

Anion Exchange Sorption of Some Transition Metals in Thioglycolic Acid at Different pH Values

M SITA RAMA REDDY & ANIMESH K GHOSE*

Chemistry Department, University of Allahabad, Allahabad 211 002

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Distribution coefficients of Fe(III), Cr(III), Pd(II), Ni(II), Co(II), Mo(IV), V(V) and dioxouranium(VI) have been determined in thioglycolic acid by batch equilibrium method. The sorption of the coloured complexes of these metals is pH dependent. The sorption of these metal complexes has been investigated at pH 2.5, 4.5 and 9.0 using a strongly basic anion exchanger Dowex 1-X8 (20-50 mesh, Cl⁻ form). Co(II) at pH 9.0; Fe(III), Co(II) at pH 4.5; and V(V), Cr(III), Fe(III), Co(II) at pH 2.5 show low sorption whereas other metal ions show appreciable sorption. Separation factors have been determined from the distribution coefficient (K_d) values as a function of thioglycolic acid concentration and suitable analytical conditions for the separation of the metal ions have been described. The important separations that can be effected in this media are: (i) Fe(III) from other metals at pH 4.5; (ii) Co(II) from other metals at pH 9.0; and (iii) Fe(III), Co(II), Cr(III), V(V) or dioxouranium(VI) from Mo(IV), Ru(II) or Pd(II) at pH 2.5.

Thioglycolic acid (TGA) also known as mercaptoacetic acid (HSCH₂COOH) is a well known reagent for the determination of iron, irrespective of its oxidation state in dilution upto 1:10⁷. TGA forms stable coloured complexes with iron, molybdenum, cobalt, nickel, chromium, uranium, vanadium, ruthenium, palladium, selenium and tellurium¹⁻⁸. However, its use in adsorption chromatography is very scanty^{7,9-11}. In the light of its interesting complexation reactions, a detailed study of the distribution coefficients of some transition metal ions using batch equilibrium technique has been made and the results are presented in this paper. Its use as a complexing agent is advantageous because the spectrophotometric determination of metal ions can be performed directly after equilibration.

Materials and Methods

Dowex 1-X8 (Cl⁻ form; 20-50 mesh) was treated with 1 mol/dm³ HCl and NaOH alternatively and washed with a large excess of water. It was converted into chloride form by passing 2 mol/dm³ HCl, excess of chloride ion removed by washing with water, dried under suction and stored in an air tight glass bottle. The capacity was 2.75 meq/g of the resin.

All the chemicals used were of reagent grade. Standard solutions of metal ions were prepared from their nitrates (BDH, AR), except those of molybdenum and vanadium which were prepared from ammonium molybdate and ammonium metavanadate respectively. Stock solution (10%) of thioglycolic acid was prepared from a pure Riedel product. Liquor ammonia (BDH, AR) was employed for pH adjustments.

A digital pH meter (Systronics, India) was used for pH measurements and Beckman model DU spectrophotometer was employed for absorbance studies.

Distribution coefficients—Solutions containing a constant amount of metal ion and varying concentrations of ligand were prepared and pH adjusted by adding ammonia, keeping the total volume constant (25 ml). Resin (1 g) was added to the flasks containing these solutions which were shaken mechanically for 1 hr. The solutions were filtered and analysed for total metal contents spectrophotometrically. The distribution coefficients were calculated by the relation

$$K_d = \frac{\text{meq of metal ion per g of resin}}{\text{meq of metal ion per ml of solution}}$$

All the experiments were carried out at room temperature 30 ± 2°C. The relative experimental error is ± 5 to ± 10% for lower and higher K_d values respectively.

Results and Discussion

The colour and adsorption maxima of the coloured species of TGA with different metal ions at various pHs are given in Table 1. The K_d values for the extraction of different metal ions at different pH values are given in Table 2 and the separation factors are given in Tables 3-5. Thioglycolic acid forms coloured complexes with metal ions having different charges. It has been recorded that no complexation occurs by the replacement of the first proton (carboxylic) of TGA but complexation occurs by the replacement of the second proton (thiol)^{1,2}.

Since, complexing agent which has a tendency to form anionic complex with a particular metal ion enhances its affinity towards anionic resins, the complexed metal ion in TGA medium could be selectively taken up by the anion exchanger and thus it is separated from other metal ions which remain in solution phase.

By observing the distribution coefficients at different pH values and at various concentrations of TGA three types of sorption order were found: (i) Co(II), dioxouranium(VI) at pH 2.5; and Ni(II), Cr(III) at pH 4.5 show an increase in K_d with increase in TGA concentration; (ii) Cr(III), Fe(III), Co(II), Ni(II), Pd(II), dioxouranium(VI) at pH 9.0; and V(V) at pH 2.5 and 4.5 show a decrease in K_d with increase in TGA concentration; (iii) Fe(III), Co(II), dioxouranium at pH 4.5; and Ni(II), Pd(II) at pH 2.5 show constant values of K_d even with increase in TGA concentration.

At pH 9.0 all the metals except Co(II) show higher K_d values at all concentrations of TGA, thus it can be retained by the resin when passed alongwith other metal ions. But at higher concentrations of TGA, Fe(III) and Cr(III) also show low sorption and may leave the column bed in preference to V(V), Ni(II), Mo(IV), Ru(III), Pd(II) and dioxouranium(VI).

Table 1—Colour and Absorption Maxima of Metal Ions

Metal ion	Colour at pH			λ_{max} (nm)
	2.5	4.5	9.0	
V(V)	Colourless	Green blue	Blue	400
Cr(III)	Red	Green blue	Blue	475
Fe(III)	Colourless	Colourless	Purple red	535
Ni(II)	Colourless	Red	Red	515
Mo(IV)	Yellow	Yellow	Yellow orange	365
UO ₂ ²⁺	Colourless	Yellow	Yellow	395
Co(II)	Colourless	Yellow red	Red	358
Pd(II)	Yellow	Yellow	Yellow	325

At pH 4.5 Fe(III) can be comfortably separated from all other metals under study due to its negligible sorption in comparison to other metal ions. Cr(III) at TGA concentration of 0.4 and 1.2 mol/dm³ has low

Table 2—Distribution Coefficients (K_d) in Thioglycolic Acid at Different pH Values

Metal ion	K_d at [TGA] $\times 10^{-5}$ (mol dm ⁻³)					
	0.4	1.2	2.0	4.0	6.0	8.0
At pH 2.5						
V(V)	31	31	16	13	13	8
Cr(III)	5	4	4	3	2	1
Fe(III)	5	4	4	3	2	1
Co(II)	4	6	7	10	13	20
Ni(II)	66	66	66	66	66	66
Mo(IV)	>10 ³	>10 ³	>10 ³	>10 ³	>10 ³	>10 ³
Ru(III)	>10 ³	>10 ³	>10 ³	>10 ³	>10 ³	>10 ³
Pd(II)	231	231	231	231	231	231
UO ₂ ²⁺	1	33	44	51	58	66
At pH 4.5						
V(V)	475	157	118	108	66	39
Cr(III)	8	15	41	171	>10 ³	>10 ³
Fe(III)	10	10	10	10	10	10
Co(II)	37	36	28	26	25	22
Ni(II)	160	213	>10 ³	>10 ³	>10 ³	>10 ³
Mo(IV)	>10 ³	>10 ³	>10 ³	>10 ³	>10 ³	171
Ru(III)	>10 ³	>10 ³	>10 ³	>10 ³	>10 ³	>10 ³
Pd(II)	253	253	212	212	212	183
UO ₂ ²⁺	167	167	167	167	167	167
At pH 9.0						
V(V)	>10 ³	>10 ³	>10 ³	>10 ³	>10 ³	>10 ³
Cr(III)	10 ³	10 ³	10 ³	145	41	24
Fe(III)	>10 ³	>10 ³	102	43	34	22
Co(II)	8	6	4	3	2	1
Ni(II)	10 ³	367	259	202	119	101
Mo(IV)	>10 ³	>10 ³	>10 ³	>10 ³	>10 ³	>10 ³
Ru(III)	>10 ³	>10 ³	>10 ³	>10 ³	>10 ³	>10 ³
Pd(II)	225	225	225	225	225	51
UO ₂ ²⁺	167	167	167	167	167	167

Table 3—Separation Factors in Thioglycolic Acid at pH 2.5

Metal ion	$(\alpha_M)^{-1}$ at [TGA] $\times 10^{-5}$ mol dm ⁻³									
	0.4		1.2		2.0		4.0		8.0	
	UO ₂ ²⁺	Fe=Cr	Fe=Cr	Co	Fe=Cr	Co	Fe=Cr	Co=V	Fe=Cr	Fe=Cr
V(V)	31.0	6.2	7.7	5.1	4.0	—	4.3	—	6.5	8.0
Cr(III)	5.0	—	—	—	—	—	—	—	—	—
Fe(III)	5.0	—	—	—	—	—	—	—	—	—
Co(II)	4.0	—	—	—	—	—	3.3	—	6.5	20.0
Ni(II)	66.0	13.2	16.5	11.0	16.5	9.4	22.2	5.0	33.0	66.0
Mo(IV)	v	v	v	v	v	v	v	v	v	v
Ru(III)	v	v	v	v	v	v	v	v	v	v
Pd(II)	231.0	46.2	57.7	38.5	57.7	33.0	77.0	17.7	115.5	231.0
UO ₂ ²⁺	—	—	8.2	5.5	11.0	6.2	17.0	4.0	29.0	66.0

v = very high; (—) = very low

Table 4—Separation Factors in Thioglycolic Acid at pH 4.5

Metal ion	$(\alpha_M)^{-1}$ at $[TGA] \times 10^{-5} \text{ mol dm}^{-3}$											
	0.4		1.2		2.0		4.0		6.0		8.0	
	Cr	Fe	Fe	Cr	Fe	Co	Fe	Co	Fe	Co	Fe	Co
V(V)	59.3	47.3	15.7	10.4	11.8	4.2	10.8	4.1	6.6	2.6	3.9	—
Cr(III)	—	—	—	—	4.1	—	17.1	6.5	v	v	v	v
Co(II)	4.6	3.7	3.6	2.4	—	—	2.6	—	2.5	—	2.2	—
Ni(II)	20.0	16.0	21.3	14.2	v	v	v	v	v	v	v	v
Mo(IV)	v	v	v	v	v	v	v	v	v	v	17.1	6.8
Ru(III)	v	v	v	v	v	v	v	v	v	v	v	v
Pd(II)	31.6	25.3	25.3	16.8	21.2	7.5	21.2	8.1	21.2	8.4	18.3	8.3
UO ₂ ²⁺	20.8	16.7	16.7	11.1	16.7	5.9	16.7	6.4	16.7	6.7	16.7	7.5

v=very high; (—)=very low

Table 5—Separation Factors in Thioglycolic Acid at pH 9.0

Metal ion	$(\alpha_M)^{-1}$ at $[TGA] \times 10^{-5} \text{ mol dm}^{-3}$										
	0.4		1.2		2.0		4.0		6.0		8.0
	Co	Co	Co	Co	Co	Fe	Cr	Co	Fe	Cr	
V(V)	v	v	v	v	v	v	v	v	v	v	v
Cr(III)	v	v	v	48.3	20.5	—	—	24.0	—	—	—
Fe(III)	v	v	25.5	14.3	17.0	—	—	22.0	—	—	—
Ni(II)	v	61.6	64.7	67.3	59.5	3.5	2.7	101.0	4.5	4.1	
Mo(IV)	v	v	v	v	v	v	v	v	v	v	v
Ru(III)	v	v	v	v	v	v	v	v	v	v	v
Pd(II)	28.1	37.5	56.2	75.0	112.5	6.6	5.2	51.0	2.3	2.1	
UO ₂ ²⁺	v	v	v	v	133.5	4.9	4.0	167.0	7.5	3.9	

v=very high; (—)=very low

values of sorption and hence leaves the column first in preference to other metal ions. V(V) at TGA concentration of 6.0 and 8.0 mol/dm³ also shows low sorption and, this, can be separated.

At pH 2.5 Co(II), Fe(III) and Cr(III) have negligible sorptions and can be separated from strongly sorbed V(V), Mo(IV), Ru(III), Pd(II) and dioxouranium(VI) under the experimental conditions. At the same time separation of dioxouranium(VI) from V(V) may also be possible at lower concentrations.

Se(IV) and Te(IV) form yellow complexes with TGA but these two metals turn black immediately when they come in contact with the resin, due to the reduction of the complexes to metallic form. The present study can be applied for the analysis of steels and alloys which contain Mo(IV), Fe(III), V(V), etc.

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