2. EQUILIBRIUM STUDIES OF CINCHONA ALKALOID SULFATES WITH SULFONIC ACID RESINS IN DIFFERENT IONIC FORMS.

2 EQUILIBRIUM STUDIES OF CINCHONA ALKALOID SULFATES WITH SULFONIC ACID RESINS IN DIFFERENT IONIC FORMS :

Introduction :

In this section equilibria of quinidine sulfate and cinchonine sulfate with styrene divinylbenzene copolymer based sulfonic acid cation exchange resins of different degree of crosslinking and in different ionic forms have been studied at room temperature (~30 °C).

Experimental :

Resins : Dowex 50W (Dow Chemical Co.) styrene divinylbenzene copolymer based sulfonic acid cation exchange resins of relative degree of crosslinking (% nominal divinylbenzene content) as 2, 4 and 8 (further referred to as X2, X4 and X8).

Amberlite IR-200 (Rohm and Haas Co.) (further referred to as IR-200) of -10, +60 mesh ; this is presumably styrene divinylbenzene copolymer based sulfonic acid cation exchange resin of relative degree of crosslinking about 20 but has an expanded structure.

Moisture and capacity of the resins : (1,2)

The resins were washed with distilled water, cycled thrice between sodium chloride and hydrochloric acid, regenerated with large excess of hydrochloric acid, washed free of acid, filtered, airdried and stored in good containers.

Moisture content was determined by heating weighed samples ($\backsim$0.5 gms.) of airdry resin in clean, dry weighing bottles, in an oven (100-103^{o}C) to a constant weight

For the estimation of the capacity of the resins, weighed samples ($\backsim$ 0.5 gms.) of airdry resins were contacted with 50 cc. of 1N barium chloride solution in well stoppered flasks with frequent shaking. After two or three days, the liberated acid was estimated by titration with standard sodium hydroxide solution and then the capacity was calculated. Preliminary work had indicated that increase in contact time did not increase the amount of acid liberated. Table (2.1) gives the values for % moisture content and capacity of different resins in the hydrogen form.

Different ionic forms of the resins :

The different ionic forms of the resins were obtained by passing excess of the salt or hydroxide solution through the resin bed. The resin was then washed, filtered, airdried, moisture content determined and the capacity of the airdry form of the resin caculated from the ovendry capacity in the hydrogen form.

Chemicals :

Quinidine sulfate (B.P Howard, London) was crystallised three times from hot water. Cinchonine sulfate was prepared by dissolving cinchonine (pure crystals ; Riedel, Germany) in aqueous sulfuric acid and crystallising out the sulfate ; this was then crystallised twice from hot water.

Solution :

The stock solution of alkaloid sulfate was first prepared in distilled water and the concentration in gram equivalent per liter was evaluated by both sulfate estimation (as barium sulfate) and by determining the optical density of the solution after suitable dilution with distilled water at the invarient wavelengths (3) (296.5 mµ for quinidine sulfate and 294.5 mµ for cinchonine sulfate) with Beckman Model DU Spectrophotometer using 10 mm. matched quartz cells.

Procedure :

To study the equilibria of the alkaloid sulfate, weighed amounts of airdry resins were placed in contact with suitable volumes of an aqueous alkaloid sulfate solution of known concentration, in well stoppered flasks with frequent shaking at room temperature ($\sim 30^{\circ}$ C).

Preliminary work was carried out to find out the time after which further uptake did not take place. After sufficiently more time than this, the solutions were analysed for alkaloid sulfate concentration in the equilibrium mixture by taking out a known suitable volume from each flask and diluting to a suitable volume with distilled water. Optical density of this solution was measured at the invarient wavelength.

The total sulfate in the equilibrium mixture was estimated gravimetrically for each resin and it showed no measurable difference in the initial and equilibrium values. The exchange equilibrium values were not measurably different when either the amount of alkaloid sulfate solution was held constant and the amount of added resin varied or when the amount of added resin was held constant and the amount of alkaloid sulfate solution was varied, provided the ratio of the initial concentration (in meq./liter) of the resin to the initial concentration of the alkaloid sulfate, was the same. Preliminary work also indicated that for small changes in temperature the value of P_R was not significantly affected.

<u>Nomenclature</u> :

$[A]_i$ = initial concentration of alkaloid sulfate solution in meq./liter,

W = weight of airdry resin taken in grams,

v = volume of alkaloid sulfate solution added in cc.,

C = capacity of the resin in meq. per gram of airdry resin,

D_i = optical density, at the invarient wavelength, of the initial concentration of alkaloid sulfate solution after suitable dilution,

D_o = optical density, at the same wavelength, of the solution at equilibrium after the same extent of dilution as in above,

$[\bar{A}]_e$ = $[A]_i \cdot (D_i - D_o) / D_i$ = the meq. of alkaloid in the resin phase per liter of solution, at equilibrium,

$\left[H\right]_i$ $= W.C.10^3 / v$ = the meq. of resin per liter of the solution in the hydrogen form, initially,

P_A $= 100. \left[\bar{A}\right]_e / \left[A\right]_i$ = the % exchange of alkaloid sulfate at equilibrium,

P_R $= 100. \left[\bar{A}\right]_e / \left[H\right]_i$ = the % resin capacity exchanged at equilibrium,

Results :

Table 2.1

Capacity of different resins

Resin	% Moisture	Capacity in meq./gm.of the ovendry resin.
X2	20.4	5.2
X4	24.0	5.12
X8	27.0	5.09
IR-200	25.5	4.78

Table 2.2

Equilibrium of aqueous quinidine sulfate with the resin X2 in different ionic forms.

Ionic form	$[H]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
Li^+	0.78	1.88	0.51	27.1	65.4
	1.16	1.88	0.77	41.0	66.4
	1.60	1.88	1.06	56.4	66.3
	1.94	1.88	1.28	68.1	66.0
Na^+	0.87	2.08	0.54	26.0	62.0
	1.44	2.08	0.89	42.8	61.8
	1.74	2.08	1.08	51.9	62.1
	2.18	2.08	1.35	64.9	61.9
NH_4^+	0.94	1.91	0.53	27.8	56.5
	1.48	1.91	0.82	43.0	55.4
	1.91	1.91	1.08	56.5	56.5
	2.30	1.91	1.28	67.0	55.7

Table 2.2 (Contd.)

Ionic form	$[H]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
K^{+}	0.89	1.92	0.50	26.0	56.2
	1.49	1.92	0.82	42.7	55.0
	1.85	1.92	1.05	54.7	56.8
	2.19	1.92	1.25	65.1	57.1
Mg^{+2}	0.79	1.85	0.35	18.3	44.3
	1.29	1.85	0.56	30.3	43.4
	1.96	1.85	0.86	46.5	43.9
	2.30	1.85	1.03	55.7	44.8
	2.70	1.91	1.21	63.4	44.8
	3.08	1.91	1.37	71.7	44.5
	3.44	1.91	1.50	78.5	43.6
Zn^{+2}	1.25	1.96	0.52	26.5	41.6
	1.81	1.96	0.74	37.8	40.9
	2.47	1.96	1.04	53.1	42.1
	3.13	1.96	1.31	66.8	41.9
	3.72	1.96	1.53	78.1	41.1
Al^{+3}	2.36	1.85	0.66	35.7	28.0
	2.98	1.85	0.83	44.9	27.9
	3.53	1.85	0.96	51.9	27.2
	4.10	1.85	1.10	59.5	26.8
	4.71	1.85	1.32	71.4	28.0
	5.35	1.85	1.49	80.5	27.8

Table 2.3

Equilibrium of aqueous quinidine sulfate with the resin X4 in different ionic forms.

Ionic form	$[H]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
Li^+	0.75	1.88	0.39	20.7	52.0
	1.32	1.88	0.68	36.2	51.5
	1.92	1.88	0.99	52.7	51.6
	2.79	1.88	1.42	77.3	50.9
Na^+	0.78	2.08	0.33	15.9	42.3
	1.30	2.08	0.56	26.9	43.1
	1.95	2.08	0.83	39.9	42.6
	2.95	2.08	1.26	60.6	42.7
	3.92	2.08	1.69	81.3	43.1
NH_4^+	0.92	1.91	0.45	23.6	48.9
	1.54	1.91	0.74	38.8	48.1
	2.30	1.91	1.10	57.6	47.8
	3.47	1.91	1.68	87.9	48.5
K^+	0.88	1.92	0.34	17.7	38.6
	1.48	1.96	0.57	29.1	38.5
	2.33	1.96	0.89	45.4	38.2
	3.09	1.92	1.23	64.1	39.8
	3.56	1.96	1.41	71.9	39.6

Table 2.3 (Contd.)

Ionic form	$[H]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
Mg^{+2}	1.14	1.92	0.36	18.8	31.6
	1.51	1.92	0.49	25.5	32.4
	1.90	1.92	0.61	31.8	32.1
	2.85	1.92	0.90	46.9	31.6
	3.38	1.91	1.11	58.1	32.8
	3.81	1.91	1.25	65.5	32.8
	4.22	1.91	1.38	72.3	32.7
Zn^{+2}	1.35	1.96	0.41	20.9	30.4
	2.02	1.96	0.61	31.1	30.2
	2.68	1.96	0.81	41.3	30.2
	3.35	1.96	1.02	52.0	30.4
	4.02	1.96	1.20	61.2	29.9
	4.75	1.96	1.42	72.4	29.9
	5.38	1.96	1.63	83.2	30.3
Al^{+3}	1.53	1.89	0.30	15.9	19.6
	2.06	1.89	0.40	21.2	19.4
	2.51	1.89	0.49	25.9	19.5
	3.05	1.89	0.59	31.2	19.3
	3.52	1.89	0.72	38.1	20.5
	4.02	1.89	0.81	42.3	20.1

Table 2.4

Equilibrium of aqueous quinidine sulfate with the resin X8 in different ionic forms.

Ionic form	$[H]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
Li^+	0.76	1.88	0.27	14.4	35.5
	1.13	1.88	0.40	21.3	35.4
	2.52	1.88	0.88	46.8	34.9
	3.14	1.88	1.11	59.0	35.4
	3.81	1.88	1.36	72.3	35.7
Na^+	0.87	2.06	0.26	12.6	29.9
	1.45	2.06	0.41	19.9	28.3
	2.08	2.06	0.59	28.6	28.4
	3.28	2.06	1.00	48.5	30.5
	4.37	2.06	1.27	61.7	29.1
	5.43	2.06	1.57	76.2	28.9
NH_4^+	0.93	1.89	0.33	17.5	35.5
	1.50	1.89	0.52	27.5	34.7
	2.25	1.89	0.78	41.3	34.7
	3.41	1.89	1.14	60.3	33.4
	4.51	1.89	1.53	81.0	33.9
K^+	0.89	1.96	0.23	11.7	25.9
	1.42	1.96	0.36	18.4	25.4
	2.29	1.96	0.59	30.1	25.6
	3.29	1.96	0.83	42.4	25.3
	4.32	1.96	1.18	60.2	27.3

Table 2.4 (Contd.)

Ionic form	$[H]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
Mg^{+2}	1.27	1.92	0.27	14.1	21.3
	2.55	1.92	0.53	27.6	20.8
	3.78	1.92	0.78	40.6	20.6
	4.45	1.91	0.91	47.6	20.5
	5.08	1.91	1.05	55.0	20.7
	5.73	1.91	1.18	61.8	20.6
	6.35	1.91	1.32	69.1	20.8
Zn^{+2}	2.10	1.96	0.42	21.4	20.0
	3.40	1.96	0.69	35.2	20.3
	4.76	1.96	0.95	48.5	20.0
	5.43	1.96	1.11	56.6	20.5
	6.14	1.96	1.27	64.8	20.7
	7.13	1.96	1.46	74.5	20.5
Al^{+3}	2.85	1.85	0.50	27.0	17.5
	3.91	1.85	0.68	36.8	17.4
	4.94	1.85	0.87	47.0	17.2
	5.85	1.85	1.07	57.8	18.3
	6.81	1.85	1.21	65.4	17.8
	7.93	1.85	1.44	77.8	18.1
	8.86	1.85	1.57	84.8	17.7

Table 2.5

Equilibrium of aqueous quinidine sulfate with the resin IR-200 in different ionic forms.

Ionic form	$[H]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
Li^+	2.87	1.88	0.73	38.8	25.4
	3.84	1.88	0.97	51.6	25.3
	4.74	1.88	1.16	61.7	24.5
	6.58	1.88	1.53	81.4	23.3
Na^+	2.14	2.06	0.49	23.8	22.9
	3.88	2.06	0.79	38.3	20.4
	6.38	2.06	1.22	59.2	19.1
	7.76	2.06	1.41	68.4	18.2
NH_4^+	2.07	1.91	0.55	28.8	26.6
	3.11	1.91	0.74	38.8	23.8
	4.15	1.91	0.95	49.7	22.9
	6.24	1.91	1.30	68.1	20.8
	7.28	1.91	1.44	75.4	19.8
	8.34	1.91	1.58	82.7	18.9
K^+	1.34	1.96	0.26	13.3	19.4
	3.06	1.96	0.57	29.1	18.7
	4.01	1.96	0.73	37.2	18.2
	5.06	1.96	0.87	44.4	17.2

Table 2.5 (Contd.)

Ionic form	$[H]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
Mg^{+2}	2.92	1.85	0.46	24.9	15.8
	3.98	1.85	0.61	33.0	15.3
	4.89	1.85	0.70	37.8	14.3
	5.86	1.85	0.80	43.2	13.7
	7.80	1.85	0.97	52.4	12.4
	10.8	1.85	1.21	65.4	11.2
Zn^{+2}	2.99	1.96	0.44	22.4	14.7
	4.38	1.96	0.61	31.1	13.9
	5.95	1.96	0.82	41.8	13.8
	7.52	1.96	0.97	49.5	12.9
	10.10	1.96	1.26	64.3	12.5
	11.90	1.96	1.38	70.4	11.6
	12.90	1.96	1.47	75.0	11.4
Al^{+3}	1.94	1.89	0.27	14.3	13.9
	3.30	1.89	0.45	23.8	13.6
	4.29	1.89	0.56	29.6	13.0
	5.81	1.89	0.74	39.1	12.7
	7.78	1.89	0.93	49.2	12.0
	9.68	1.89	1.15	60.8	11.9
	11.60	1.89	1.30	68.8	11.2

Table 2.6

Equilibrium of aqueous cinchonine sulfate with the resin X2 in different ionic forms.

Ionic form	$[H]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
Li^+	0.76	2.12	0.65	30.7	85.5
	1.21	2.12	1.05	49.5	86.8
	1.50	2.12	1.30	61.3	86.7
	1.94	2.12	1.67	78.8	86.1
Na^+	1.13	2.15	0.92	42.7	81.4
	1.36	2.15	1.12	52.1	82.3
	1.80	2.15	1.48	68.9	82.2
	2.25	2.15	1.85	86.0	82.2
NH_4^+	0.90	1.96	0.69	35.2	76.7
	1.13	1.96	0.86	43.9	76.1
	1.34	1.96	1.02	52.0	76.1
	1.79	1.96	1.36	69.4	76.0
	2.25	1.96	1.69	86.2	75.1
K^+	0.98	2.13	0.68	31.9	69.4
	1.27	2.13	0.87	40.8	68.5
	1.71	2.13	1.16	54.5	67.8
	1.99	2.13	1.34	62.9	67.3

Table 2.6 (Contd.)

Ionic form	$[H]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
Mg^{+2}	0.66	2.05	0.47	22.9	71.2
	0.77	2.05	0.54	26.3	70.1
	1.15	2.05	0.77	37.6	66.9
	1.53	2.05	0.98	47.8	64.0
	1.92	2.05	1.21	59.0	63.0
Zn^{+2}	0.82	2.15	0.58	27.0	70.7
	1.25	2.15	0.76	35.3	60.8
	1.83	2.15	1.07	49.8	58.5
	3.21	2.15	1.60	74.4	49.8
	3.76	2.15	1.69	78.6	44.9
Al^{+3}	1.03	2.09	0.43	20.6	41.8
	1.57	2.09	0.62	29.7	39.5
	1.97	2.09	0.76	36.4	38.6
	2.37	2.09	0.91	43.5	38.4
	2.91	2.09	1.06	50.7	36.4
	3.46	2.09	1.22	58.4	35.3
	4.08	2.09	1.31	62.7	32.1

Table 2.7

Equilibrium of aqueous cinchonine sulfate with the resin X4 in different ionic forms.

Ionic form	$[H]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
Na^+	0.79	2.43	0.51	21.0	64.6
	1.31	2.43	0.83	34.2	63.4
	1.96	2.43	1.28	41.8	65.3
	2.94	2.43	1.89	77.8	64.3
NH_4^+	0.87	2.06	0.58	28.3	66.7
	1.37	2.06	0.92	44.7	67.2
	1.71	2.06	1.14	55.3	66.7
	2.18	2.06	1.43	69.4	65.6
	2.34	1.96	1.57	79.1	67.1
K^+	0.88	2.13	0.54	25.4	61.4
	1.48	2.13	0.89	41.8	60.1
	2.26	2.13	1.34	62.9	59.3
	3.32	2.13	2.01	94.4	60.5

Table 2.7 (Contd.)

Ionic form	$[H]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
Mg^{+2}	0.75	2.05	0.35	17.1	46.7
	1.14	2.05	0.52	25.4	45.6
	1.54	2.05	0.72	35.1	46.8
	2.10	2.05	0.98	47.8	46.7
	2.78	2.05	1.27	61.9	45.7
Zn^{+2}	1.42	2.15	0.65	30.2	45.8
	2.89	2.15	1.13	52.6	39.1
	3.84	2.15	1.45	67.5	37.8
	4.77	2.15	1.66	77.2	34.8
	5.56	2.15	1.81	84.2	32.6

Table 2.8

Equilibrium of aqueous cinchonine sulfate with the resin X8 in different ionic forms.

Ionic form	$[H]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
NH_4^+	0.95	2.21	0.46	20.8	48.4
	1.70	2.21	0.82	37.1	48.2
	2.26	2.21	1.09	44.0	48.2
	3.38	2.21	1.61	72.9	47.6
K^+	0.96	2.21	0.43	19.5	44.8
	2.12	2.21	0.97	43.9	45.8
	3.29	2.21	1.43	64.7	43.5
	4.26	2.21	1.85	83.7	43.4
Mg^{+2}	0.78	2.05	0.28	13.7	35.9
	1.92	2.05	0.66	32.9	34.4
	2.59	2.05	0.86	42.0	33.2
	2.90	2.05	0.95	46.3	32.8
	3.18	2.05	1.03	50.2	32.4

Table 2.8 (Contd.)

Ionic form	$[H]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
Zn^{+2}	2.16	2.15	0.66	30.7	30.6
	2.77	2.15	0.82	38.2	29.6
	3.87	2.15	1.10	51.2	28.4
	4.55	2.15	1.27	59.1	27.9
	5.75	2.15	1.57	73.0	27.3
Al^{+3}	1.95	2.09	0.49	23.5	25.1
	2.60	2.01	0.64	30.6	24.6
	3.27	2.01	0.80	38.3	24.5
	3.91	2.01	0.93	44.5	23.8
	4.54	2.01	1.07	51.2	23.6
	5.50	2.01	1.28	61.3	22.8
	7.81	2.01	1.75	81.8	22.4

Table 2.9.

Equilibrium of aqueous cinchonine sulfate with the resin IR-200 in different ionic forms.

Ionic form	$[H]_i$	$[A]_i$	$[\bar{A}]_e$	P_A	P_R
Na^+	1.94	2.43	0.65	26.8	33.5
	2.92	2.43	0.91	37.4	31.2
	3.87	2.43	1.12	46.1	28.9
	5.82	2.43	1.53	63.0	26.3
	7.76	2.43	1.81	74.5	23.3
NH_4^+	2.08	2.00	0.54	27.0	26.0
	3.10	2.00	0.77	38.5	24.8
	4.18	2.00	1.03	51.5	24.6
	7.29	2.00	1.52	76.0	20.8
	8.32	2.00	1.66	83.0	20.0
Al^{+3}	1.94	2.15	0.47	21.9	14.2
	3.31	2.15	0.58	27.0	13.7
	4.25	2.15	0.77	35.8	13.2
	5.83	2.15	1.00	46.5	12.9
	7.75	2.15	1.38	64.2	11.8
	11.7	2.15	1.54	71.7	11.3

Discussion :

The synthetic organic ion exchange resins (4,5) consist of an irregular, three dimensional network of hydrocarbon chains, to which ionogenic groups are attached and the surplus electric charge is balanced by mobile counter ions. The hydrocarbon network is hydrophobic but the ionogenic groups are hydrophilic. Hence when the resin particle is placed in water, it sorbes water and swells to a limited extent. The amount of water sorbed and the extent of swelling depends on the degree of crosslinking and the counter ions. The selectivity coefficients for alkali metal ions with resins in hydrogen form in sulfate solutions had been studied earlier (6). When calculations were carried out for exchange in solutions of the cinchona alkaloid sulfates studied, with resins in different ionic forms, the calculated values of P_R were either practically constant or varied to a small extent (7) when P_A was varied. The results were not measurably different when either the amount of alkaloid sulfate solution was held constant and the amount of added resin varied or when the amount of added resin was held constant and the amount of alkaloid sulfate solution was varied, provided the ratio of the initial concentration (in meq./liter) of the resin to the initial concentration of the alkaloid sulfate, was the same. It is suggested that the value of the equilibrium constant for the exchange (8-16) of the cation QH^+ is large and the equilibrium

$MR + QH^{+} \rightleftharpoons RQH + M^{+}$ is shifted very much to the right ; however, all the replaceable metallic ions in the resin phase are not accessible for exchange or the available capacity is only a fraction of the total capacity probably due to the size of the organic counter ions. It is likely that the marked shift of the equilibrium to the right is aided by the operation of nonexchange interactions (1,15,16) and that the interactions tend to increase the extent of exchange with increase in $[\bar{A}]_e$. This may be feasible to some extent by further expansion of and / or further separation between some segments in the swollen (4-5) or expanded resin network and should depend on the degree of crosslinking and the extent to which exchange has already occured. If the further expansion and / or segment separation is sufficient to accommodate some more organic cations by exchange, P_R should increase with increase in $[\bar{A}]_e$ or decrease in P_A. On the other hand, if the further expansion and / or segment separation is too small to accommodate some organic cations by exchange, P_R should remain practically constant with increase in $[\bar{A}]_e$ or decrease in P_A.

For resins X2, X4 and X8 in the alkali metal forms, that is lithium, sodium and potassium for both the alkaloid sulfates the values of P_R are in the order Li $\gg$ Na $\gg$ K which is also the order of increasing naked ionic radii and decreasing water content of the swollen resin (4-5).

For resins in divalent ionic forms, magnesium and zinc, the order is Mg > Zn which is also the order of increasing naked ionic radii.

For resins in the ionic form of ions of different valance the order of the P_R values is monovalent > bivalent > trivalent ; that is, the value of P_R decreases with increase in valance of the counterion .

The values of P_R for the resin X2 in NH_4 form for both the alkaloid sulfates may be considered to be between the values of P_R for sodium and potassium forms. But as the degree of crosslinking increases, that is for the resins X4 and X8, the values of P_R for NH_4 form lie between the values for Li and Na forms of the respective resins.

The effect of the degree of crosslinking is significant. The values of P_R for both the alkaloid sulfates decrease as X increases. This is so for each of the ionic forms of the resins. This could be attributed to the decrease in the swelling of the resin as the degree of crosslinking increases ; hence the number of accessible exchange sites for the alkaloid in the interior of the resin decreases.

In general, the results indicate that the P_R values with quinidine sulfate for a resin in a particular ionic form are significantly lower than those for cinchonine sulfate for the same resin in the same ionic form. This should be attributed to the difference in the size of quinidine as compared to that of cinchonine.

Conclusion :

It may be concluded that the value of P_R decreases with increase in the size of the alkaloid molecule, increase in the degree of crosslinking, increase in the ionic radius of the metallic counter ion of the same group (Li, Na and K) and increase in the charge of the metallic counter ion of the same period (Na, Mg and Al).

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