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Ion Exchange Kinetics of α-, β- and γ-Picolines: Thermodynamic Parameters

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The study of ion exchange and sorption equilibria is of great importance to study the ion exchange resin solute solvent systems. Kinetic study of a system is generally undertaken to know the mechanism of the process, to determine the rate controlling step and to calculate the thermodynamic parameters. This study reports the uptake of α-, β- and γ-picolines by strongly acidic cation exchange resin, Dowex 50 WX8 (–20, +50) in H^+ form from aqueous methanolic media of different composition. The variables studied are the rate of stirring, temperature and solvent medium. The study shows that the systems obey the first order rate laws with respect to α-, β- and γ-picolines. This paper also reports the thermodynamic parameters: the apparent energy of activation ΔE, the entropy of activation ΔS and the free energy of activation ΔG, for different systems studied.

INTRODUCTION

The study of ion exchange equilibria is of great importance for knowing the behaviour of ion exchange resin-solute-solvent systems. The rates at which these equilibria approach are equally important in many cases. Kinetic studies allow one to calculate the thermodynamic quantities and these in turn help to understand the mechanism of uptake of solutes by ion exchange resins. The kinetics of uptake of nicotine and nicotinamide[1, 2] and of monochlorophenols[3] were reported earlier. This paper describes the kinetics of uptake of α-, β- and γ-picolines by strongly acidic cation exchange resin, Dowex 50 WX8 (–20, +50) in H^+ form from aqueous methanolic media of different composition.

EXPERIMENTAL

Resins and Chemicals

Dowex 50 WX (Dowex Chemical Co., Midland, Mich.) styrene DVB copolymer based strongly acidic cation exchange resin, of relative degree of crosslinking 8, was conditioned, regenerated to H^+ form, air dried, and its capacity was determined. The per cent moisture, air dry capacity in meq/gm and particle size of the resin were 22.00, 3.42 and –20, +50 B.S.S. α-, β- and γ-picolines and methanol were of analytical reagent grade and were used directly.

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Solution

Solutions of desired concentration were prepared by dissolving weighed amount of each compound in appropriate solvents. Concentration of the solution was then rechecked by UV absorption with Shimadzu UV visual recording spectrophotometer model-240, Japan, using 10 mm matched quartz cells.

Procedure

A known amount of dry resin (*ca.* 0.5 g) was kept in a three-neck round-bottom pyrex flask (1 litre) clamped in a constant temperature bath (± 0.02°C). The central opening of the flask was fitted with a quick-fix metallic piece with a pyrex glass stirrer with regulator and a counter for measuring the rate of stirring. A known volume of the solution (800 mL), previously brought to bath temperature, of the solute was poured into the flask through the side opening and the stopper was replaced. The steop watch was started when about half of the solution was added. The stirrer was switched on as soon as the addition of the solution was complete (*ca.* 20 secs). After a definite time the stirrer was switched off for about 5 to 8 secs., in order to allow the resin particles to settle down. A suitable volume was quickly withdrawn into well stoppered clear and dry test tubes and the stirrer was restarted. Further samples were taken similarly. In one run not more than six samples of 5 mL each or 3 samples of 10 mL each were withdrawn. To obtain more points the run was repeated as many times as needed.

The contents of the test tubes were analysed by measuring their UV absorption.

RESULTS AND DISCUSSION

The process of uptake of pyridine and picolines by strongly acidic cation exchange resin was found to be partly through base exchange and partly through sorption, aided by hydrogen bonding between the solute molecule and the resin particles.[4, 5]

The kinetics of α-, β- and γ-picolines obeyed the first order rate law in aqueous methanols of different composition (0 to 100% V/V). The intial part of the first order plot was found to be linear but a gradual deviation from linearity was observed in the later part (Fig. 1). This is similar to the observation made by Bhat and coworkers with nicotinamide[2]. Deviation from linearity may be attributed to gradual decrease in the diffusion of solute inside the resin particle in the later part of exchange/sorption reaction and by the kinetic concept of *Shell progressive reaction mechanism* or the *ash layer mechanism*[6–10].

Effects of solute concentration and rate of stirring

Kinetic study of α-, β- and γ-picolines at concentrations ranging from 0.5 to 5.0×10^{-3} mol dm^{-3} at three different temperatures (293, 303 and 313 K) showed that the rate of uptake is independent of solute concentrations. This was true in all the solvent media studied.

When the contents of the system were not stirred the rates of uptake were too slow to measure. However, the rates almost doubled when the stirring speed was increased from 200 to 700 r.p.m. and then remained constant. This shows that as

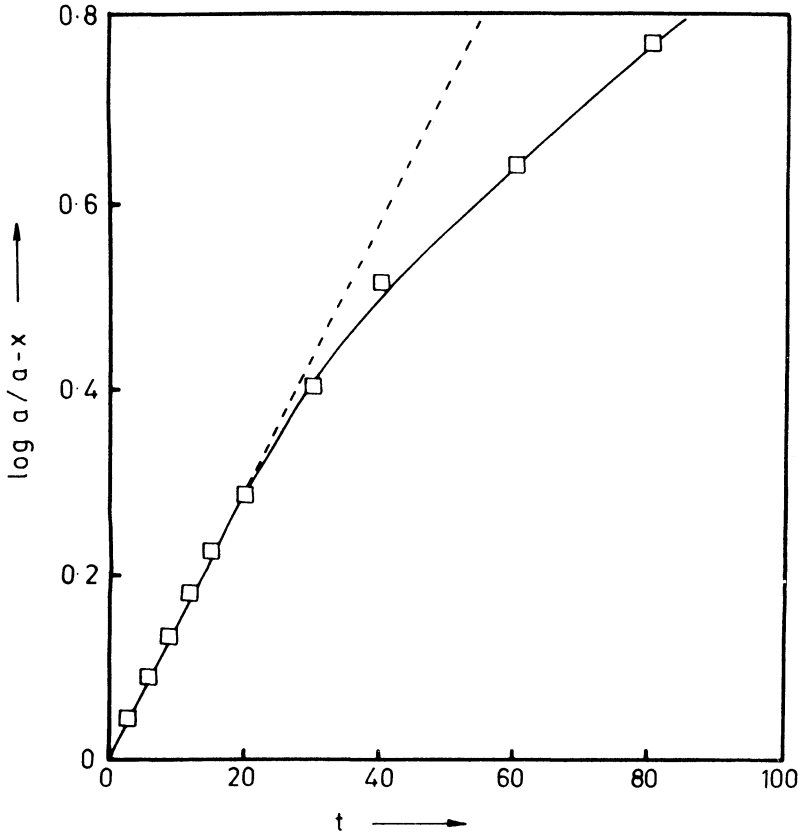

Fig. 1. First order plot for the uptake of γ-picoline in 50% aqueous methanol

the speed of agitation increases the thickness of the thermodynamic film adhering to the resin particles decreases and the film attains a constant thickness above 700 r.p.m. Constancy of sorption rate above 700 r.p.m. indicates that the mechanism of uptake of picolines may not be through film diffusion.

Temperature Coefficient and Thermodynamic Parameters

Table-1 gives the rate constants at three different temperatures and the value of $t_{1/2}$. All the three compounds show a decreasing tendency in the value of k as the amount of methanol increases up to 60 per cent in the binary solvent and then increases. Ion exchange kinetics is very complicated in the sense that several factors that determine the value of k act parallelly and simultaneously. Some of these factors such as solubility of the solute inside and outside the resin particle, solute-solvent interaction, solute-resin matrix interaction, solvent-resin matrix interaction, swelling of the resin particle, etc. determine the overall value of k. While some of these factors for a given solute-solvent resin system may try to decrease the value of k others will try to increase the value of k. In this system factors that influence the decrease in uptake of the solute predominate as the methanol content increases up to 60 per cent and thereafter factors that increase

the uptake operate to a greater extent. The table also shows that the rate constants of α- and β-picolines are comparable at all the temperatures and that of γ-picoline is distinctly higher. The time required for the uptake of half the amount of picolines by the resin ($t_{1/2}$) increases with increasing methanol content up to 60 per cent and then drastically decreases. The values of $t_{1/2}$ for α- and β- picolines are once again comparable while that of γ-picolines is lower. This study shows that the process of uptake of picolines by Dowex 50WX8 resin reaches equilibrimum about 3 times more quickly in methanolic medium than in water.

TABLE-1

VARIATION OF SORPTION RATE FOR α-, β- and γ-picolines by Dowex 50WX8 IN H^+ FORM WITH CHANGE IN PER CENT METHANOL

S. No.	Per cent methanol in water	Temp. in K	α-Picoline		β-Picoline		γ-Picoline	
			$t_{1/2}$ min	$K_1 \times 10^2$ min^{-1}	$t_{1/2}$ min	$K_1 \times 10^2$ min^{-1}	$t_{1/2}$ min	$K_1 \times 10^2$ min^{-1}
1.	0	293	15.5	4.50	15.0	4.52	14.5	4.80
2.	0	303	14.5	4.77	14.0	4.84	13.5	5.22
3.	0	313	13.5	5.18	13.0	5.20	12.5	5.62
4.	10	293	17.5	4.02	19.0	3.86	15.0	4.50
5.	10	303	16,0	4.34	17.5	4.21	14.0	4.88
6.	10	313	15.0	4.72	15.0	4.60	13.5	5.23
7.	20	293	19.0	3.84	18.5	3.80	18.0	4.05
8.	20	303	17.0	4.15	17.0	4.17	16.0	4.47
9.	20	313	16.0	4.38	16.0	4.31	15.0	4.74
10.	30	293	20.0	4.75	19.5	3.70	18.0	3.88
11.	30	303	18.0	4.10	18.0	3.92	17.0	4.16
12.	30	313	16.5	4.35	17.0	4.18	16.0	4.48
13.	40	293	23.5	3.26	25.5	3.18	20.5	3.49
14.	40	303	21.0	3.36	24.5	3.25	19.0	3.83
15.	40	313	21.0	3.63	22.5	3.60	17.0	4.26
16.	50	293	25.0	3.14	26.0	3.09	20.0	3.45
17.	50	303	23.0	3.35	23.5	3.24	18.0	3.75
18.	50	313	21.0	3.56	21.0	3.54	17.0	4.12
19.	60	293	27.0	3.02	26.0	2.98	22.5	3.21
20.	60	303	24.5	3.04	24.0	3.21	21.0	3.55
21.	60	313	21.5	3.46	21.5	3.43	19.0	3.83
22.	70	293	10.0	6.90	10.0	6.86	8.5	8.05
23.	70	303	10.0	7.10	10.0	7.06	8.0	8.50
24.	70	313	9.0	7.54	10.0	7.19	8.0	9.19
25.	80	293	7.5	9.44	7.0	9.67	7.0	10.06
26.	80	303	7.0	10.21	6.5	10.48	6.0	11.17
27.	80	313	6.0	11.50	5.0	11.67	5.5	12.40
28.	90	293	5.5	12.80	5.0	12.87	4.5	15.02
29.	90	303	5.0	13.90	5.0	13.67	4.0	16.80
30.	90	313	4.5	15.18	4.5	15.08	4.0	18.36
31.	100	293	5.0	14.20	5.0	14.13	4.0	18.24
32.	100	303	4.5	15.15	4.5	15.12	3.5	19.66
33.	100	313	4.0	16.38	4.0	16.27	3.0	21.27

Table-2 gives the value of the temperature coefficient ϕ($\phi = K''/K'$ where K''

and K′ are rate constants at two different temperatures differing by 10 K) and thermodynamic parameters. The temperatures coefficient is not apppreciably different for all the three picolines. It is about 1.07. It is obvious that ϕ is not affected by the change in the compostion of the solvent.

TABLE -2(A)
EFFECT OF TEMPERATURE ON SORPTION KINETICS OF α-PICOLINES BY DOWEX 50WSX8 IN H^+ FORM IN AQUEOUS METHANOLIC MEDIA

S. No.	% methanol in water	Temp. in K	$K_1 \times 10^2$ min^{-1}	$\phi = K''/K'$	ΔE KJ $mole^{-1}$	ΔS JK^{-1} $mole^{-1}$	ΔG (303 K) KJ $mole^{-1}$
1.	0	293	4.50	—			
2.	0	303	4.77	1.060	5.384	–256.31	83.04
3.	0	313	5.18	1.085			
4.	10	293	4.02	—			
5.	10	303	4.34	1.079	5.317	–257.69	83.39
6.	10	313	4.72	1.087			
7.	20	293	3.84	—			
8.	20	303	4.15	1.080	5.263	–258.02	83.44
9.	20	313	4.38	1.055			
10.	30	293	4.75	—			
11.	30	303	4.10	1.093	5.359	–257.81	83.48
12.	30	313	4.35	1.060			
13.	40	293	3.26	—			
14.	40	303	3.36	1.030	5.468	–258.90	83.91
15.	40	313	3.63	1.080			
16.	50	293	3.14	—			
17.	50	303	3.35	1.066	5.422	–259.24	83.96
18.	50	313	3.56	1.062			
19.	60	293	3.02	—			
20.	60	303	3.04	1.072	5.468	–259.36	84.05
21.	60	313	3.46	1.067			
22.	70	293	6.90	—			
23.	70	303	7.10	1.028	3.829	–258.15	82.04
24.	70	313	7.54	1.061			
25.	80	293	9.44	—			
26.	80	303	10.21	1.081	7.811	–241.96	81.12
27.	80	313	11.50	1.092			
28.	90	293	12.80	—			
29.	90	303	13.90	1.085	7.656	–239.99	80.37
30.	90	313	15.18	1.092			
31.	100	293	14.20	—			
32.	100	303	15.15	1.066	6.317	–243.67	80.18
33.	100	313	16.38	1.081			

TABLE-2(B)
EFFECT OF TEMPERATURE ON SORPTION KINETICS OF β-PICOLINES BY DOWEX 50WX8 IN H^+ FORM IN AQUEOUS METHANOLIC MEDIA

S. No.	% methanol in water	Temp. in K	$K_1 \times 10^2$ min^{-1}	$\phi = K''/K'$	ΔE KJ $mole^{-1}$	ΔS JK^{-1} $mole^{-1}$	ΔG (303 K) KJ $mole^{-1}$
1.	0	293	4.52	—			
2.	0	303	4.84	1.070	5.359	–256.35	83.03
3.	0	313	5.20	1.074			
4.	10	293	3.86	—			
5.	10	303	4.21	1.090	5.468	–257.14	83.39
6.	10	313	4.60	1.092			
7.	20	293	3.80	—			
8.	20	303	4.17	1.097	5.468	–257.39	83.45
9.	20	313	4.31	1.033			
10.	30	293	3.70	—			
11.	30	303	3.92	1.059	5.263	–258.40	83.56
12.	30	313	4.18	1.066			
13.	40	293	3.18	—			
14.	40	303	3.25	1.022	5.359	–259.44	83.97
15.	40	313	3.60	1.107			
16.	50	293	3.09	—			
17.	50	303	3.24	1.048	5.468	–258.86	83.90
18.	50	313	3.54	1.092			
19.	60	293	2.98	—			
20.	60	303	3.21	1.077	5.359	–259.78	84.08
21.	60	313	3.43	1.068			
22.	70	293	6.86	—			
23.	70	303	7.06	1.029	1.914	–264.63	82.10
24.	70	313	7.19	1.018			
25.	80	293	9.67	—			
26.	80	303	10.48	1.083	7.658	–242.29	81.06
27.	80	313	11.67	1.113			
28.	90	293	12.87	—			
29.	90	303	13.67	1.062	7.658	–240.03	80.39
30.	90	313	15.08	1.003			
31.	100	293	14.13	—			
32.	100	303	15.12	1.070	5.932	–244.97	80.16
33.	100	313	16.27	1.076			

TABLE-2(C)
EFFECT OF TEMPERATURE ON SORPTION KINETICS OF γ-PICOLINES BY DOWEX 50WX8 IN H^+ FORM IN AQUEOUS METHANOLIC MEDIA

S. No.	% methanol in water	Temp. in K	$K_1 \times 10^2$ min^{-1}	$\phi = K''/K'$	ΔE KJ $mole^{-1}$	ΔS JK^{-1} $mole^{-1}$	ΔG (303 K) KJ $mole^{-1}$
1.	0	293	4.80	—			
2.	0	303	5.22	1.087	6.698	–251.33	82.85
3.	0	313	5.62	1.076			
4.	10	293	4.50	—			
5.	10	303	4.88	1.084	6.891	–251.24	83.01
6.	10	313	5.23	1.071			
7.	20	293	4.05	—			
8.	20	303	4.47	1.103	6.698	–252.37	83.26
9.	20	313	4.74	1.060			
10.	30	293	3.88	—			
11.	30	303	4.16	1.072	6.937	–253.04	83.41
12.	30	313	4.48	1.076			
13.	40	293	3.49	—			
14.	40	303	3.83	1.097	6.937	–253.38	83.60
15.	40	313	4.26	1.112			
16.	50	293	3.45	—			
17.	50	303	3.75	1.086	6.891	–254.05	83.66
18.	50	313	4.12	1.098			
19.	60	293	3.21	—			
20.	60	303	3.55	1.105	6.857	–251.41	83.83
21.	60	313	3.83	1.078			
22.	70	293	8.05	—			
23.	70	303	8.50	1.055	5.418	–240.53	81.59
24.	70	313	9.19	1.081			
25.	80	293	10.06	—			
26.	80	303	11.17	1.110	8.037	–236.27	80.93
27.	80	313	12.40	1.110			
28.	90	293	15.02	—			
29.	90	303	16.80	1.118	8.326	–241.20	79.91
30.	90	313	18.36	1.092			
31.	100	293	18.24	—			
32.	100	303	19.66	1.077	6.414	–241.20	79.49
33.	100	313	21.27	1.081			

The apparent energy of activation (ΔE) was calculated using Arrhenius equation. The entropy of activation (ΔS) and the free energy of activation (ΔG) were calculated using the formula given by Adomson[11]. For α- and β-picolines apparent energies of activation are very close while ΔE for γ-picoline has a little

higher value. For all the three compounds ΔE remains unaffected by the composition of the solvent medium up to 60 per cent of methanol and then it decreases considerably at 70 per cent and increases again. Low values of the energy of activation indicate that non-exchange interactions must be playing a greater role in the uptake of picolines by Dowex 50 WX8 resin than the exchange interactions. The behaviour of entropy of activation and the free energy of activation is similar to that of energy of activation.

Conclusion

Kinetic study of the uptake of α-, β- and γ-picolines and their thermodynamic parameters indicate that the mechanisms of uptake of these compounds are quite similar. The amount of methanol in the solvent has no effect on the uptake upto 60 per cent of the methanol content but above 60 per cent the effect of solvent medium is quite appreciable.

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