Ion Exchange Kinetics of Aniline with Gel Type Sulphonic Acid Cation Exchange Resins: Mechanism of Uptake

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The mechanism of uptake of aniline by Dowex 50W X8 (–100, +200) resin in H$^+$ form from different pH medium and different composition of aqueous methanolic solvent medium has been studied. The mechanism of uptake of aniline takes place through particle diffusion and chemical reaction, the latter predominating in the earlier part, the former in the middle part and neither in the later part of the process of uptake.

INTRODUCTION

The study of ion-exchange and sorption equilibrium is of great importance to study the ion exchange resin-solute-solvent system. The rates at which these equilibria are approached are equally important in many case. This paper describes the mechanism of uptake of aniline in aqueous media of different pH and aqueous methanol of different composition by strongly acidic cation exchange resin. Dowex 50W X8 in H$^+$ form[1]. Preliminary work[2] has shown that ion exchange kinetics of this compound in aqueous media of different pH follows second order rate equation. But in aqueous methanols second order law fits well only in 10% and 20% aqueous methanol media. For 30% and above the uptake follows the first order rate equation.

EXPERIMENTAL

Dowex 50W (Dow Chemical Co., Midland, Mich.) styrene DVB copolymer based sulfonic acid cation exchange resin of relative degree of crosslinking 8 was taken in H$^+$ form, after proper conditioning, regeneration and air-drying. The mesh size, moisture content and the capacity of the resin were (–100, +200), 22.00 and 3.42 meq/g respectively. Aniline AnalaR (BDH, England) was used directly without further purification. Solutions of desired concentration were prepared by dissolving weighed amounts of aniline in aqueous solvent of different pH and aqueous methanol of different composition. Concentration of the solution was checked by UV absorption and pH of the solutions were measured with the help of systronics pH meter type 324. A known amount of air dry resin (3.0 g) was kept in a clean and dry three neck round bottom pyrex flask, clamped in a constant temperature bath (± 0.02°C). The central opening of the flask was fitted with a

quickfit metallic piece with a pyrex glass stirrer with regulator and a counter for measuring the rate of stirring. A known volume of the solution (750 mL), previously brought to the bath temperature, was poured into the flask through the side opening and the stopper was replaced. The stop watch was started when about half of the solution was added. The stirrer was switched on as soon as the addition of solution was complete (*ca.* 20 sec.). After a definite time, the stirrer was switched off for about 5 to 8 seconds in order to allow the resin to settle down. A suitable volume was quickly taken out into well stoppered clean and dry test tube and the stirrer was restarted. Further samples were taken out similarly at regular intervals. In one run not more than six samples of 5 mL each or three samples of 10 mL each were taken out. To obtain more points, the run was repeated as many times as required. The contents of the test tubes were analysed by measuring their UV absorption at wavelength of maximum absorption.

RESULTS AND DISCUSSION

A cation exchange reaction may be considered as

$$A^+ + BR \rightleftharpoons AR + B^+$$
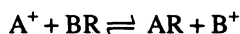
where A^+ and B^+ are exchanging univalent counter ions and R is the insoluble, indiffusible anionic framework of the resin (the resin matrix). The process of ion exchange consists[3-5] of the following five steps:

(a) Transport of A^+ ions through the solution to the exchanger particles;

(b) Diffusion of A^+ ions through the exchanger particles to the reaction sites;

(c) Chemical reaction between A^+ ions and BR at the sites of the reaction in the interior of the particles;

(d) Diffusion of the displaced B^+ ions out of the interior towards the surface of the exchanger; and

(e) Transport of B^+ ions from the surface of the particles into the bulk of the solution.

Any one or more of these steps could be rate controlling.

There is always a thin region around each particle in which mixing of the system is imperfect due to hydrodynamic factors. This region is referred to as Nernst film through which ions can traverse only by free diffusion. The steps (a) and (e) are commonly called film diffusion. The step (c) is called the chemical process of exchange.

For particle diffusion controlled kinetics[6,7] during the earlier part of the exchange process, F should increase linearly with $\sqrt{t}$ according to

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

where, $F = Q_t/Q_\infty$, Q_t being the amount absorbed at time t and Q_∞ the ultimate (*i.e.* at $t = \infty$) amount absorbed, r is the radius of the resin particle and D is the diffusion coefficient of species.

The departure from linearity at $F = 0.5$ should be less than 2.0 per cent[8]. Fig. 1 gives plot of F against $\sqrt{t}$ for aniline in aqueous medium at pH 9.0 and Fig. 2
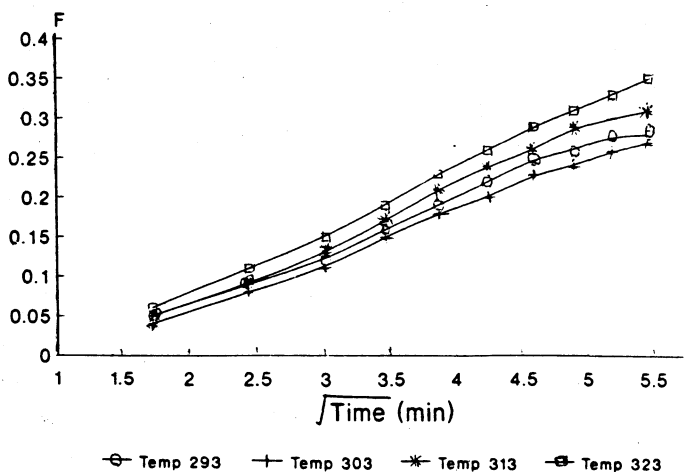
Fig. 1.   F v/s √time for aniline at pH 9.0 by the resin 50W X8 in H⁺ form
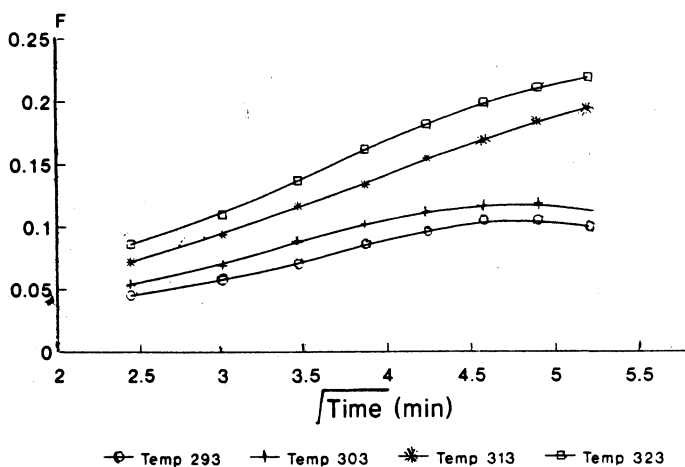

Fig. 2.   F v/s √time for aniline in 70% MeOH by the resin 50W X8 in H⁺ form

gives the plot for aniline in 70 per cent (v/v) aqueous methanol medium. In all aqueous methanols the graphs exhibit similar shapes. However, the slope of the graph changes with $\sqrt{t}$ as the methanolic content of the solvent varies. In each solvent medium, for each temperature, there is a range of F value between which the graph can be considered to be a straight line. The values of F in this range is different at different temperatures. This indicates that during the linear part of the graph, the particle diffusion is rate controlling in the process of uptake of aniline by resin X8. In the initial and final parts of the reaction the contribution by particle diffusion to the overall uptake of aniline seems to be negligible.

The shapes of the graphs obtained by plotting F Vs √t for aniline in aqueous media of different pH are similar to the shapes of graph in aqueous methanols.

If the rate of uptake is governed by film diffusion, the kinetic equation for infinite bath conditions is[8]

$$\log (1 - F) = \frac{Rt}{2.303}$$

where R is a parameter of the system given by

$$R = \frac{3D_0}{r\delta k}$$

D_0 is the diffusion coefficient of the ions in the solution, δ = thickness of the stagnant solution film, k = distribution coefficient of the entering ions between the solution and resin particles.

In the case of aniline and anilinium ions, their large size compared to the size of H^+ ions in the solution which gives a doubtful meaning to D_0. Further, it was observed that rate of uptake suggests that the film diffusion control is ruled out.

In chemical reaction is rate controlling, the degree of exchange versus time can be expressed by an equation which has the same form as that for liquid film diffusion control.

$$\log (1 - F) = \frac{St}{2.303}$$

where S = function of the rate constant of forward and back reactions at the ion exchange sites and of the ion concentration in the solution. Tables 1 and 2 give the values of S at different time intervals for aniline uptake by resin X8 from aqueous solution of pH 9, and 70 per cent aqueous methanolic solution at four

TABLE-1

KINETIC DATA FOR THE SORPTION OF ANILINE BY
DOWEX 50W X8 IN H^+ FORM AT pH = 9.0

S.No.	t in min	$F = Q_t/Q_\infty$				$S = \dfrac{-2.303 \times \log (1 - F) \times 10^2}{t}$ min^{-1}			
		293 K	303 K	313 K	323 K	293 K	303 K	313 K	323 K
1.	3	0.05	0.04	0.05	0.06	1.71	1.36	1.71	2.07
2.	6	0.09	0.08	0.09	0.11	1.57	1.39	1.57	1.94
3.	9	0.12	0.11	0.13	0.15	1.42	1.30	1.55	1.81
4.	12	0.16	0.15	0.17	0.19	1.46	1.36	1.56	1.76
5.	15	0.19	0.18	0.21	0.23	1.41	1.33	1.57	1.75
6.	18	0.22	0.20	0.24	0.26	1.38	1.24	1.53	1.68
7.	21	0.25	0.23	0.26	0.29	1.37	1.25	1.44	1.63
8.	24	0.26	0.24	0.29	0.31	1.25	1.14	1.43	1.55
9.	27	0.28	0.26	0.30	0.33	1.22	1.11	1.32	1.48
10.	30	0.28	0.27	0.31	0.35	1.09	1.05	1.24	1.43

different temperatures. It shows that in aqueous medium in the early part of the reaction the values of S are fairly constant. This indicates that the chemical reaction is rate controlling. But in the latter part, the decreasing S values suggest the influence of particle diffusion on the uptake of aniline. However, in aqueous alcoholic medium the S values decrease continuously with time indicating the parallel operation of particle diffusion and chemical reaction in the process of uptake of aniline by Dowex 50W X8 resin in H^+ form.

TABLE-2

KINETIC DATA FOR THE SORPTION OF ANILINE BY
DOWEX 50W X8 IN H^+ FORM IN 70% MeOH

S.No.	t in min	$F = Qt/Q_\infty$				$S = \dfrac{-2.303 \times \log(1-F) \times 10^3}{t} \, min^{-1}$			
		293 K	303 K	313K	323 K	293 K	303 K	313 K	323 K
1.	6	0.045	0.054	0.072	0.086	7.67	9.25	12.45	14.98
2.	9	0.057	0.069	0.094	0.110	6.52	7.95	10.97	12.95
3.	12	0.070	0.089	0.117	0.137	6.06	7.79	10.40	12.31
4.	15	0.086	0.102	0.134	0.162	6.01	7.18	9.61	11.80
5.	18	0.096	0.112	0.155	0.182	5.61	6.61	9.37	11.18
6.	21	0.105	0.117	0.169	0.199	5.29	5.93	8.83	10.58
7.	24	0.105	0.119	0.184	0.211	4.62	5.28	8.47	9.87
8.	27	0.100	0.113	0.195	0.219	3.90	4.44	8.02	9.14

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