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CHROMATOGRAPHIC SEPARATION OF VANADIUM (IV) FROM VANADIUM (V) AND IRON (II) FROM IRON (III)

K RAVINDHRANATH

Department of Chemistry, Engineering College, Bapatla-522 100, Guntur DT.,A.P., India

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Chromatographic separations of quadrivalent vanadium ions from quinquevalent vanadium ions and ferrous ions from ferric ions, are described. In the case of Iron, the bi- and tri-valent ions are first converted quantitatively into their respective chelates of α-nitroso-β-napthol or 2-2′-bipyridyl. Thus obtained chelates are subjected to chromatographic migration. Unitary, binary and ternary solvent systems of diverse nature are used as eluents. Conditions are optimized to get quick, simple and quantitative separations. The dgeree of quantitativeness of separations is assessed by estimating the resolved species (ions or chelates) of different valency states of vanadium and iron spectrophotometrically.

Key Words : Chromatography; Separation and Analysis; V(IV)—from V(V); Fe(II)—from Fe(III)

INTRODUCTION

THE previous works[1–3] available on the chromatographic separation of V(IV) from V(V) are inconclusive and qualitative in nature. Though, there are some works available in separating the ferrous from ferric in their simple ionic forms[3–6], the new chromatographic line of work of converting the species of different valency states of iron, viz., ferrous and ferric, into their respective chelates and submitting thus obtained chelates for chromatography, is not reported in the literature. Such chelation, before actual chromatographic migration, is expected to enhance the physico-chemical differences between the ions and thereby facilitate the quick, easy and quantitative separations.

The present work is a comprehensive report on the separation of V(IV) from V(V) and Fe(II) from Fe(III) with respect to observations and their interpretations. Of the various complexing and chelating agents studied as 'via media', α-nitroso-β-napthol and 2-2′-bipyridyl were found to be successful in achieving quick and quantitative separations of Fe(II) from Fe(III).

EXPERIMENTAL

Preparation of Solutions :

(*a*) *V(IV) and V(V) Solutions* : Solutions of V(IV) and V(V) were prepared from $VOSO_4$ and V_2O_5 respectively and standardized. The acidity of the

solutions was kept at 4N with respect to H_2SO_4. The species expected to be present are $VO_2SO_4^-$ and $VO(SO_4)_2^-$ for V(V) and VO^{2+} for V(IV).

(*b*) *Fe(II) and Fe(III) α-nitroso-β-naptholates* : Aliquots containing know amounts of iron (ferrous of ferric or a mixture of both the ions) were adjusted to *p*H 4 with dil. acetic acid. Then the aqueous solutions were subjected to repeated extractions with $CHCl_3$ containing 0.1 per cent of α-nitroso-β-napthol. Under these conditions, the conversion of ions into their complexes is quantitative and any fluctuations in the red-ox ratio of the valences are practically negligible.

(*c*) *Fe(II) and Fe(III) Bipryidyls* : To an aliquot of ferrous or ferric or an admixture of both, excess of 1 per cent alcoholic solution of 2-2′-bipyridyl was added and the resulting solutions were diluted to a definite volume, adjusting the *p*H to 3 with dil. HCl or dil. NaOH.

Technique

Rutter's[7] technique of circular paper chromatography was adopted using circular discs of Whatman No. 1 Chromatographic grade filter paper of 12 cm diameter. Individual species (ionic or chelates) of the same valency state or mixture of species (ionic or chelates) of different valency states, were spotted at the centre of the paper discs using Micrometer Syringe. The spots were air dried and eluted with unitary, binary and ternary solvent systems of diverse nature. In the case of separation of Iron (II) from Iron (III) via bipyridyls, the spots were to be eluted without drying because Iron (III) bipyridyl was found to be partially reduced to Iron (II) bipyridyl on drying. The elution of wet spots prevented the partial reduction.

Some of the important results are presented in the Tables I & II.

Detection

V(IV) and V(V) revealed themselves as deep yellow and black bands respectively with the spraying reagent, 1 per cent alcoholic solution of 8-hydroxyquinoline. As Fe(III) (α-nitroso-β-naptholate)$_3$, Fe(II) (α-nitroso-β-naptholate)$_2$.$2H_2O$ and ferrous bipyridyl have dark brown, intensive green and deep red colours respectively, no spraying reagent is needed and the chelates revealed themselves by their own colours. Ferric bipyridyl appeared as blue with aqueous potassium ferrocyanide.

Results and Discussion

Separation of V(IV) from V(V)

Successful quantitative separations are found :-

(*i*) In *n*PrOH *t*BuOH or Acetone containing 5 per cent of Conc. HNO_3 (*vide* Table I, item Nos. 1-3).

TABLE I

Migratory Behaviour of V(IV) *and* V(V)

QUALITY SPOTTED : 50 μg each of V(IV) & V(V) as V

Sl. No.	Eluents		R_f Values*		Estimation†	
			V(IV)	V(V)	V(IV)	V(V)
1.	*n*PrOH : Con. HNO_3	(95 : 5)+	0.32	0.72	50.62	50.45
2.	*t*BuOH : Con. HNO_3	(95 : 5)+	0.30	0.65	50.31	50.52
3.	Acetone : Con. HNO_3	(95 : 5)+	0.31	0.62	49.61	50.64
4.	Acetone : Con. HCl	(95 : 5)+	0.28	0.51^f & 0.47^s	49.51	49.61
5.	*n*PrOH : Con. HCl	(95 : 5)+	0.34	0.75^f & 0.63^s	49.30	50.22
6.	EtOH : *n*PrOH	(40 : 60)+	0.42^d	0.72	50.44	50.35
7.	EtOH : *t*BuOH	(40 : 60)+	0.25^d	0.68	50.24	50.21
8.	EtOH : *i*BuOH	(60 : 40)+	0.20^d	0.72	49.30	49.47
9.	EtOH : *i*AmOH	(60 : 40)+	0.15^d	0.68	50.12	49.85
10.	Water: nPrOH	(40 : 60)	0.78	0.42 & 0.82	—	—
11.	Water : tBuOH	(40 : 60)+	0.57	0.29 & 0.77	50.46	50.28
12.	Water : Acetone	(40: 60)+	1.00	0.40	50.38	50.24
13.	EtOH : Acetone : Con. HNO_3	(20 : 75 : 5)+	0.29	0.53	50.27	50.17
14.	EtOH : EtOAc : Con. HNO_3	(40 : 55 : 5)+	0.25	0.60	49.78	49.82
15.	EtOH : *i*BuOAc : Con. HNO_3	(40 : 55 : 5)+	0.16	0.50	49.53	49.63
16.	EtOH : *i*AmOAc: Con. HNO_3	(40 : 55 : 5)+	0.20	0.44	50.39	50.29
17.	EtOH : Ether : Con. HNO_3	(40 : 55 : 5)+	0.25	0.53	50.33	49.97
18.	EtOH : MeEtCO : Con. HNO_3	(40 : 55 : 5)+	0.31	0.62	49.65	49.85

* average value of four runs; *d*–diffusion; *f*–faint band; *s*–strong band

'+' — good separation; † average value of four estimations.

(*ii*) In Acetone or *n*PrOH containing 5 per cent of Conc.HCl (*vide* Table I, item Nos. 4 & 5).

(*iii*) In the binary blends of EtOH with other aliphatic alcohols at the optimum composition (40 : 60) or (60 : 40) (*vide* Table I, item Nos. 6–9).

(*iv*) In aqueous solutions of *t*BuOH and Acetone at optimum 60 per cent (*vide*) Table I : item Nos. 11 & 12).

(*v*) In ternary solvent systems containing EtOH as one component at optimum percentages (*vide* Table I : item Nos. 13–18).

In most of these eluents, V(V) shows relatively greater mobility than V(IV). It is probably due to the fact that the species of V(V) are relatively easily solvated than the V(IV) species.[8,9]

Separation of Iron (II) from Iron (III)

a. Separation via α-nitroso-β-naptholates—The solvent systems tried for the separation are presented in Table No. II : A. The separations are achieved :

TABLE II

Migratory Behaviour of iron (II) & iron (III) α-nitroso-β-naphtholates and iron (II) & iron (III) bipyridyls

Sl. No.	Eluents		R_f Values*		Estimaton†	
			Fe(II)	Fe(III)	Fe(II)	Fe(III)
A :	*via α-nitroso-β-naptholates* :					
1.	$CHCl_3$		1.00	1.00		
2.	Benzene+, Toluene+, CCl_4+, or PHCl+		0.12*d* to 0.63*d*	1.00	19.50 to 20.24	10.40 to 20.15
3.	$CHCl_3$: Pet. ether	(30 : 70)	0.28	1.00	20.23	20.34
4.	$CHCl_3$: Heptane	(20 : 80)+	zero	1.00	19.56	19.62
5.	$CHCl_2$: Benzene	(20 : 80)+	0.55	1.00	20.14	20.34
6.	$CHCl_3$: CCl_4	(20 : 80)+	0.35	1.00	20.62	20.45
7.	*i*BuOAc : Toluene	(4 : 96)+	0.59	1.00	20.42	19.67
8.	*i*AmOAc : Toluene	(4 : 96)+	0.64	1.00	20.15	20.25
9.	Acetone : Toluene	(1 : 99)+	0.36	1.00	19.42	19.67
10.	Acetone : Hexane	(4 : 96)+	0.62	1.00	20.29	20.54
B :	*via bipyridyls* :					
1.	Water		0.20*d*	zero	—	—
2.	1.ON Ammonia		0.21*d*	zero	—	—
3.	Neutral sat. solution of KCl		1.00	1.00*d*	—	—
4.	1.ON Ammonia sat. with KCl+		1.00	zero	20.20	20.42
5.	*t*BuOH : Water	80 : 20+	0.15 & 0.36	zero	20.35	20.44
		60 : 40+	0.35 & 0.79	zero	19.40	19.64
		40 : 60	0.25*d* & 1.00	zero	—	—
		20 : 80	0.26*d* & 1.00	zero	—	—
6.	Acetone : Water	80 : 20+	0.14 & 0.26	zero	20.21	19.70
		60 : 40+	0.66 & 1.00	zero	20.43	20.52
		40 : 60	0.35*d* & 1.00	zero	—	—
		20 : 80	0.37*d* & 1.00	zero	—	—

* —Average value of four runs; *d* — diffusion; '+' — good separation; † average value of four estimations

(*i*) in non-donor active solvents like Benzene, Toluene, CCl_4 and C_6H_5Cl, wherein the ferric complex sharply migrated to the solvent front while ferrous complex seldom migrated (*vide* Table II : A : item No. 2).

(*ii*) in the binary blends of donor active solvents with aromatic or aliphatic hydrocarbons at optimum compositions, wherein both the complexes show sharp band-type of migration; ferric complex shows greater migration than ferrous complex (*vide* Table No. II:A : item Nos. 3–10).

These observations can be accounted from the structural differences of the two complexes. Ferrous complex is a coordination unsaturated chelate having two water molecules coordinated to the central metal ion, Fe (α-nitroso-β-naptholate)$_2$.$2H_2O$ while ferric complex is a coordination saturated chelate having no vacancy left in the coordination sites of the central metal ion, Fe (α-nitroso-β-naptholate)$_3$.[10–13] So, ferrous complex is expected to be dissolved in donor-active

organic solvents which either block or displace coordinated water molecules of the complex and not in non-donor active solvents. Hence, ferrous complex shows sharp band-type migration in donor active solvents or in binary blends containing an optimum amount of donor active solvent and not in the non-donor active solvents. On the other hand, ferric complex having closely packed structure is soluble in solvents of diverse nature wherein the chelating agent dissolves. Hence, the complex shows sharp band-type migration both in donor active solvents like ketones and esters and also in non-donor active solvents like Benzene, Toluene, CCl_4 and PhCl.

(*b*) *Separations via Bipyridyl Complexes*—Eluents tried for separation are presented in Table No. II : B. The successful separations are found :

(*i*) in 1. ON ammonia saturated with KCl wherein the ferrous complex migrates sharply to the solvent front leaving ferric as its hydroxide at the origin (*vide* Table No. II : B : item No. 4).

(*ii*) in aq. acetone or aq. *t*BuOH containing 20–40 per cent of water wherein the ferrous complex shows sharp double band migration while ferric remains at the origin (*vide* Table No. II : B : item Nos. 5 & 6)

In neutral water or in 1. ON ammonia, the paper is negatively charged due to dissociation of functional groups of cellulose.[14–15] So, the positively charged ferrous bipyridyl, $Fe(dip)_3^{2+}$, is strongly adhered to the paper due to electrostatic attraction but if the eluents loaded with KCl are used, the electrostatic adsorption is palliated and hence the ferrous complex shows sharp migration in the water or 1. ON ammonia loaded with KCl. In these eluents ferric remains essentially at the origin because of its precipitation as hydroxide.

In the binary blends, the mechanism changes from electrostatic adsorption to that of physical adsorption,[14,15] because the decrease in the percentage of water content in the blends, decreases the dielectric constant and hence dissociation of –OH groups of cellulose is less favoured. So the migration of the ferrous complex is expected in these binary blends only when the adsorption is physical in nature and the eluents possess adequate physical forces to desorb and solubilize the complex. 20–40 per cent of water in the blend is found to be optimum because ferrous moves off from the centre as two sharp bands while ferric remains as its hydroxide at the origin. Above this optimum range, electrostatic adsorption also comes into play along with the physical adsorption and hence some part of ferrous complex remains at the origin due to the electrostatic adsorption while the rest moves off sharply due to the desorption of the physically adsorbed complex and subsequent solubilization by the eluents.

Estimation

Regions corresponding to the separated species (ionic or chelates) were cut out from the paper chromatogram and extracted with 0.1N H_2SO_4. The washings were combined and concentrated to a definite volume. Spectrophotometrically,

the amount of Vanadium was estimated by oxine method[16] and Iron by O-phenanthroline method.[17] Results are presented in the Table Nos. I & II. The percentage of error ranges from-1.40 per cent to + 1.28 per cent for the separations of V(IV) from V(V) and—3.00 per cent to + 3.10 per cent for the separations of Fe(II) from Fe (III). Quantitative separations are found with the eluents marked with '+' in the Table Nos. I & II.

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