

Chelation ion-exchange properties of salicylic acid-urea-formaldehyde copolymers

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Abstract. Chelation ion-exchange properties of copolymers prepared from salicylic acid, urea and formaldehyde by condensation in presence of acid catalyst were studied for Cu^{2+} , Fe^{3+} , UO_2^{2+} , Mn^{2+} , Zn^{2+} and Co^{2+} ions. A batch equilibration method was adopted to study the selectivity of metal ion uptake. This method involved the measurement of distribution of a given metal between the copolymer sample and a solution containing the metal ions. The study was carried out over a wide pH range and in media of various ionic strengths. The copolymer showed a higher selectivity for UO_2^{2+} , Cu^{2+} and Fe^{3+} ions than Mn^{2+} , Co^{2+} and Zn^{2+} ions.

Keywords. Chelation ion exchange; batch equilibration; distribution ratio.

1. Introduction

Salicylic acid and its bi-substituted derivatives are well-known complexing agents and find many applications in analytical chemistry of inorganic species. The salicylic acid formaldehyde polymer has been reported to show a chelation ion-exchange capacity (Donaruma 1962; Degeiso *et al* 1962a, 1963). It is obvious that copolymers prepared from salicylic acid are also a subject of an extensive investigation for their chelation properties.

We report in this paper the systematic study of the selectivity and capacity of salicylic acid(S)-urea(U)-formaldehyde (F) copolymers (SUF) in the ion-exchange reaction. The SUF copolymers used here were prepared by condensation of (S) and (U) in different molar-proportions with (F) in presence of aq. HCl at 100°C for 5 hr (Joshi and Patel 1981). The batch equilibration method (Gregor *et al* 1952, 1953) was employed to study the effect of various electrolytes on the metal uptake, rate of metal uptake and the distribution ratio of the metal ions between polymeric material and solution at different pH.

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2. Experimental

2.1. Preparation of salicylic acid-urea-formaldehyde copolymers

The copolymers SUF-1 and SUF-2 were prepared by taking the molar proportion of S : U : F to be equal to (1 : 1 : 2) and (3 : 1 : 4) respectively ; by condensation in the presence of 2M aq. HCl at 100° C for 5 hr (Joshi and Patel 1981). The copolymers were washed with large amounts of hot water, soxhlet extracted with ether and purified by dissolving in 8% NaOH and reprecipitating with 1 : 1 (V/V) conc. HCl/water. Finally the copolymers were washed with hot water and dried in vacuum at room temperature. The purified copolymers were finely ground to pass a 300 mesh screen and used in all experiments described in the present text.

2.2. Determination of metal uptake in the presence of different electrolytes

In order to study the effect of the nature of the electrolyte and its concentration on the amount of the metal ions taken up by the copolymer sample, SUF-1 copolymer sample 25 mg each, were weighed into a 100 ml glass stoppered conical flask. 44 ml of each 0.01, 0.05, 0.1, 0.5 and 1 M NaNO₃ were added to the samples. The pH of the suspensions was adjusted to 2.5 by addition of 0.1 M HNO₃ or 0.1 M NaOH and stirred for a period of 24 hr at room temperature. This treatment would swell the copolymer samples. Then 0.1 M metal solution (1 ml) was added to each one of the above suspensions and the pH was adjusted to the required value by the use of appropriate concentration (1 M-0.01 M) of NaOH or HNO₃. The slurries were stirred at room temperature continuously for 24 hr, filtered and washed with distilled water. The filtrates and washings were combined and the metal was estimated by titrating against standard EDTA. A blank experiment was similarly carried out without adding the copolymer sample. The blank was also estimated for the metal ion content. The metal ion uptake by the copolymer in the presence of sodium nitrate of known concentrations was obtained from difference between the blank reading and the reading in the actual experiment. This experiment was repeated in the presence of different electrolytes of known concentrations for different metal ions (table 1). The same procedure was applied to the SUF-2 copolymer sample.

2.3. Evaluation of the rate of metal uptake

With a view to estimate the time required to reach the state of equilibrium under given experimental conditions with each metal ion, a series of experiments of the type described above were carried out. The metal ion Fe³⁺, Cu²⁺ and UO₂²⁺ taken up by the chelating copolymer was estimated from time to time (table 2) at 25° C in the presence of 44 ml of 1M NaNO₃ solution, while the selectivity of Mn²⁺, Co²⁺, and Zn²⁺ was determined in the presence of 44 ml of 0.01 M NaNO₃ solution, as the copolymer in the presence of these last three metal ions was found to be more stable with respect to solubility than in the 1 M NaNO₃. It is assumed that under the given conditions, the state of equilibrium is established in 24 hr. The rate of metal uptake is expressed as percentage attainment of the state of equilibrium by expressing it as the amount of metal ion taken up after a certain time in relation to that in the state of equilibrium (*cf.* table 2).

2.4. Evaluation of distribution of metal ions at different pH

The distribution of each one of the six metal ions Cu^{2+} , UO_2^{2+} , Fe^{3+} , Mn^{2+} , Zn^{2+} and Co^{2+} between polymer phase and aqueous phase was estimated at 25°C . 1M NaNO_3 was used for the first three metal ions and 0.01M NaNO_3 was used for the last three metal ions. The experiments were carried out as described above in the pH range 1 to 7. The distribution coefficient D was calculated according to

$$D = \frac{\text{amount of metal on the copolymer}}{\text{amount of metal in the solution}} \times \frac{\text{volume of solution}}{\text{weight of copolymer}}$$

The results are shown in table 3.

3. Results and discussion

3.1. Effect of electrolytes on the metal uptake

It is known that chelation reactions can be carried out most efficiently in the presence of a buffer system of higher capacity to maintain a certain pH value. At the same time metal-buffer reactions can shift the position of the equilibrium of metal polymer interaction especially where chelates of low stability are formed. Hence, to find out which electrolyte system has maximum metal uptake, the influence of ClO_4^- , NO_3^- , Cl^- and SO_4^{2-} was examined at various concentrations on position of the equilibrium. Table 1 reveals that the amount of Cu^{2+} , UO_2^{2+} and Fe^{3+} taken up by SUF-1 and SUF-2 copolymer samples increases with increasing concentration of ClO_4^- , NO_3^- and Cl^- and decreases with increasing concentration of SO_4^{2-} (Degeiso *et al* 1962a), whereas, uptake of Mn^{2+} , Co^{2+} and Zn^{2+} ions by the above copolymers increases with decreasing concentration of ClO_4^- , NO_3^- , Cl^- and SO_4^{2-} . This may be explained in terms of stability constants (Degeiso *et al* 1962a) of the chelates with these copolymers. Sulphate might form rather strong chelates with Fe^{3+} , UO_2^{2+} and Cu^{2+} ions, while perchlorate, nitrate and chloride might form weak chelates and therefore might not influence the position of the Fe^{3+} , UO_2^{2+} and Cu^{2+} salicylate equilibrium as much as sulphate. This trend has also been observed by others (Degeiso *et al* 1962a; Patel and Pate, 1979). The amount of metal uptake is more in SUF-2 than in SUF-1. However, the difference in uptake in both the copolymers is less as compared to their difference in molar ratio of salicylic acid : urea. Our results indicate that for the copolymers under study, higher pH was not suitable when concentrated electrolytes were used. The effect was more predominant in SUF-2 than in SUF-1 copolymer. The copolymer containing a higher salicylic acid-to-urea molar ratio was less stable with respect to solubility in concentrated electrolyte solution at higher pH. Hence it may be concluded that a higher concentration of urea in the copolymer improves, to some extent, the stability of the copolymer when used as an ion-exchanger, without affecting the metal uptake significantly.

3.2. Rate of metal uptake

Table 2 shows the dependence of the rate of metal ion uptake on the nature of the metal. The term "rate" refers to changes with time in the concentration of

Table 1. Evaluation of the effect of different electrolytes in the uptake of several metal ions $[M^{n+}(\text{NO}_3)_m] = 0.1 \text{ mol. l}^{-1}$

Metal ion	Electrolyte mol. l ⁻¹	pH	Weight in meq × 10 of the metal ion taken up in the presence of				
			NaClO ₄	NaNO ₃	NaCl	Na ₂ SO ₄	
Cu ⁺⁺	1.00		0.28 ^b (0.45) ^c	0.23 ^b (0.29) ^c	0.26 ^b (0.31) ^c	0.065 ^b (0.14) ^c	
	0.50		0.2 (0.34)	0.14 (0.21)	0.16 (0.26)	0.077 (0.18)	
	0.10	5.0	0.17 (0.24)	0.1 (0.18)	0.11 (0.24)	0.14 (0.24)	
	0.05		0.16 (0.19)	0.075 (0.17)	0.095 (0.21)	0.16 (0.26)	
	0.01		0.15 (0.19)	0.07 (0.16)	0.08 (0.2)	0.19 (0.265)	
Fe ³⁺	1.00		0.30 (0.36)	0.15 (0.22)	0.18 (0.24)	0.04 (0.11)	
	0.50		0.28 (0.34)	0.13 (0.19)	0.14 (0.20)	0.06 (0.11)	
	0.10	2.0	0.25 (0.32)	0.12 (0.17)	0.12 (0.18)	0.1 (0.13)	
	0.05		0.24 (0.31)	0.11 (0.15)	0.11 (0.17)	0.12 (0.17)	
	0.01		0.21 (0.30)	0.09 (0.14)	0.10 (0.15)	0.13 (0.20)	
UO ₂ ⁺⁺	1.00		0.39 (0.48)	0.35 (0.44)	0.37 (0.46)	0.22 (0.28)	
	0.50		0.35 (0.44)	0.32 (0.40)	0.34 (0.42)	0.27 (0.33)	
	0.10	4.0	0.27 (0.36)	0.25 (0.32)	0.32 (0.31)	0.32 (0.38)	
	0.05		0.24 (0.33)	0.23 (0.28)	0.29 (0.26)	0.35 (0.41)	
	0.01		0.22 (0.32)	0.23 (0.26)	0.26 (0.25)	0.35 (0.43)	

	1.00	0.01 (0.015)
	0.50	0.015 (0.035)	0.02 (0.03)	0.015 (0.025)	0.025 (0.03)	..
Mn ²⁺	0.10	0.03 (0.08)	0.025 (0.06)	0.035 (0.045)	0.03 (0.045)	..
	0.05	0.08 (0.11)	0.07 (0.08)	0.06 (0.075)	0.05 (0.065)	..
	0.01	0.09 (0.13)	0.075 (0.09)	0.08 (0.095)	0.075 (0.085)	..
	1.00	0.02 (..)	0.01 (..)	0.015 (..)	0.01 (..)	..
	0.50	0.03 (0.035)	0.025 (0.035)	0.045 (0.02)	0.025 (0.025)	..
Co ²⁺	0.10	0.055 (0.075)	0.045 (0.06)	0.04 (0.05)	0.045 (0.055)	..
	0.05	0.06 (0.09)	0.06 (0.075)	0.06 (0.065)	0.055 (0.065)	..
	0.01	0.085 (0.11)	0.07 (0.08)	0.075 (0.09)	0.06 (0.08)	..
	1.00	0.03 (0.035)	0.025 (0.025)	0.01 (0.02)	0.01 (0.025)	..
	0.50	0.045 (0.05)	0.04 (0.045)	0.02 (0.035)	0.025 (0.03)	..
Zn ²⁺	0.10	0.06 (0.065)	0.05 (0.06)	0.03 (0.045)	0.03 (0.035)	..
	0.05	0.07 (0.08)	0.055 (0.06)	0.05 (0.065)	0.05 (0.06)	..
	0.01	0.08 (0.09)	0.065 (0.07)	0.07 (0.085)	0.06 (0.075)	..

* Volume of electrolyte solution : 44 ml, volume of metal ion solution † 0.1 mol. l⁻¹ ; volume ; 1 ml ; time : 24 hr ; temp ; room temp.
 ‡ SUF-1 ; § SUF-2.

Table 2. Comparison of the rates of metal (M^{n+}) ion uptake^a.

Time in hr	Percentage of the amount of metal ions taken up ^b					
	Cu ²⁺	Fe ³⁺	UO ₂ ²⁺	Mn ²⁺	Co ²⁺	Zn ²⁺
0.5	62 ^c (71) ^d	51 ^c (55) ^d	40 ^c (46) ^d	19 ^c (21) ^d	13 ^c (15) ^d	16 ^c (16) ^d
1	71 (80)	64 (74)	69 (71)	33 (41)	23 (28)	28 (35)
2	85 (85)	83 (84)	93 (86)	41 (60)	42 (45)	45 (58)
3	91 (89)	93 (92)	98 (94)	59 (69)	55 (60)	57 (69)
4	94 (92)	96 (94)	99 (96)	70 (81)	64 (70)	68 (78)
5	94 (95)	98 (95)	99 (98)	78 (90)	73 (83)	80 (87)
6	95 (96)	98 (96)	99 (98)	81 (94)	81 (91)	87 (94)
7	95 (96)	98 (97)	...	93 (94)	89 (93)	91 (94)
8	85-	94-	95-

^a $[M^{n+}(NO_3)_n] = 0.1 \text{ mol. l}^{-1}$; volume: 1 ml. $[NaNO_3] = 1 \text{ mol. l}^{-1}$; volume: 44 ml for Cu²⁺, Fe³⁺ and UO₂²⁺ ions. $[NaNO_3] = 0.01 \text{ mol. l}^{-1}$; volume: 44 ml for Mn²⁺, Co²⁺ and Zn²⁺ ions; pH: 5 for Cu²⁺; 2.0 for Fe³⁺, 4.0 for UO₂²⁺ and 5.5 for Mn²⁺, Co²⁺ and Zn²⁺; temp: room temp.

^b Related to the amount of metal ions in the state of equilibrium (100%).

^c SUF-1; ^d SUF-2.

the metal ions in the aqueous solution in contact with the polymer, keeping in view the stability of the copolymers under study it was not possible to study the rate of metal uptake at high pH and in same concentration of electrolytes as discussed above of the various metal ions under study. The rate of uptake of Cu²⁺ during the first hour in both the copolymers is the highest. After 1 hr the rates of uptake of UO₂²⁺ and Fe³⁺ increase and are found to be higher than that of Cu²⁺ ion. Equilibrium is reached in the shortest possible time of 4 hr. For Cu²⁺ the equilibrium time is 5 hr. Mn²⁺, Zn²⁺ and Co²⁺ require almost the same time 7 hr. The overall rate of metal uptake follows the order UO₂²⁺ > Fe³⁺ > Cu²⁺ > (Mn²⁺ ≈ Co²⁺ ≈ Zn²⁺) for both the copolymers, but it is comparatively higher in SUF-2 than in SUF-1 copolymer (table 2).

3.3. Distribution ratio of metal ions at different pH

The effect of pH on the amount of metal ion distributed between two phases can be explained by the examination of results shown in table 3. The results indicate that the relative amount of metal ions taken up by the polymeric material increases with increasing pH of the medium. The study was carried out only up to pH 7 to prevent hydrolysis of the metal ions at higher pH. Both the copolymers are taking up UO₂²⁺ more selectively than any other metal ions under study. Cu²⁺ and Fe³⁺ ions are also taken up by the copolymers more selectively than Mn²⁺, Co²⁺ and Zn²⁺ which are taken up poorly. Hence, the results of this type of study are helpful in selecting the optimum pH for a selective uptake of a particular metal ion from a mixture of different metal ions. For example, the results for SUF-2 copolymer suggest the optimum pH 2 for the separation of Fe³⁺ and

Table 3. Distribution ratios D^a of different metal ions as a function of the pH.

pH	Distribution ratio of the metal ions					
	Cu ²⁺	Fe ³⁺	UO ₂ ²⁺	Mn ²⁺	Co ²⁺	Zn ²⁺
1.5	..	141.5 ^b (218.9) ^c
1.75	...	232.9 (320.2)
2.0	...	360.0 (528.6)	30.5 (46.1)
2.5	55.6 (92.7)	519.4 (651.0)
3.0	128.5 (163.6)	36.7 (65.0)	27.4 (74.0)	13.0 (46.0)
3.5	117.5 (334)	...	473.6 (489.1)
4.0	385.0 (616.1)	...	786.8 (1118.9)	65.2 (104.0)	74.9 (140.0)	46.0 (74.9)
5.0	553.0 (699.0)	149.0 (222.0)	114.8 (156.0)	94.0 (135.0)
5.5	156.0 (233.0)	...
6.0	188.9 (268.0)	...	135.0 (188.9)
7.0	222.4 (305)

$$^a D = \frac{\text{amount of metal on the copolymer}}{\text{amount of metal in the solution}} \times \frac{\text{volume of solution}}{\text{weight of copolymer}}; [M^{n+} (\text{NO}_3)_n] = 0.1$$

mol. l^{-1} ; volume : 1 ml; $\text{NaNO}_3 = 1 \text{ mol } l^{-1}$; volume : 44 ml for Cu²⁺, Fe³⁺ and UO₂²⁺; $\text{NaNO}_3 = 0.01 \text{ mol. } l^{-1}$; volume 44 ml for Mn²⁺, Co²⁺ and Zn²⁺; temp. : room temp.; time : 24 hr (equilibrium state).

^b SUF-1 :

^c SUF-2.

UO₂²⁺, at which the distribution ratio D of Fe³⁺ is 528 and that of UO₂²⁺ is 46. The observed order of distribution ratios of metal ions measured in the range of pH 1.5 to 7 is : UO₂²⁺ > Cu²⁺ > Fe³⁺ > Mn²⁺ > Co²⁺ > Zn²⁺.

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