850	0.769	0.823	1.000	0.871	0.974
10	0.153	0.358	0.925	0.975	0.794	0.974	1.000	0.897	1.000
20	0.256	0.512	0.975	1.000	0.820	1.000	1.000	0.948	1.000
30	0.435	0.589	1.000	1.000	0.846	1.000	1.000	1.000	
40	0.435	0.615	1.000	1.000	0.871	1.000	1.000	1.000	
50	0.641	0.820	1.000	1.000	0.923				
60	0.8461	0.948	1.000	1.000	1.000				
120	0.892	0.948							
180	0.948	0.988							
240	1.000	1.000							
300	1.000	1.000							
360	1.00	1.000							

a = 0% Acetone + 0.05 M TA
b = 10% Acetone + 0.05 M TA
c = 30% Acetone + 0.5 M TA
d = 50% Acetone + 0.05 M TA

Table 2.15 Dependence of fractional exchange (F) on temperature

Metal ion Sr(II) 0.004 M

Time in (min)	Fractional attainment of equilibrium(F)											
	Temperature in ^{o}K											
	308				313				318			
	a	b	c	d	a	b	c	d	a	b	c	d
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.00	0.00	0.2631	0.2631	0.375	0.375	0.736	0.736	0.789	0.894	0.947	1.000
10	0.470	0.508	0.550	0.789	0.421	0.631	0.842	0.868	0.894	0.947	1.000	1.000
20	0.588	0.705	0.732	0.805	0.578	0.710	0.842	0.921	0.960	1.000	1.000	
30	0.651	0.725	0.750	0.813	0.631	0.710	0.973	1.000	1.000	1.000		
40	0.714	0.735	0.850	0.910	0.684	0.736	1.000	1.000	1.000			
50	0.818	0.835	0.949	0.971	0.736	0.789	1.000					
60	0.882	0.886	0.960	1.000	0.789	0.894	1.000					
120	0.935	0.960	1.000	1.000	0.947	1.000						
180	0.980	0.985	1.000	1.000	1.000	1.000						
240	0.980	1.000										
300	1.000	1.000										
360	1.000	1.000										

a = 0% Acetone + 0.05 M TA
b = 10% Acetone + 0.05M TA
c = 30% Acetone + 0.05M TA
d = 50% Acetone + 0.05M TA

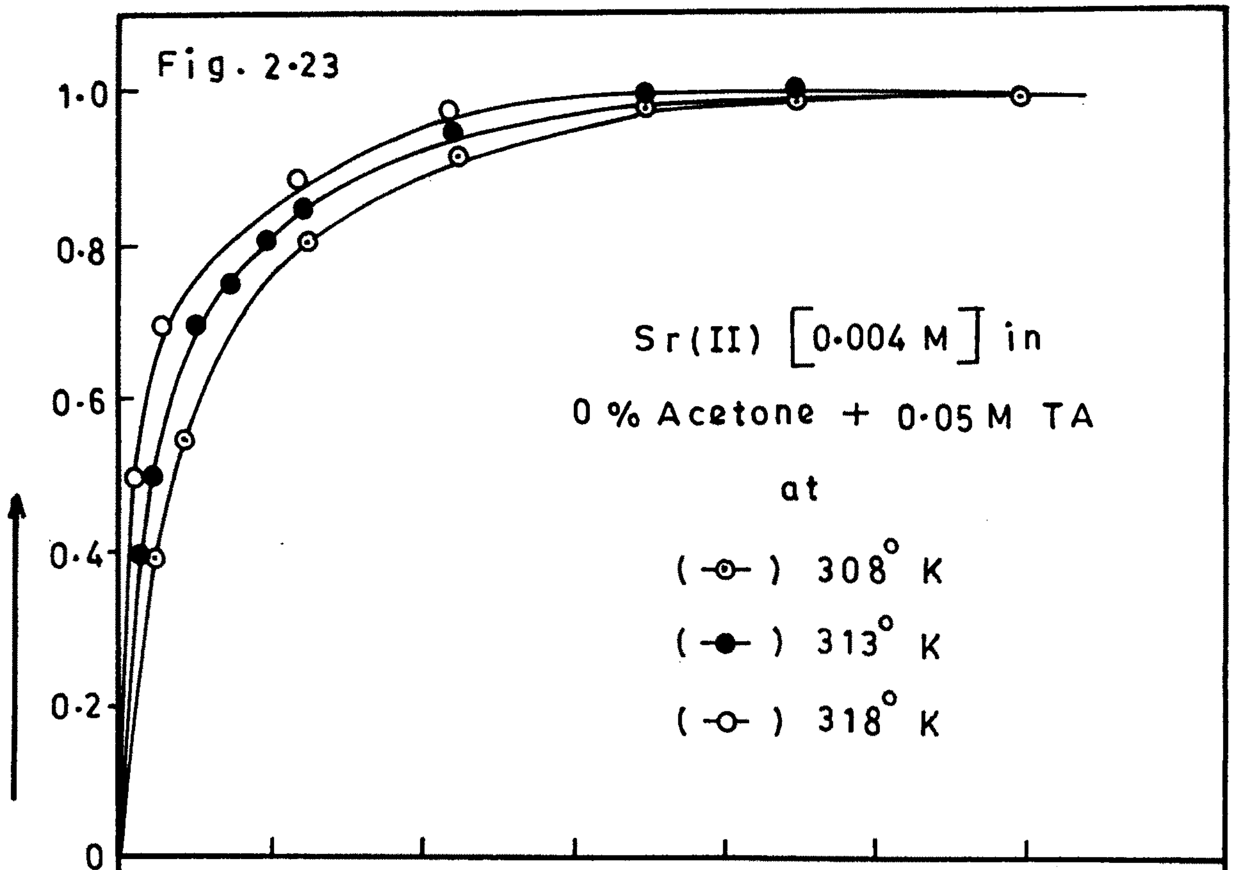


Fig. 2.23

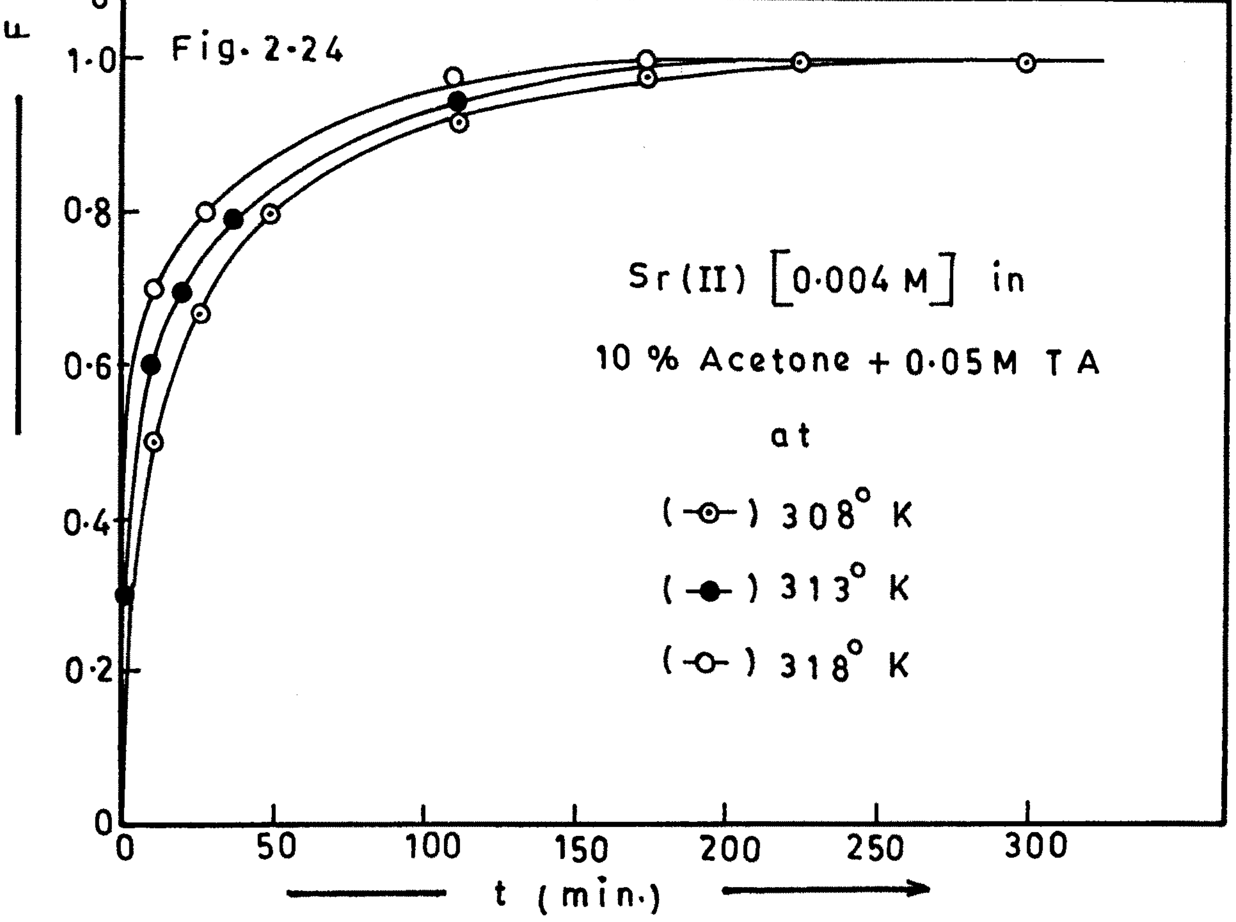


Fig. 2.24

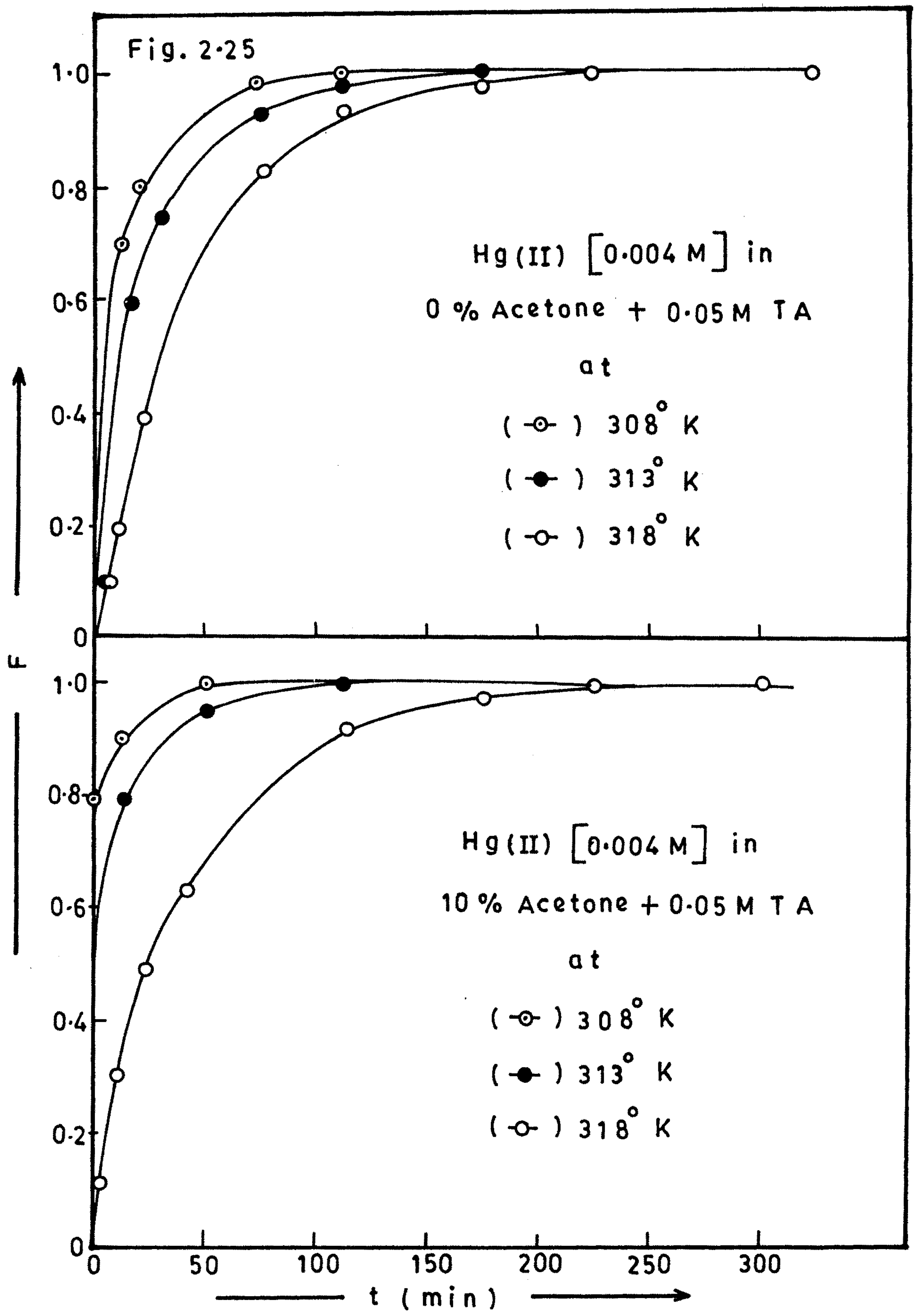


Fig. 2·25

Hg(II) [0·004 M] in
0 % Acetone + 0·05 M TA
at
(-⊙-) 308° K
(-●-) 313° K
(-○-) 318° K
Hg(II) [0·004 M] in
10 % Acetone + 0·05 M TA
at
(-⊙-) 308° K
(-●-) 313° K
(-○-) 318° K
F
1·0
0·8
0·6
0·4
0·2
0
0
50
100
150
200
250
300
t (min)

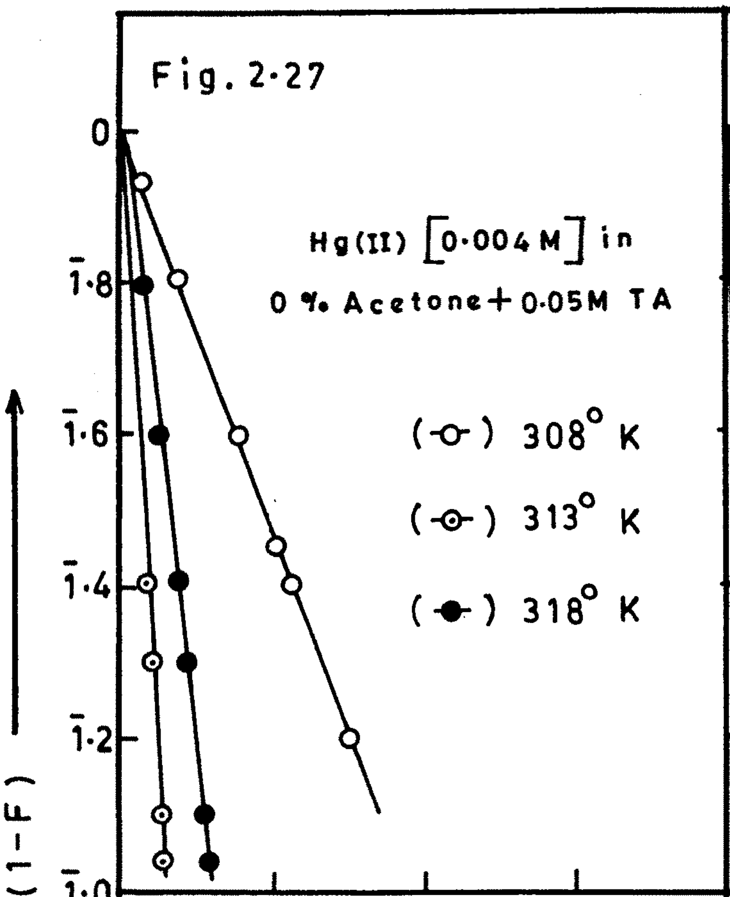


Fig. 2·27

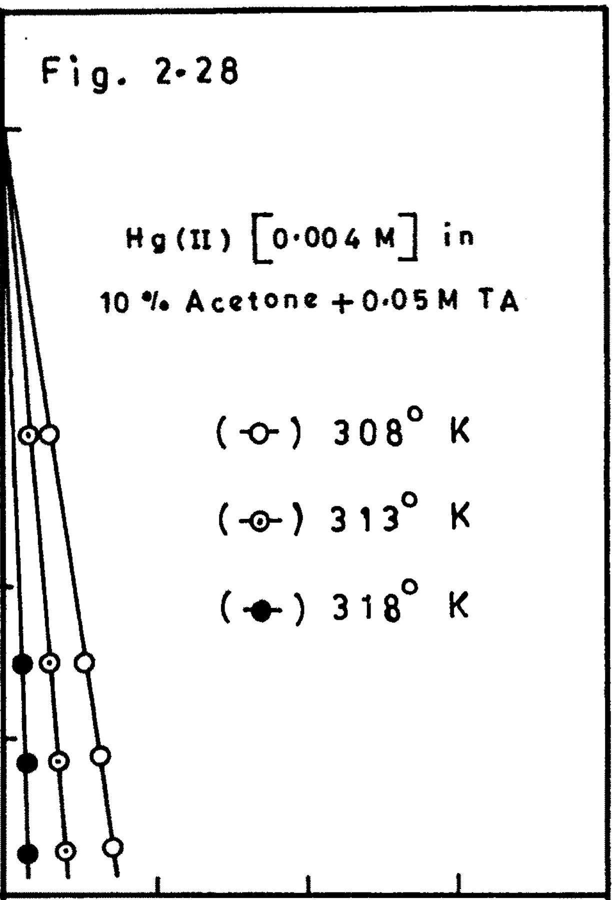


Fig. 2·28

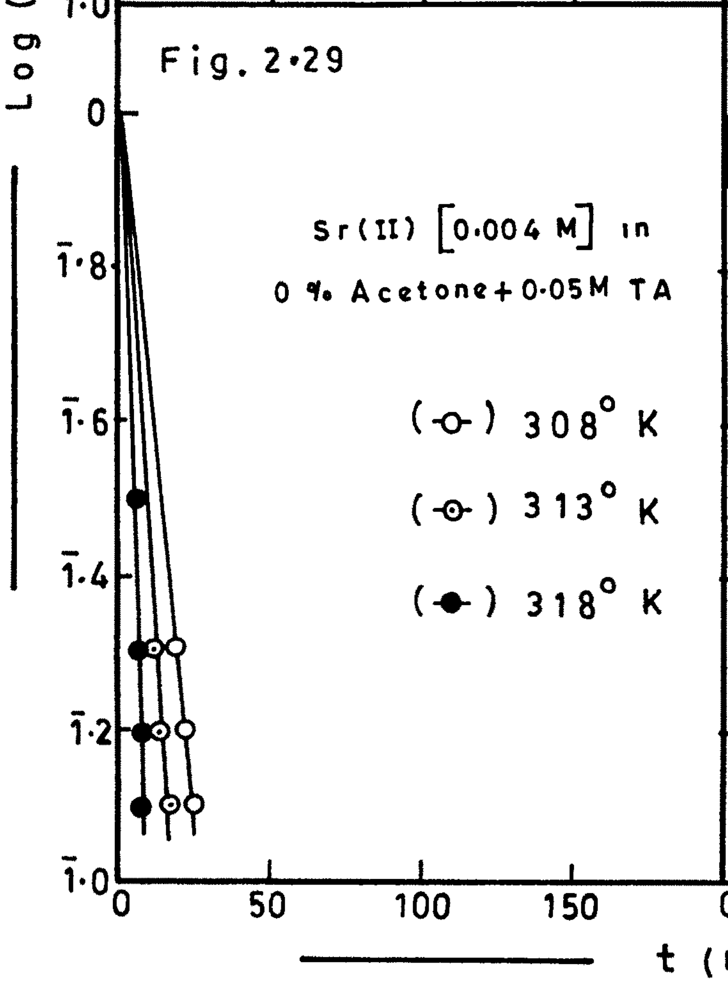


Fig. 2·29

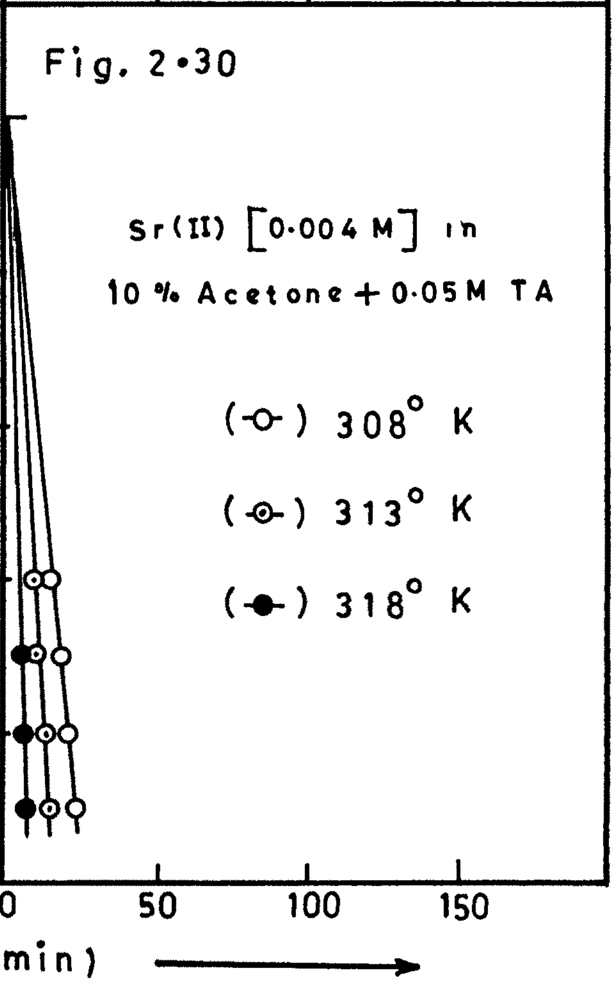
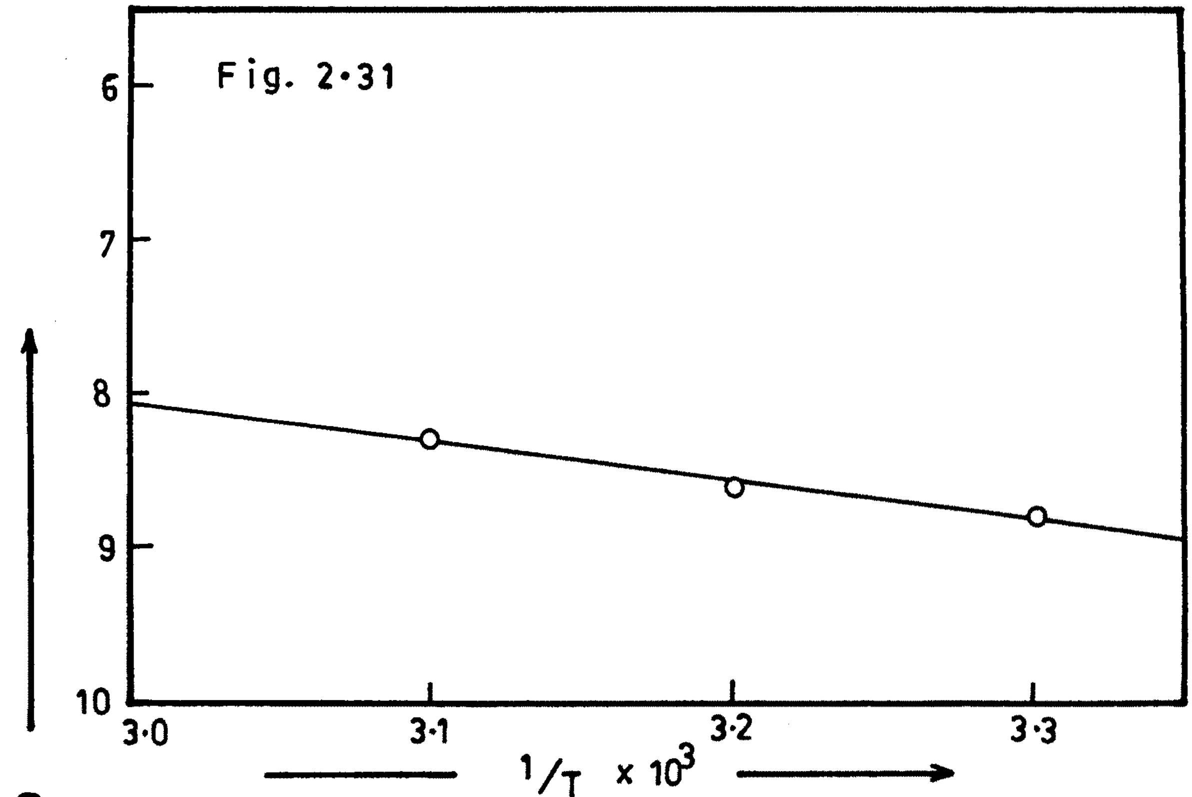
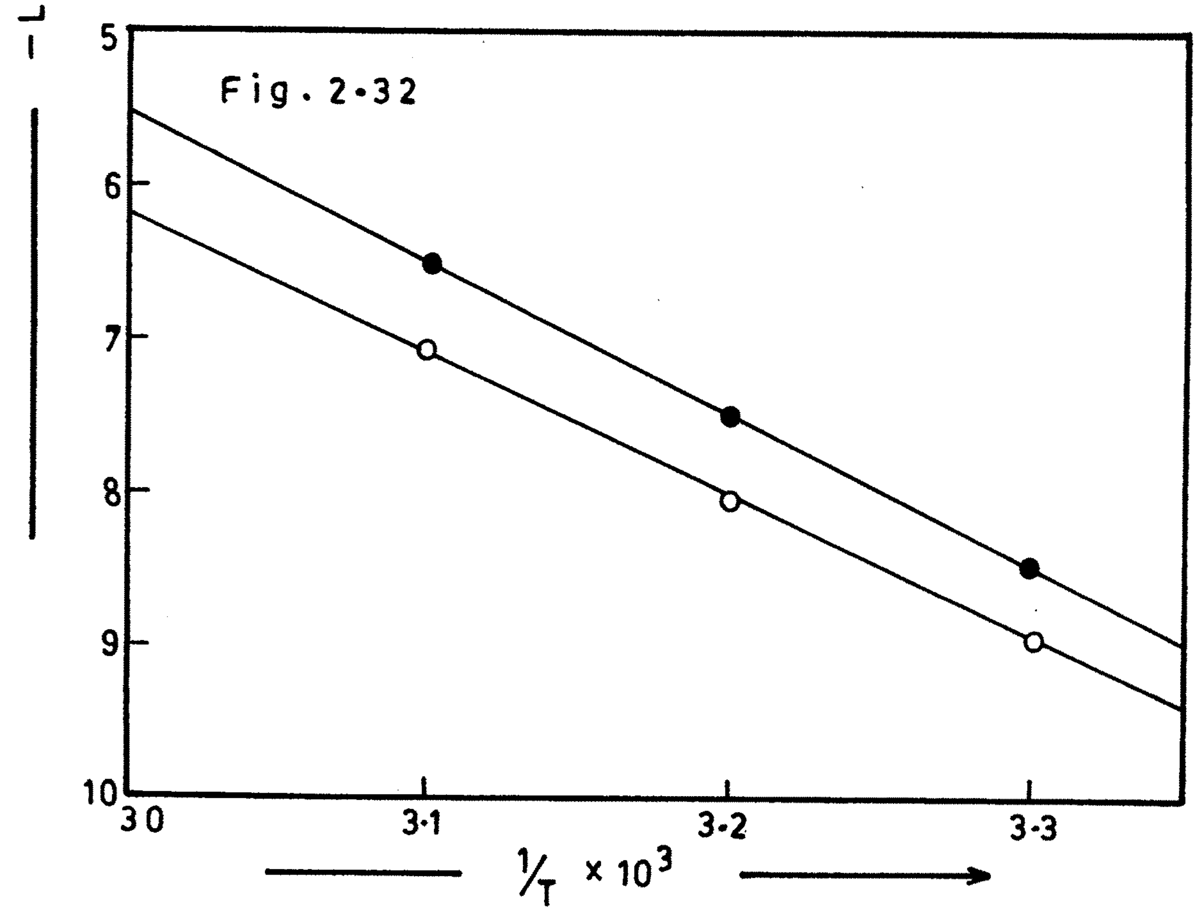


Fig. 2·30



Sr(II) → (-○-) 0 % Acetone



Hg (II) → (-○-) 0 % , (-●-) 10 % Acetone.

Table 2.16 Kinetic Parameters calculated for the exchange of Hg and Sr(0.004 M) on Dowex 21K(Cl^-) in aqueous acetone (0.10%) tartaric acid (0.05 M) at various temperatures

Metal ion	Acetone percentage (v/v)	Temperature (^oK)	t ½ (min)	D x 10^7 Cm^2/	B x 10^2 s^{-1}	Rate constant K x 10^2 (min^{-1})	Parabolic diffusion constant K
Hg	0	303	45	0.88	0.795	1.07	0.083
		308	3	1.33	1.35	1.28	0.088
		313	2	2.00	1.40	1.77	0.118
	10	303	20	1.35	1.35	0.88	0.060
		308	3	1.33	1.34	1.53	0.116
		313	2	2.00	1.40	1.77	0.118
Sr	0	303	10	0.300	0.30	0.88	0.0623
		308	5	0.400	0.385	0.89	0.0740
		313	2	2.00	1.40	1.77	0.118
Sr	10	303	7	0.285	0.290	0.76	0.066
		308	5	0.400	0.385	0.89	0.074
		313	2	2.000	1.40	1.77	0.118

Table 2.17: Dependence of Fractional exchange (F) on state of solution.

Metal ion Hg(II) 0.004 M
Tartaric Acid 0.05 M

Time in (min)	Fractional attainment of equilibrium (F)							
	Acetone percentage (V/V)							
	0		10		30		50	
	a	b	a	b	a	b	a	b
0	0.00	0.000	0.000	0.000	0.000	0.000	0.000	0.000
5	0.110	0.615	0.153	0.765	0.775	0.974	0.850	0.974
10	0.153	0.717	0.353	0.975	0.925	0.974	0.975	0.974
20	0.256	0.871	0.512	0.975	0.975	0.974	1.000	1.000
30	0.435	0.973	0.589	1.000	1.000	1.000	1.000	1.000
40	0.435	0.974	0.615	1.000	1.000	1.000	1.000	1.000
50	0.641	1.000	0.820	1.000	1.000			
60	0.846	1.000	0.948	1.000	1.000			
120	0.892	1.000	0.948	1.000	1.000			
180	0.948	1.000	0.988	1.000	1.000			
240	1.000	1.000	1.000	1.000	1.000			
300	1.000	1.000	1.000	1.000	1.000			
360	1.000	1.000	1.000	1.000	1.000			

a = Stationary state of solution
b = Agitated state of solution

Table 2.18 Values of Energy of Activation (Ea), Pre-exponential constant (Do) and entropy of actigation (ΔS) for Hg(II) and Sr(II) (0.004 M) (0.05M tartaric acid).

Metal ion	Acetone %	Dox 10^7 Cm^2/Sec^{-1}	Ea KJ mol^{-1}	ΔS J mol^{-1} deg^{-1}
Hg	0	1.582	32	- 34.13
	10	3.200	38	- 33.25
Sr	0	1.25	5.72	- 34.31
	10	1.25	3.81	- 34.31

Effect of Temperature :

The exchange of Hg and Sr (0.004 M) on Dowex 21 K (Cl^-) in aqueous acetone (0,10 %) tartaric acid (0.05 M) media was studied at 303, 308 and 313 °K. The effect of temperature on fractional attainment of equilibrium (F), half exchange time ($t_{1/2}$), interdiffusion coefficient (D), parabolic diffusion constant (K) and B values is seen from the values presented in Table 2.16.

The variations of F versus t at 303, 308, 313°K in 0 and 10 % acetone (0.05 M) tartaric acid are presented in Figs. 2·23 to 2·26. It is observed that the uptake of Hg and Sr (0.004 M) ions is increased at higher temperatures. The equilibrium periods for Hg exchanges are 4 hrs at 303°K (0-10% acetone) and these periods shoot upto 50 and 20 minutes respectively (0-10%) at 308°K and 30 and 10 minutes respectively (0-10%) at 313°K. The equilibrium periods for Sr exchanges are 4 hrs at 303°K (0-10% acetone) and these periods shoot upto 3 and 2 hrs respectively (0-10%) at 308°K and 30 and 20 minutes respectively (0-10%) at 313°K. It is also observed that the rates of adsorption of Hg and Sr at 10% acetone is greater than that without acetone.

The values of half exchange time t ½ decreases and those of interdiffusion coefficient increase with rise in temperature. It is concluded that the rate of exchange is enhanced by the temperature. The energies of activation (Ea) were calculated from Log D versus $\frac{1}{T}$ plots (Figs. 2.31 2.32) and the values presented in Table 2.16. Suggest that the rates of metal ions are activated by the energy supplied by temperature.

The values of energy of activation for $[Hg(Tart)_2]^{2-}/Cl^-$ exchanges are 32 and 38 K J mole^{-1} at 0 and 10 percentages of acetone respectively and for $[Sr(Tart)_2]^{2-}/Cl^-$ exchanges the values are 5.72 and 3.81 K J mol^{-1} at 10 percentage of acetone. The values of Ea for particle diffusion mechanism in standard ion exchange resins were found[34,35] to be 25.1 to 41.84 K ion J mole^{-1}. The values of Ea for the systems under study are in good agreement with the above values indicating that the exchanges are mostly governed by particle diffusion mechanism.

The pre-exponential constant, (Do) is related with the energy of activation ΔS^* as follows :

$$Do = 2.72\ (KB\ Td^2/h)\quad \exp\ (\Delta S^*/R\ )$$

where KB = Boltzmann constant, T = 303°K , d = ionic jump (distance between two successive positions of ions in the process of diffusion)taken as equal to 5 x 10^{-10} M, h =planks 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 natural molecules into charged species accompany a decrease in entropy due to the immobilization 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 methanol[36]. The negative value of entropy are indeed what one would expect in reaction involving ionisation of neutral molecules[37]. Since the transformation of the outer to the inner complex involves ionisation 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 stage[38]. The negative entropy indicates that the activated complex is less probable[38].

Rate Constants :

Log (1-F) versus time (t) for the exchange systems are plotted and are presented in Figs. 2.2 to 2.3. 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 Tables 2.12 to 2.14. The values of rate constant (K) are in agreement with the following over all 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 tartaric acid are in the following sequence:

$$Hg > Sr > Pb$$

c) The rate constant increases as the concentration of metal ions is increased from 0.002 to 0.008 M solutions.

d) The rate of ion exchange increases with the increase in temperature from 303° to 313°K (Table 2.16) suggesting that the mobility of the ion increases with increasing temperature The uptake increases with time.

The findings are similar to the finding of the distribution coefficients (Chapter-III) of the metal ions in these media. The distribution coefficient increases with the rise in percentage of acetone. The distribution coefficients of the metal ions showed the following order.

$$K_D \text{ Hg} > K_D \text{ Sr} > K_D \text{ Pb}$$

State of Mixed Media :

Kinetics of exchange of Hg (0.004 M) on Dowex 21 K(Cl^-) in 0,10,30,50 percentage of Acetone containing TA (0.05 M) were studied in stationary and agitated states of media. The experimental procedure is the same but was carried in stationery i.e. without stirring the media and agitated i.e.stirring the media by a mechanical stirror. The value of fractional exchange (F) is presented in Table 2.17.

It is observed that in solution not containing acetone the equilibrium is attained in 4 hrs in stationary state and the same is observed in 50 minutes in agitated state. In media containing 10 percent acetone the equilibrium is attained at 4 hrs, 20 min respectively at stationary and agitated stated. In media containing 30-50 percent acetone equilibrium periods are not considerably affected by states of media. It may be generaly noted that at lower ~~tempe~~ percentages of acetone the equilibrium of exchange is attained quickly and the rate of exchange is also enhanced in agitated where as state no sizable effect is seen at higher percentage of acetone.

The reaction rate depends[7] on (a) Concentration (b) Order of the collisions needs for reaction (c) rate of brining dissolved ions upto and away from the surface of the exchanger granules, (d) rate of diffusion of ions in and out of the granules and (e) the activation energy of the exchange process. All the experimental conditions being same except the stationary and agitated states the factors responsible for the reaction (a), (b), (d) and (e) will be the same. It may be calculated that the factor (C) i.e. rate of bringing dissolved ions upto and away from the surface of the exchanger granules is playing major role in increasing rate of exchange in agitated state. The uptake of Ag^+ ions by metakaolinite was studied by E.A. Daniels, Experiments were aimed at studying the uptake as a function of temperature of the system, time of contact, concentration of $AgNO_3$ in the mixture and the studies were carried out at stationary and agitated states.

The equilibrium at agitated state was found to be quicker and more than that of steady state. The higher value of the Langmuir constant for the agitated system is the result of greater degree of interaction of Ag^+ under the agitated condition of equilibria, The obvious reasons being greater exposed surface area and higher concentration gradient of Ag^+

at the particle solution surface. The studies[33] of kinetics of exchanges of Ag^{+}, Zn^{2+} and Cr^{3+} in the chelating resin Dowex A-1 also revealed that from the requirement in the heterogeneous reaction system, the whole reaction system was vigorously stirred (400 ppm) to neglect the effect of agitation on the rate of exchange reaction. The evaporational losses[41] due to stirring may be a minor point affecting the rate of exchange.

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