Sodium Alizarin-3-Sulphonate as a Chromophoric Reagent. V[1])

Colorimetric Determination of Vanadium (V)

By Surendra Nath Sinha and Arun K. Dey

With 3 Figures

Abstract

The formation of a red coloured chelate (λ_{max} 455 mμ) between ammonium vanadate and sodium alizarin-3-sulphonate has been taken advantage of, in the colorimetric determination of pentavalent vanadium on a micro-scale. The colour formation is instantaneous and the colour intensity is constant between 5 °C and 70 °C and pH 3.5 and 5.8. The system adheres to Beers Law over a range of 0.10 to 3.67 p. p. m. of vanadium. The sensitivity is 0.051 γ/cm^2 (Sandell) and 0.51 γcm^2 (Practical) Copper, beryllium, bismuth, iron, aluminum, cerium, uranium, thorium, tungsten, molybdenum, carbonate, borate, citrate, and tartrate interfere in the determination.

In a large number of publications from these laboratories[2-5]) the chromophoric properties of sodium-alizarin-3-sulphonate with various metal ions have been reported. Some of these colour producing reactions have been used in the colorimetric determinations of metals viz., uranium[6]), copper[7]), tungsten[8]), molybdenum[9]) and thorium[10]). Dey and coworkers[11-12]) observed the formation of a red coloured chelate (λ_{max} 455 mμ) between vanadium (V) and the reagent. They found the composition 1:2

[1]) Part IV: S. N. Sinha and A. K. Dey, Z. analyt. Chem. (in press).

[2]) S. K. Banerji and A. K. Dey, J. Sci. Ind. Research (India) 20 B, 58 (1961).

[3]) S. K. Banerji and A. K. Dey, J. Ind. Chem. Soc. 38, 121 (1961).

[4]) S. K. Banerji and A. K. Dey, Z. analyt. Chem. 179, 30 (1961).

[5]) A. K. Dey, A. K. Mukherji and S. K. Banerji, XVII Int. Cong. Pure Appl. Chem., Munich, Abstract A 1072 (1959).

[6]) A. K. Mukherji and A. K. Dey, Z. analyt. Chem. 160, 98 (1958).

[7]) A. K. Mukherji and A. K. Dey, Bull. Chem. Soc. Japan 31, 521 (1958).

[8]) S. N. Sinha and A. K. Dey, Z. analyt. Chem. 185, 182 (1961).

[9]) S. N. Sinha and A. K. Dey (communicated).

[10]) S. N. Sinha and A. K. Dey (communicated).

[11]) S. K. Banerji and A. K. Dey, Z. anorg. Chem. 309, 226 (1961).

[12]) R. L. Seth and A. K. Dey, J. Ind. Chem. Soc. 39, 724 (1962).

of the metal and the reagent in the chelate and the stability constant was determined by them and log K found to be 8.6 ± 0.3.

In the present communication we have described our attempt to utilize the chelate formation for the colorimetric determination of vanadium (V) on a micro-scale.

Experimental

Spectrophotometric Measurements

Absorbance measurements were carried out with a Unicam SP 500 spectrophotometer. The colorimetric measurements were made with a Klett Summerson photoelectric colorimeter as described earlier[8]). pH measurements were made with a Leeds and Northrup line operated pH indicator.

Reagents

Solutions of sodium alizarin-3-sulphonate and ammonium vanadate (E. MERCK sample) were prepared in double distilled water.

All other reagents used were of analytical grade.

All measurements were made at 25 °C.

Beer's Law

A series of mixtures were prepared by adding varying amounts (2, 4, 6, 8 . . . 18 ml) of ammonium vanadate to a fixed volume (20 ml) of the reagent solution and the pH was adjusted to 4.5 ± 0.2. The total volumes were raised to 50 ml by the addition of water and the mixtures were allowed to equilibrate for 10 minutes. The colour intensity was measured with a photoelectric colorimeter using a blue filter Klett No. 44 (transmission 410—480 mμ). Figs. 1 and 2 show that the system adheres to Beer's Law over the range of 0.10 to 3.67 p. p. m. of vanadium.

Rate of Colour Formation

The rate of colour formation does not depend upon reaction time and takes less than 5 minutes to assume its full colour intensity.

Effect of Temperature on the stability of colour

A mixture containing 1.0×10^{-4} M ammonium vanadate and 2.0×10^{-4} M Alizarin Red S was kept for 48 hours and no change in the absorbance value was observed even after this period. The same mixture was heated to various degrees of temperature and there was no marked change in the colour intensity over a wide range of temperature upto 70 °C (Table I).

Table I

Concentration of ammonium vanadate $= 1.0 \cdot 10^{-4}$ M
Concentration of Alizarin Red S $= 2.0 \cdot 10^{-4}$ M
pH of the mixture $= 4.5 \pm 0.2$

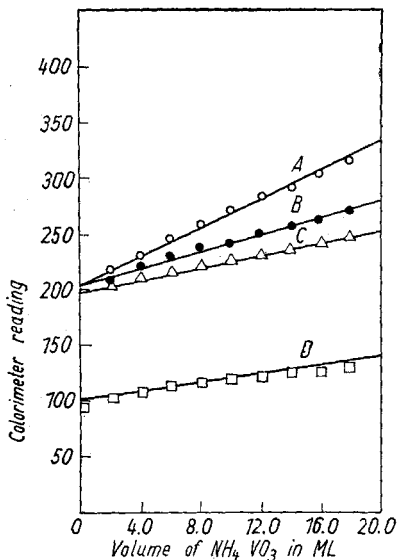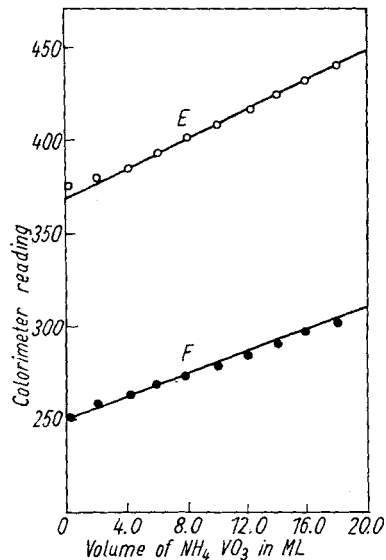| Temperature °C	5	10	20	30	40	50	60	70	80	90	95
Colorimeter Reading	305	305	305	305	305	305	305	305	280	250	225

Fig. 1   Fig. 2

Figs. 1 and 2. Adherence to Beer's Law. (Total value 50 ml.)
A 20 ml $5.0 \cdot 10^{-4}$ M Alizarin Red S, x ml $2.0 \cdot 10^{-4}$ M NH_4VO_3
B 20 ml $5.0 \cdot 10^{-4}$ M Alizarin Red S, x ml $1.0 \cdot 10^{-4}$ M NH_4VO_3
C 20 ml $5.0 \cdot 10^{-4}$ M Alizarin Red S, x ml $5.0 \cdot 10^{-5}$ M NH_4VO_3
D 20 ml $2.5 \cdot 10^{-4}$ M Alizarin Red S, x ml $5.0 \cdot 10^{-5}$ M NH_4VO_3
E 20 ml $1.0 \cdot 10^{-3}$ M Alizarin Red S, x ml $1.0 \cdot 10^{-4}$ M NH_4VO_3
F 20 ml $6.66 \cdot 10^{-4}$ M Alizarin Red S, x ml $6.66 \cdot 10^{-5}$ M NH_4VO_3

Influence of pH

The colour is stable between pH 3.5 to 5.8 as represented in Fig. 3.

Sensitivity

The sensitivity is 0.051 γ/cm^2 at 455 mμ (Sandell).

Four solutions containing 0.51 p. p. m. of vanadium showd the absorbance values 0.009, 0.010, 0.010 and 0.010 unit respectively. Hence the practical sensitivity, based on a absorbance value of 0.010 unit is 0.51 γ/cm^2.

15*

Table II
Concentration of ammonium vanadate $= 6.60 \cdot 10^{-5}$ M
Concentration of Alizarin Red S $= 4.00 \cdot 10^{-4}$ M
pH of the mixture $= 4.5 \pm 0.2$

Foreign ion	Added as	Concentration of ion p. p. m.	Observed change in absorbance %	Tolerance limit p. p. m.
Li^+	LiCl	210	+ 3	Large excess
		140	+ 2	
Ag^+	$AgNO_3$	216	+ 4	
		108	+ 2	Large excess
Pb^{2+}	$Pb(NO_3)_2$	140	− 5	
		55	− 2	55
Hg^{2+}	$HgCl_2$	900	− 6	
		300	− 2	Large excess
Bi^{3+}	$Bi(NO_3)_3$	Interferes at all concentrations		0
Cu^{2+}	$CuSO_4$	Interferes at all concentrations		0
Cd^{2+}	$CdSO_4$	560	+ 3	
		336	+ 2	Large excess
ASO_3^{3-}	H_3ASO_3	240	− 4	
		112	+ 2	Large excess
Sb^{3+}	$SbCl_3$	372	− 3	
		248	+ 2	Large excess
Fe^{2+}	$(NH_4)_2Fe(SO_4)_2$	Interferes at all concentrations		0
Fe^{3+}	$FeCl_3$	Interferes at all concentrations		0
Al^{3+}	$Al(NO_3)_3$	Interferes at all concentrations		0
Cr^{3+}	$CrCl_3$	208	+ 3	
		146	+ 2	Large excess
Zn^{2+}	$ZnCl_2$	520	− 4	
		260	− 2	Large excess
Mn^{2+}	$MnSO_4$	165	− 3	
		77	− 2	77
Co^{2+}	$Co(NO_3)_2$	356	+ 3	
		236	+ 2	Large excess
Ni^{2+}	$NiSO_4$	475	+ 3	
		356	+ 2	Large excess
Ba^{2+}	$BaCl_2$	1370	− 5	
		548	− 2	Large excess
Sr^{2+}	$Sr(NO_3)_2$	704	+ 3	
		528	+ 2	Large excess

Table II (Continuation)

Foreign ion	Added as	Concentration of ion p. p. m.	Observed change in absorbance %	Tolerance limit p. p. m.
Ca^{2+}	$CaCl_2$	400	+ 6	
		136	+ 2	Large excess
Mg^{2+}	$MgSO_4$	.240	− 3	
		144	− 2	Large excess
Be^{2+}	$BeSO_4$	Interferes at all concentrations		0
Zr^{4+}	$ZrOCl_2$	728	− 6	
		154	− 2	Large excess
Ce^{3+}	$Ce_2(SO_4)_3$	Interferes at all concentrations		0
Ce^{4+}	$Ce(SO_4)_2$	Interferes at all concentrations		0
MoO_4^{2-}	$(NH_4)_2MoO_4$	Interferes at all concentrations		0
CrO_4^{2-}	K_2CrO_4	208	+ 4	
		104	+ 2	Large excess
WO_4^{2-}	Na_2WO_4	Interferes at all concentrations		0
SO_3^{2-}	H^2SeO_3	790	− 10	
		158	− 2	Large excess
TeO_3^{2-}	K_2TeO_3	640	+ 6	
		219	+ 2	Large excess
UO_2^{2+}	UO_2SO_4	Interferes at all concentrations		0
Th^{4+}	$ThCl_4$	Interferes at all concentrations		0
Au^{3+}	$AuCl_3$	156	− 6	
		45	− 2	45
F^-	NaF	768	− 4	
		384	− 2	Large excess
Cl^-	KCl	875	− 3	
		672	− 2	Large excess
Br^-	KBr	1200	− 3	
		800	− 2	Large excess
I^-	KI	740	− 4	
		380	− 2	Large excess
ClO_3^-	$KClO_3$	1554	− 5	
		630	− 2	Large excess
NO_2^-	$NaNO_2$	880	− 4	
		440	− 2	Large excess
NO_3^-	$NaNO_3$	1320	− 5	
		550	− 2	Large excess

Table II (Continuation)

Foreign ion	Added as	Concentration of ion p. p. m.	Observed change in absorbance %	Tolerance limit p. p. m.
CNS^-	KCNS	1360	— 2	
		910	— 2	Large excess
SO_4^{2-}	K_2SO_4	1150	— 4	
		580	— 2	Large excess
SO_3^{2-}	$Na_2S_2O_3$	780	— 4	
		400	— 2	Large excess
$S_2O_8^{2-}$	$K_2S_2O_8$	1375	— 3	
		940	— 2	Large excess
CO_3^{2-}	Na_2CO_3	Interferes at all concentrations		0
Acetate	$NaC_2H_3O_2$	1240	— 6	
		420	— 2	Large excess
Oxalate	$K_2C_2O_4$	2200	— 6	
		792	— 2	Large excess
Citrate	Na_3Cit	Interferes at all concentrations		0
Tartrate	K_2Tart	Interferes at all concentrations		0
$B_4O_7^{2-}$	$Na_2B_4O_7$	Interferes at all concentrations		0
PO_4^{3-}	NaH_2PO_4	1440	— 5	
		590	— 2	Large excess

Foreign ions

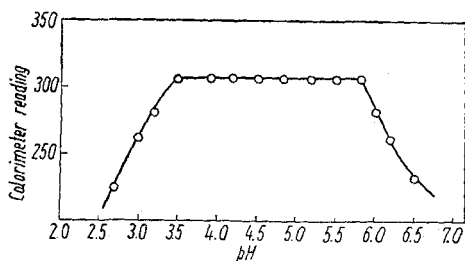The effect of various cations and anions was studied and the tolerance limits in each case determined. Tolerance limit is the concentration of foreign ion which affects the absorbance of the system by less than $\pm$ 2 percent. From the following table it may be seen that Cu(II), Be(II), Bi(III), Fe(II), Fe(III), Al(III), Ce(III), Ce(IV), UO_2(II), Th(IV), W(VI), Mo(VI), carbonate, borate, citrate, and tartrate interfere at all concentrations.

Fig. 3. Variation of colour intensity with pH. $NH_4VO_3 = 1.0 \cdot 10^{-4}$ M; Alizarin Red S = $2.0 \cdot 10^{-4}$ M

Recommended Procedure

In order to determine vanadium using Alizarin Red S, the interfering substances should be removed as usual. The pure sample of vanadium then

be diluted suitably and treated with an excess of freshly prepared solution of the reagent. The pH should be maintained between 3.5 to 5.8 and the colour intensity may be measured with a photoelectric colorimeter employing an appropriate filter or with a spectrophotometer.

Allahabad (India), Chemical Laboratories, University of Allahabad.