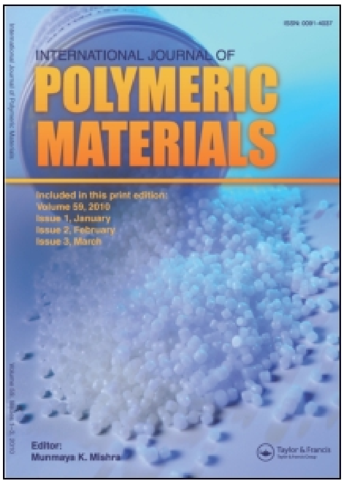

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Methyl Methacrylate-8-quinolinyl Acrylate Copolymers-II: Ion-exchange Study

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Methyl Methacrylate-8-quinolinyl Acrylate Copolymers-II: Ion-exchange Study

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The chelating ion-exchange properties of the methylmethacrylate (MMA)-8-quinolinyl acrylate (8-QA) copolymers, synthesized using different monomer feed ratios, were estimated by batch equilibration method. Five metal ions *viz.*, Cu^{+2}, Ni^{+2}, Co^{+2}, Zn^{+2} and Fe^{+3} were used to evaluate the capability of MMA-8-QA copolymers as a cation exchangers. The ion-exchange study was carried out under three different experimental variables *viz.*, pH of the aqueous medium, electrolyte and its ionic strength and shaking time. It was observed that due to the presence of a pendant ester-bound quinolinyl group, the copolymers are capable of exchanging the tested cations from their aqueous solutions.

Keywords: Ion-exchange properties; batch equilibration method; ionic strength

INTRODUCTION

Ion exchangers have been used commercially on a worldwide basis for almost a century due to inverse applications in many fields such as water softening and deionization [1], sugar purification [2], extraction of

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uranium [3], glycerol refining [4], isolation and purification of antibiotics [5], in hydrometallurgy for separation and purification of metals [6] and waste water treatment and pollution control [7]. Since long, a considerable interest has been developed in the synthesis of ion-exchange resins having special properties and containing specific functional groups. These resins are expected to work under crucial conditions of pH, temperature and at the same time selective in adsorption of specific metal ions. In our earlier communication we have reported the synthesis and characterization of MMA-8-QA copolymers [8]. In the present article, we have studied the ion-exchange properties of MMA-8-QA copolymers by batch equilibration method. The effect of various experimental parameters; such as pH of the medium, shaking time and electrolytes and its ionic strength; on the metal ion uptake capacity of the polymers has also been discussed.

EXPERIMENTAL

Batch equilibration method [9, 10] was adopted for the determination of the ion-exchange properties using different experimental variables such as electrolyte and its concentration, pH of the medium and time. Five metal ions *viz.*, Cu^{+2}, Ni^{+2}, Co^{+2}, Zn^{+2} and Fe^{+3} were tested in the form of aqueous metal nitrate solution. The general experimental procedure is given below.

The finely powdered and dried polymer sample (50 mg) was suspended in the 40 ml of electrolyte solution of specific ionic strength. The pH of the suspension was adjusted to required value either by 0.1 M HNO_3 or 0.1 M NaOH. The conical flask with this content was stoppered and mechanically shaked for 24 hrs to allow the sweeling of the polymer at room temperature. To this, 0.1 M metal nitrate solution (2 ml) was added and the pH was adjusted to the required value. The content was mechanically stirred for 24 hrs and then filtered and washed with distilled water. The filtrate and the washing was collected in the conical flask and the unadsorbed metal was estimated by back titration with standard EDTA solution using appropriate indicator. A separate blank experimental (without adding polymer sample) was also carried out in the same manner. From the difference between a sample and a blank reading the amount of metal adsorbed by the polymer was calculated and expressed in terms of milli equivalent per gram of the polymers (m.eq. g^{-1}).

RESULTS AND DISCUSSION

The presence of pendant quinolinyl group in the polymer chain imparts ion-exchange properties to the polymer. Tables I and II shows the results of effect of pH on the metal binding capacity of the synthesized polymers. It is observed that the relative amount of metal ion adsorped by the polymers increases with increasing pH of the medium. The results of distribution ratios (Tabs. III and IV) also

TABLE I Effect of pH on Cu^{+2}, Ni^{+2}, Zn^{+2} and Co^{+2} metal ion binding capacity of 8-QA homo- and copolymers

Metal ion (0.1 M, 2 ml)	*Sample code no.*	*Metal ion uptake (m.eq. g^{-1}) pH of the medium*					
		3.0	**3.5**	**4.0**	**5.0**	**5.5**	**6.0**
	P-1	0.92	1.58	2.04	2.54	2.62	2.78
	P-2	0.48	0.81	0.98	1.28	2.24	2.26
$Cu(NO_3)_2$	P-3	0.28	0.32	0.51	0.83	0.98	1.00
	P-4	0.10	0.12	0.18	0.26	0.38	0.40
	P-5	0.06	0.06	0.08	0.16	0.21	0.28
	P-6	–	–	0.04	0.10	0.14	0.16
	P-1	0.92	1.08	2.60	3.52	3.70	3.72
	P-2	0.48	0.88	1.12	2.01	2.38	2.40
$Ni(NO_3)_2$	P-3	0.46	0.48	0.67	0.98	1.04	1.08
	P-4	0.32	0.40	0.51	0.60	0.68	0.70
	P-5	0.10	0.16	0.18	0.26	0.30	0.36
	P-6	–	0.02	0.06	0.10	0.12	0.16
	P-1	0.58	0.72	1.23	1.94	2.00	2.04
	P-2	0.28	0.32	0.58	1.60	1.78	1.80
$Zn(NO_3)_2$	P-3	0.22	0.36	0.38	0.66	0.72	0.80
	P-4	0.06	0.08	0.08	0.20	0.29	0.32
	P-5	–	–	0.06	0.08	0.12	0.16
	P-6	–	–	–	0.08	0.08	0.10
	P-1	0.78	0.88	1.62	2.42	2.50	2.58
	P-2	0.43	0.52	1.02	1.98	2.10	2.13
$Co(NO_3)_2$	P-3	0.18	0.22	0.29	0.46	0.50	0.51
	P-4	0.08	0.14	0.18	0.22	0.27	0.29
	P-5	–	0.06	0.06	0.08	0.11	0.14
	P-6	–	–	0.04	0.08	0.08	1.00

Weight of polymer : 50 mg; Electrolyte : 1.0 M $NaNO_3$ (40 ml).

TABLE II Effect of pH on Fe^{+3} metal ion binding capacity of 8-QA homo- and copolymers

Sample code no.	*Metal ion uptake (m.eq. g⁻¹) pH of the medium*					
	1.5	**2.0**	**2.5**	**3.0**	**3.5**	**4.0**
P-1	0.98	1.52	1.78	2.23	2.25	2.27
P-2	0.68	0.77	1.02	1.98	2.01	2.02
P-3	0.38	0.42	0.70	0.92	0.98	1.01
P-4	0.22	0.26	0.38	0.52	0.64	0.65
P-5	0.08	0.18	0.20	0.28	0.34	0.36
P-6	–	0.06	0.06	0.08	0.08	0.10

Weight of polymer: 50 mg; Metal ion : 0.1 M $Fe(NO_3)_3$ (2 ml); Electrolyte : 1.0 M $NaNO_3$ (40 ml).

TABLE III Distribution ratio of Cu^{+2}, Ni^{+2}, Zn^{+2} and Co^{+2} ions adsorbed by the polymer and remained in the solution at equilibrium

Metal ion (0.1 M, 2 ml)	*Sample code no.*	*Distribution ratio (K_D) pH of the medium*					
		3.0	**3.5**	**4.0**	**5.0**	**5.5**	**6.0**
	P-1	116	220	308	422	442	485
	P-2	57	100	124	170	351	356
$Cu(NO_3)_2$	P-3	32	37	60	103	124	127
	P-4	11	14	20	30	44	47
	P-5	07	07	09	18	24	32
	P-6	–	02	04	11	16	18
	P-1	109	131	405	660	723	730
	P-2	54	104	137	282	356	360
$Ni(NO_3)_2$	P-3	51	54	77	117	126	131
	P-4	35	44	56	68	78	81
	P-5	11	17	19	28	33	40
	P-6	–	02	06	11	13	17
	P-1	66	83	153	269	280	288
	P-2	30	35	66	210	240	244
$Zn(NO_3)_2$	P-3	22	39	42	76	83	93
	P-4	06	09	09	22	32	35
	P-5	02	04	06	08	13	17
	P-6	–	02	02	02	02	04
	P-1	91	104	213	364	382	399
	P-2	48	58	123	276	299	305
$Co(NO_3)_2$	P-3	19	24	32	51	56	57
	P-4	08	15	19	24	29	32
	P-5	–	06	06	08	12	15
	P-6	–	02	04	08	11	15

Weight of polymer : 50 mg; Electrolyte : 1 M $NaNO_3$ (40 ml).

indicates that at equilibrium, the distribution of each metal between the polymeric phase and aqueous phase increases with increasing pH of the medium. The data clearly indicates that Ni^{+2}, get adsorped

TABLE IV Distribution ratio of Fe^{+3} ions adsorbed by the polymer and remained in the solution at equilibrium

Sample code no.	*Distribution ratio (K_D) pH of the medium*				
	1.5	**2.0**	**2.5**	**3.0**	**3.5**
P-1	75	122	146	192	194
P-2	50	58	78	166	168
P-3	28	30	52	70	75
P-4	16	19	28	38	47
P-5	06	13	14	20	24
P-6	03	04	04	06	06

Weight of polymer : 50 mg; Electrolyte : 1 M $NaNO_3$ (40 ml); Metal : 0.1 M $Fe(NO_3)_3$ (2 ml).

TABLE V Effect of electrolyte concentration on metal ion adsorption capacity of 8-QA homo- and copolymers

Sample code no.	*Electrolyte concentration ($Mol.lit^{-1}$)*	*Metal ion uptake (m.eq. g^{-1})*				
		Cu^{+2}	**Ni^{+2}**	**Zn^{+2}**	**Co^{+2}**	**Fe^{+3}**
	0.05	1.62	1.88	3.92	0.92	4.22
P-1	0.10	1.84	2.00	3.02	1.16	3.88
	0.50	2.32	2.96	2.04	2.04	2.46
	1.00	2.56	3.68	1.98	2.48	2.22
	0.05	1.86	1.92	2.62	1.78	2.88
P-2	0.10	1.90	1.98	2.48	1.86	2.68
	0.50	2.28	2.32	2.02	2.10	2.14
	1.00	2.32	2.40	1.90	2.20	1.96
	0.05	0.38	0.52	1.50	0.24	1.62
P-3	0.10	0.42	0.62	1.42	0.28	1.56
	0.50	0.58	0.88	0.96	0.42	1.02
	1.00	0.64	1.02	0.80	0.48	0.94
	0.05	0.14	0.20	0.88	0.10	1.02
P-4	0.10	0.16	0.30	0.72	0.12	0.94
	0.50	0.32	0.54	0.34	0.24	0.70
	1.00	0.38	0.62	0.28	0.28	0.62
	0.05	0.04	0.10	0.60	–	0.82
P-5	0.10	0.06	0.14	0.52	0.06	0.74
	0.50	0.12	0.22	0.22	0.10	0.32
	1.00	0.16	0.28	0.12	0.10	0.24
	0.05	–	–	0.18	–	0.20
P-6	0.10	–	0.04	0.10	–	0.12
	0.50	0.06	0.08	0.04	0.04	0.06
	1.00	0.10	0.12	–	0.08	–

Weight of polymer : 50 mg; Electrolyte : 1.0 M $NaNO_3$ solution (40 ml); pH of the medium : 5.5 (for Cu^{+2}, Ni^{+2}, Zn^{+2} and Co^{+2}) 3.0 (for Fe^{+3}).

selectively to the higher extent whereas Zn^{+2} adsorped to a least extent over and entire pH range studied. The lowest affinity of the Zn^{+2} ion may be attributed to the very low stability constants of Zn complexes with ligands [11]. Tables V to VII shows the results of the effect of the type and concentration of an electrolyte on the amount of different metal ion adsorption by the polymer from their solutions at room temperature. It is observed that the amount of Cu^{+2}, Ni^{+2} and Co^{+2} ions adsorption increases with increasing concentration of NO_3^{-1} and Cl^{-1} ions whereas that of Zn^{+2} decreases with increasing concentration of NO_3^{-1} and Cl^{-1} ions. But in case of SO_4^{-2}, the adsorption of all the metal ions studied decreases with increasing concentration of SO_4^{-2} ions which may be explained in terms of the stability constant of the complexes of studied metal ions with NO_3^{-1}, Cl^{-1}, and SO_4^{-2} anions [12]. Tables VIII and IX shows the results of the rate of metal uptake by the polymers as a function of time which shows that among the five metal ions studied, Zn^{+2} and Fe^{+3} ions requires the shortest time of

TABLE VI Effect of electrolyte concentration on metal ion adsorption capacity of 8-QA homo- and copolymers

Sample code no.	*Electrolyte concentration* ($Mol.lit^{-1}$)	*Metal ion uptake* ($m.eq.\ g^{-1}$) Cu^{+2}	Ni^{+2}	Zn^{+2}	Co^{+2}	Fe^{+3}
	0.05	3.86	2.14	1.12	1.28	2.02
P-1	0.10	3.20	1.98	0.96	1.10	1.32
	0.50	2.72	1.06	0.88	0.96	1.08
	1.00	2.32	0.78	0.72	0.62	0.78
	0.05	1.64	1.54	1.46	1.52	1.34
P-2	0.10	1.60	1.50	1.40	1.48	1.28
	0.50	1.42	1.28	1.08	1.20	0.62
	1.00	1.36	1.24	0.92	1.12	0.50
	0.05	1.20	1.16	1.06	1.12	0.96
P-3	0.10	1.12	1.08	0.98	1.02	0.86
	0.50	0.96	0.90	0.62	0.80	0.52
	1.00	0.86	0.84	0.52	0.74	0.42
	0.05	0.96	0.72	0.42	0.58	0.28
P-4	0.10	0.88	0.64	0.34	0.46	0.20
	0.50	0.62	0.42	0.20	0.28	0.10
	1.00	0.54	0.36	0.16	0.20	0.06
	0.05	0.40	0.32	0.12	0.20	0.08
P-5	0.10	0.34	0.24	0.08	0.12	0.04
	0.50	0.26	0.10	0.04	0.06	–
	1.00	0.20	0.04	–	–	–
	0.05	0.18	0.10	0.06	0.08	0.04
P-6	0.10	0.06	0.40	0.04	0.02	–
	0.50	0.02	–	–	–	–
	1.00	–				

Weight of polymer : 50 mg; Electrolyte : 1.0 M Na_2SO_4 solution (40 ml); pH of the medium : 5.5 (for Cu^{+2}, Ni^{+2}, Zn^{+2} and Co^{+2}) 3.0 (for Fe^{+3}).

TABLE VII Effect of electrolyte concentration on metal ion adsorption capacity of 8-QA homo- and copolymers

Sample code no.	*Electrolyte concentration (Mol.lit^{-1})*	*Metal ion uptake (meq. g^{-1})*				
		Cu^{+2}	Ni^{+2}	Zn^{+2}	Co^{+2}	Fe^{+3}
	0.05	2.56	1.42	2.02	0.56	2.92
P-1	0.10	2.72	1.92	1.82	0.94	1.28
	0.50	2.96	2.88	1.08	1.18	0.98
	1.00	3.28	3.60	0.68	1.32	0.64
	0.05	0.98	1.04	1.52	0.32	1.58
P-2	0.10	1.08	1.18	1.46	0.44	1.44
	0.50	1.56	1.60	0.62	1.08	0.76
	1.00	1.62	1.62	0.50	1.32	0.52
	0.05	0.50	0.62	0.58	0.22	0.62
P-3	0.10	0.54	0.78	0.50	0.28	0.60
	0.50	0.68	0.92	0.40	0.34	0.52
	1.00	0.72	1.02	0.32	0.42	0.46
	0.05	0.06	0.12	–	–	0.04
P-4	0.10	0.10	0.18	0.06	–	0.08
	0.50	0.22	0.30	0.10	0.04	0.18
	1.00	0.28	0.34	0.14	0.10	0.20
	0.05	–	0.04	0.06	–	–
P-5	0.10	0.04	0.08	0.02	–	–
	0.50	0.06	0.18	–	0.04	0.06
	1.00	0.10	0.22	–	0.06	0.08
	0.05	–	–	–	–	–
P-6	0.10	–	0.06	–	–	–
	0.50	0.04	0.08	–	–	0.06
	1.00	0.10	0.14	0.08	0.04	0.10

Weight of polymer : 50 mg; Electrolyte : 1.0 M NaCl solution (40 ml); pH of the medium : 5.5 (for Cu^{+2}, Ni^{+2}, Zn^{+2} and Co^{+2}) 3.0 (for Fe^{+3}).

TABLE VIII Rate of Cu^{+2}, Ni^{+2}, Zn^{+2} and Co^{+2} metal ion uptake by 8-QA homo- and copolymers as a function of time

Metal ion (0.1 M, 2 ml)	*Sample code no.*	**% attanment of equilibrium**[a] **Time (hrs)**						
		1.0	**2.0**	**3.0**	**4.0**	**5.0**	**6.0**	**7.0**
	P-1	35.9	37.2	43.5	52.1	78.8	90.2	98.4
	P-2	29.2	32.4	42.5	69.9	89.0	93.4	–
$Cu(NO_3)_2$	P-3	22.6	26.8	28.1	57.7	78.8	89.6	95.8
	P-4	21.9	24.8	32.5	63.6	82.5	98.9	–
	P-5	19.8	20.1	28.8	53.4	81.9	96.8	–
	P-6	15.1	16.2	19.9	48.9	71.8	89.3	97.2
	P-1	25.3	27.7	36.4	43.5	76.8	88.8	95.3
	P-2	26.6	28.2	33.4	58.8	78.3	87.3	94.5
$Ni(NO_3)_2$	P-3	19.6	21.6	25.1	44.3	70.1	87.8	90.0
	P-4	20.8	23.0	30.5	68.1	71.0	89.6	92.5
	P-5	19.1	20.0	30.1	50.3	73.4	87.1	89.2
	P-6	16.8	17.1	21.1	41.8	70.0	87.4	90.2

TABLE VIII (Continued)

Metal ion (0.1 *M*, 2 *ml*)	*Sample code no.*	% *attanment of equilibrium*[a] *Time (hrs)* 1.0	2.0	3.0	4.0	5.0	6.0	7.0
	P-1	42.1	43.8	68.7	82.5	96.8	–	–
	P-2	42.2	45.6	56.1	70.1	89.9	92.0	–
$ZnNO_3$	P-3	41.8	46.7	62.0	89.1	97.0	–	–
	P-4	40.1	42.3	79.0	92.9	–	–	–
	P-5	32.5	34.8	48.9	80.1	89.9	100.0	–
	P-6	29.9	30.3	41.2	92.2	100.0	–	–
	P-1	20.5	26.4	38.3	52.6	58.5	85.4	92.5
	P-2	19.9	21.6	29.8	49.2	67.8	83.8	90.3
$Co(NO_3)_2$	P-3	12.9	14.5	28.6	58.1	62.4	88.1	90.2
	P-4	11.2	12.3	18.4	30.8	69.9	87.8	92.8
	P-5	10.8	11.4	13.5	20.3	58.1	88.7	90.0
	P-6	08.6	09.2	19.5	28.6	51.2	78.8	79.8

[a] With respect to 100% equilibrium after 24 hr.
Weight of sample : 50 mg. Electrolyte : 1.0 M $NaNO_3$ (40 ml). pH of the medium : 5.5.

TABLE IX Rate of Fe^{+3} metal ion uptake by 8-QA homo- and copolymers as a function of time

Sample code no.	% *attanment of equilibrium*[a] *Time (hrs)* 1.0	2.0	3.0	4.0	5.0	6.0	7.0
P-1	52.5	58.6	72.7	90.6	100.0	–	–
P-2	58.5	60.2	82.4	96.8	98.1	–	–
P-3	50.1	58.2	72.0	89.2	95.6	97.9	–
P-4	40.8	51.2	76.8	92.1	100.0	–	–
P-5	42.5	43.1	69.3	89.9	100.0	–	–
P-6	32.5	34.8	70.1	82.5	89.9	98.2	–

[a] With respect to 100% equilibrium after 24 hr.
Weight of sample : 50 mg; Electrolyte : 1.0 M $NaNO_3$ (40 ml); Metal ion : 0.1 M $Fe(NO_3)_3$ (2 ml); pH of the medium : 3.0.

about 4 – 5 hrs whereas Cu^{+2}, Ni^{+2} and Co^{+2} requires 6 – 7 hrs to reach the state of equilibrium. Due to this difference in the uptake rate of the metals, it may be possible to used these polymers to separate Zn^{+2} and Fe^{+3} ions from their admixtures with Cu^{+2}, Ni^{+2} and Co^{+2} ions.

CONCLUSION

Since the pendent quinolinyl group plays a key role in the ion-exchange phenomena, the amount of metal adsorbed by each sample depends upon its 8-QA content. As the pH of the medium increases, the amount of metal adsorded by the polymers also increases and follows the treand of: $Ni^{+2} > Cu^{+2} > Co^{+2} > Zn^{+2}$. The Fe^{+3} adsorption was studied in the pH range of 1.5 to 3.5 and it is also increases with increasing pH. The adsorption of Cu^{+2}, Ni^{+2} and Co^{+2} at pH 5.5 increases with increasing NO_3^- and Cl^- ion concentration in the aqueous phase were as that of Zn^{+2} and Fe^{+3} decreases with increasing NO_3^- and Cl^- ion. From the results of distribution ratios it can be observed that all the polymers shows highest affinity for Ni^{+2} whereas least affinity for the Zn^{+2}. Due to the considerable difference between the adsorption capacity at different pH, rate of metal uptake and distribution ratio at equilibrium, it may be possible to use the polymers for separation of particular metal ions form their admixture.

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