



KINETIC VANADIMETRIC ESTIMATION OF D- GLUCOSE

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Abstract

Kinetic vanadimetric estimation of D-Glucose in sulphuric acid medium has been carried out after elaborating the kinetic and mechanistic features of this redox indicator reactions which can be expressed as



This reaction followed first order kinetics with respect to initial concentrations of vanadium (V), D-glucose and sulphuric acid under present experimental conditions with the formation of intermediate C- centered free radical and D-arabinose as initial reaction product. The observed decreasing absorbance with time at different initial concentrations of respective D-glucose has been used for the kinetic estimations adopting (a) Rate constant, (b) variation of absorbance at fixed time (c) variation of time at fixed absorbance of (d) One point and (e) Two point methods using respective calibration plots .The consistency and reproducibility of these results have clearly showed these kinetic vanadimetric estimations of D-glucose can be used as an alternative/additional analytical method to the existing traditional estimation methods in the present day laboratory conditions and also as advance laboratory experiments/student's projects.

Key Words: Kinetic estimation, D-Glucose, Vanadium (V) oxidation, Electron transfer reaction,

I. INTRODUCTION

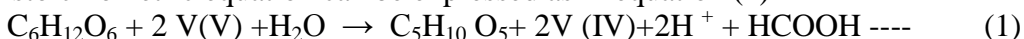
Kinetic (reaction-rate) methods have undergone wide development in the last few years. The reaction used for kinetic determination is known as “indicator reaction”, which must be thermodynamically favored and its mechanism and kinetic factors should be well explored. The rate data of such indicator reactions thus obtained is then used for estimation by employing different computational methods./1/ Vanadium (V) is commonly used in laboratory as a powerful and versatile electron transfer one equivalent reagent in number of kinetic and mechanistic studies involving various organic substrates /2/The present report regarding vanadimetric estimation of D-Glucose is a logical extension of earlier work of detailed kinetic , mechanistic and analytical studies of electron transfer reactions of metal ions with various reducing sugars and alditols./3/.

II. RESULTS AND DISCUSSION

The rate data of indicator electron transfer reaction between aldoses and vanadium (V) were obtained with using Shimadzu Pharmaspec-UV-1700, kinetic model spectrophotometer by measuring changing absorbance at 214 nm due to changing concentration of vanadium (V) in sulphuric acid medium under pseudo first order conditions.

Reaction product analysis was done in the left over reaction mixture of kinetic run. Formation of HCOOH and D-arabinose were confirmed by usual spot test ,paper chromatography and HPLC Formation of respective intermediate C-centered free radical were confirmed by induced polymerization

with acryl nitrile which is consistent with the earlier results of EPR spin trapping studies/4/. Thus the general stoichiometric equation can be expressed as in equation (1)



The linear dependence of pseudo first order rate constant $k_{obs.}(s^{-1})$ with initial concentrations of D-glucose (Table 1) have been used for kinetic vanadimetric estimations of D-glucose using methods used in earlier studies/3/

TABLE – 1 VARIATION OF ABSORBANCE WITH D-GLUCOSE CONCENTRATION

$10^4 [V (V)] = 5.0 \text{ mol dm}^{-3}$

$[H_2SO_4] = 1.45 \text{ mol dm}^{-3}$

Temperature = $296 \pm 0.5 \text{ K}$

$\lambda = 214 \text{ nm}$

10^{-2} Time (sec.)	----- 10 [D-glucose] (mol dm ⁻³) -----				
	2.00	3.00	4.00	5.00	7.00
0	1.335	1.335	1.335	1.335	1.335
3	1.274	1.245	1.216	1.192	1.151
6	1.219	1.183	1.165	1.135	1.072
9	1.16	1.142	1.125	1.090	1.014
12	1.125	1.105	1.084	1.043	0.966
15	1.093	1.073	1.051	1.010	0.918
18	1.063	1.039	1.017	0.975	0.879
21	1.035	1.011	0.984	0.942	0.840
24	1.014	0.976	0.958	0.915	0.805
27	0.994	0.962	0.935	0.886	0.775
30	0.972	0.942	0.910	0.861	0.743
33	0.959	0.923	0.887	0.835	0.715
36	0.943	0.906	0.869	0.814	0.691
39	0.925	0.891	0.850	0.795	0.670
42	0.906	0.878	0.831	0.777	0.649
$10^5 K_{obs} (s^{-1})$	12.23±0.04	14.09±0.07	15.91±0.05	18.59±0.03	24.76±0.01

10^{-2} Time in seconds	----- 10 [D-glucose] (mol dm ⁻³) -----					
	8.00	9.00	11.00	12.00	simulated - 1	simulated - 2
0	1.335	1.335	1.335	1.335	1.335	1.335
3	1.138	1.117	1.075	1.061	1.166	1.101
6	1.047	1.025	0.960	0.931	1.099	0.995
9	0.985	0.955	0.875	0.835	1.045	0.922
12	0.928	0.896	0.818	0.753	0.999	0.859
15	0.875	0.841	0.764	0.692	0.961	0.809
18	0.831	0.795	0.711	0.635	0.925	0.755
21	0.788	0.750	0.660	0.583	0.891	0.715
24	0.750	0.709	0.618	0.542	0.862	0.665
27	0.715	0.675	0.580	0.505	0.834	0.627
30	0.681	0.645	0.555	0.481	0.802	0.601
33	0.656	0.627	0.534	0.461	0.775	0.577
36	0.633	0.605	0.514	0.442	0.750	0.555
39	0.613	0.575	0.495	0.425	0.728	0.537
42	0.592	0.565	0.479	0.408	0.705	0.521

$10^5 k_{obs.}$ (s^{-1})	27.76 ± 0.09	30.27 ± 0.02	36.93 ± 0.04	42.08 ± 0.01	21.88 ± 0.03	33.22 ± 0.02
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Vanadimetric Estimation of D-glucose

(A) Rate constant method The rate of present indicator reaction has been determined by observing decreasing concentration of V(V) in terms of absorbance with time at constant temperature as
 $-d[V(V)]/dt = k_s [V(V)] [D\text{-glucose}]_0 [H_2SO_4]_0 = k_0 [A_0] [Aldose]_0$ at constant $[H_2SO_4]_0$

$$\text{Thus } k_{obs} = k_0 [D\text{-Aldose}]_0 \tag{2}$$

The estimation of simulated sample has been done from the linear variation of k_{obs} with changing concentration of D-glucose. Calibration plot was obtained between k_{obs} and $[D\text{-glucose}]$ and the concentration of simulated samples of D-glucose was determined from the “best fit” regression equations.

(A) Rate Constant Method

S.No.	10 [D-glucose] mol dm ⁻³	$10^5 k_{obs.}$ (s^{-1})
1	0.50	12.23 \pm 0.04
2	0.75	14.09 \pm 0.07
3	1.25	15.91 \pm 0.05
4	1.50	18.59 \pm 0.03
5	1.75	24.76 \pm 0.01
6	2.25	27.76 \pm 0.09
7	2.50	30.27 \pm 0.02
8	2.75	36.93 \pm 0.04
9	3.00	42.08 \pm 0.01
10	Simulated-1	21.88\pm0.03
11	Simulated-2	33.22\pm0.02

Regression Equation $10^5 k_{obs.} = 2.9362 [D\text{-glucose}] + 4.8739$ Corr. Coeff. = 0.99

Results:

10[simulated -1] (mol dm⁻³)	5.89(Calculated): 6.00 (Actual)
10[simulated -2] (mol dm⁻³)	9.86(Calculated): 10.00 (Actual)

(B) Fixed time method Fixed (C) Fixed absorbance (concentration) method

The concentration of V(V) i.e. changing absorbance $\Delta[A_t]$ with finite time interval can be expressed in terms of equation (3)

$$\Delta [Absorbance]_t / \Delta t = k_0 [Aldose] ; \text{Thus, } [Absorbance]_t = k [Aldose]_0 \tag{3}$$

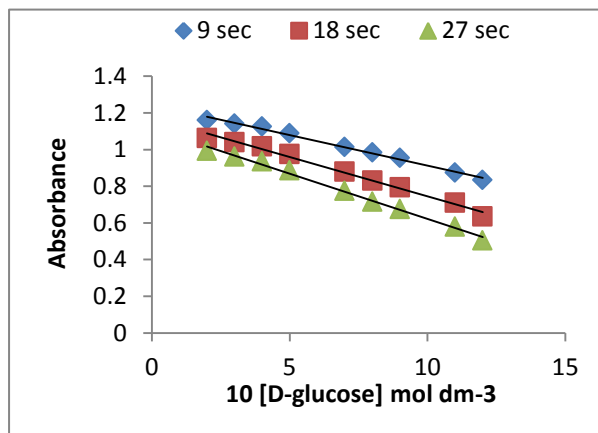
Rearranged equation (3) can be expressed as:

$$\text{Time} = k [Aldose]_0^{-1} = k [Absorbance]^{-1} \tag{4}$$

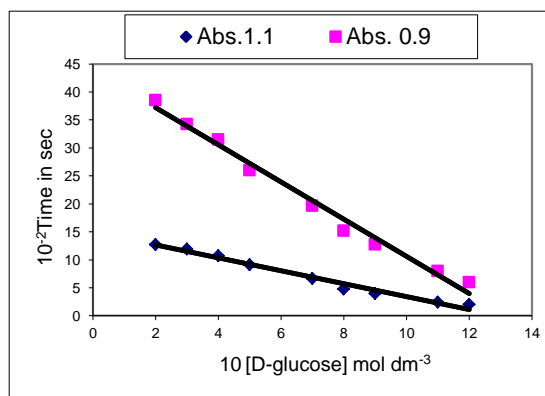
Calibration plots were then obtained between absorbance at 20 min, 40 min, and 60min and also between fixed concentration of D-glucose in terms of 1.1, 0.9 and 0.7 concentrations in the respective kinetic runs. The concentration of simulated samples of D-glucose was determined from the “best fit” regression equations.

(B & C) Fixed Time and Fixed Absorbance Method

10 [D-glucose] (mol dm ⁻³)	Absorbance at fixed 10 ⁻² time (sec)			10 ⁻² time(sec)at fixed absorbance	
	9	18	27	1.1	0.9
2	1.161	1.063	0.994	12.75	38.51
3	1.142	1.040	0.962	11.90	34.24
4	1.125	1.017	0.935	10.70	31.50
5	1.090	0.975	0.886	9.10	26.00
7	1.014	0.879	0.775	6.65	19.64
8	0.985	0.831	0.715	4.75	15.20
9	0.955	0.795	0.675	3.95	12.70
11	0.875	0.711	0.580	2.45	8.00
12	0.835	0.635	0.505	2.00	6.00
simulated -1	1.045	0.925	0.834	7.25	21.75
10[simulated -1] (mol dm ⁻³)	6.04	5.93	5.94	6.07	6.09
simulated -2	0.922	0.755	0.627	3.15	10.25
10[simulated -2] (mol dm ⁻³)	9.96	9.81	9.93	10.16	10.06



Absorbance at fixed 10⁻²time



Time at fixed absorbance

Regression Equations

$A_{900} = -0.0331 [D\text{-glucose}] + 1.245$	Corr. Coeff. = 0.99
$A_{1800} = -0.0427 [D\text{-glucose}] + 1.1739$	Corr.Coeff. = 0.99
$A_{2700} = -0.0494 [D\text{-glucose}] + 1.1177$	Corr. Coeff. = 0.99
$t_{1.1} = - 1.1545 [D\text{-glucose}] + 14.882$	Corr.Coeff. = 0.98
$t_{0.9} = - 3.3128 [D\text{-glucose}] + 43.605$	Corr.Coeff. = 0.98

Results:

10 [simulated -1] (mol dm ⁻³) (Fixed Time Method)	5.97 ± 0.04 (Calculated): 6.00 (Actual)
10[simulated -2] (mol dm ⁻³)	9.90 ± 0.06 (Calculated): 10.00 (Actual)

10 [simulated -1] (mol dm ⁻³) (Fixed Abs. Method) 10[simulated -2] (mol dm ⁻³)	6.08 ± 0.01 (Calculated): 6.00 (Actual) 10.11 ± 0.05(Calculated):10.00(Actual)
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(D) One point (fixed absorbance) method

It is always not possible to perform large number of kinetic runs when a small amount of sample is available for estimation. Then simplified kinetic estimation of D-glucose was also employed. Reaction mixtures with known and simulated sample of D-glucose were taken and at fixed absorbance 1.1, 0.9 and 0.7 at respective time intervals were determined.

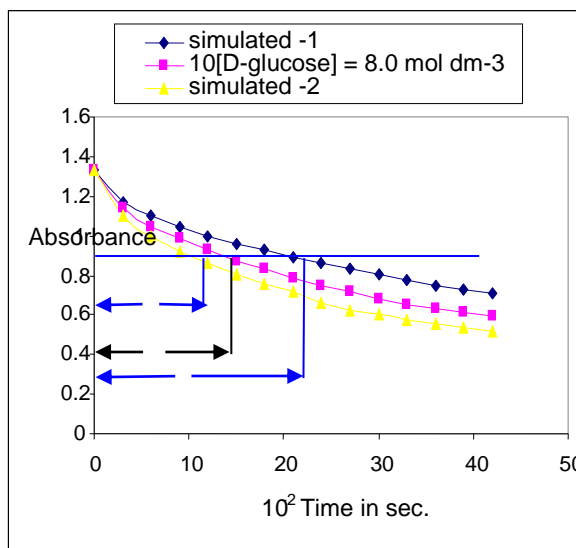
Thus (time)_{known} ∝ [Aldose]⁻¹ or (Absorbance)⁻¹

and (time)_{simulated} ∝ [Aldose]⁻¹ or (Absorbance)⁻¹

$$(time)_{known} / (time)_{simulated} = (Absorbance)_{simulated} / (Absorbance)_{known} \quad (5)$$

(D) One Point Method

10 ⁻² Time (sec.)	10 [D-glucose](mol dm ⁻³)		
	6.00	8.00	10.00
0	1.335	1.335	1.335
3	1.166	1.138	1.101
6	1.099	1.047	0.995
9	1.045	0.985	0.922
12	0.999	0.928	0.859
15	0.961	0.875	0.809
18	0.925	0.831	0.755
21	0.891	0.788	0.715
24	0.862	0.750	0.665
27	0.834	0.715	0.627
30	0.802	0.681	0.601
33	0.775	0.656	0.577
36	0.750	0.633	0.555
39	0.728	0.613	0.537
42	0.705	0.592	0.521



Fixed Absorbance	10 ⁻² Time (sec.)	10[Standard] mol dm ⁻³	10[Simulated Sample] mol dm ⁻³ C ₁ = (t ₂ C ₂ /t ₁)
0.9	t ₁ = 20.75	C ₂ = 8.00	C ₁ = 5.91
	t ₂ = 15.20		(C _{Actual} = 6.00)
	t ₁ = 11.85	C ₂ = 8.00	C ₁ = 10.16
	t ₂ = 15.20		(C _{Actual} = 10.00)
	t ₁ = 6.20	C ₂ = 8.00	C ₁ = 6.14
	t ₂ = 4.75		(C _{Actual} = 6.00)

1.1	$t_1 = 3.81$ $t_2 = 4.75$	$C_2 = 8.00$	$C_1 = 9.97$ $(C_{Actual} = 10.00)$
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Results:

10[simulated -1] (mol dm ⁻³)	6.03 ± 0.12(Calculated): 6.00 (Actual)
10[simulated -2] (mol dm ⁻³)	10.07 ± 0.09 (Calculated):10.00 (Actual)

(E) Two point (Difference in Absorbance) method

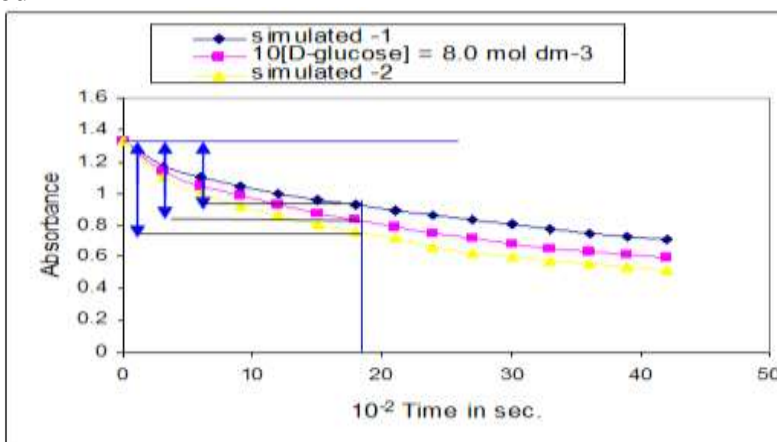
This method can yield better estimation results as this requires determination of change in absorbance at fixed time intervals of 20min, 40min, and 60 min for the known and simulated samples of D-glucose.

Thus $(\Delta \text{time})_{\text{known}} \propto \Delta[\text{D-glucose}]^{-1}$ or $(\Delta \text{Absorbance})^{-1}$

and $(\Delta \text{time})_{\text{simulated}} \propto \Delta[\text{D-glucose}]^{-1}$ or $(\Delta \text{Absorbance})^{-1}$

$$(\Delta \text{time})_{\text{known}} / (\Delta \text{time})_{\text{simulated}} = (\Delta \text{Absorbance})_{\text{simulated}} / (\Delta \text{Absorbance})_{\text{known}} \quad (6)$$

(E) Two Point Method



10 ⁻² Fixed Time (sec.)	Absorbance ΔA	10[Standard] mol dm ⁻³	10[Simulated Sample] mol dm ⁻³ $C_1 = (\Delta A_1 C_2 / \Delta A_2)$
9.0	$\Delta A_1 = 0.175$	$C_2 = 8.00$	$C_1 = 6.05$
	$\Delta A_2 = 0.249$		$(C_{Actual} = 6.00)$
	$\Delta A_1 = 0.343$	$C_2 = 8.00$	$C_1 = 10.17$
	$\Delta A_2 = 0.249$		$(C_{Actual} = 10.00)$
18.0	$\Delta A_1 = 0.288$	$C_2 = 8.00$	$C_1 = 5.97$
	$\Delta A_2 = 0.403$		$(C_{Actual} = 6.00)$
	$\Delta A_1 = 0.561$	$C_2 = 8.00$	$C_1 = 10.09$
	$\Delta A_2 = 0.403$		$(C_{Actual} = 10.00)$

27.0	$\Delta A_1 = 0.382$		$C_1 = 5.95$
	$\Delta A_2 = 0.523$	$C_2 = 8.00$	($C_{Actual} = 6.00$)
	$\Delta A_1 = 0.691$		$C_1 = 9.98$
	$\Delta A_2 = 0.523$	$C_2 = 8.00$	($C_{Actual} = 10.00$)

Results:

10[simulated -1] (mol dm⁻³)	5.99 ± 0.04 (Calculated): 6.00 (Actual)
10[simulated -2] (mol dm⁻³)	10.08 ± 0.07 (Calculated):10.00 (Actual)

The results of the kinetic vandimetric estimation of D-glucose has been summarized in table -2

TABLE-2 Summary of the Kinetic Vanadimetric Estimation of D-glucose

Estimation Method		10[simulated-1] mol dm ⁻³	10[simulated-2] mol dm ⁻³
A	Rate Constant Method	5.89	9.86
B	Fixed Time Method	5.97	9.90
C	Fixed Absorbance Method	6.08	10.11
D	One Point Method	6.03	10.07
E	Two Point Method	5.99	10.08
Average Value		5.99±0.05	10.00±0.10
Actual Value		6.00	10.00

III. CONCLUDING REMARKS

The present report is a part of detailed study to use rate data obtained during electron transfer reactions between aldoses and other reducing sugars including alditols with one equivalent metal ions(vanadium(V) in present case) for their estimations in simulated /real samples. The results of present and earlier reports/3/ show clearly the pseudo first order kinetic conditions can be successfully employed for the kinetic estimations of aldoses with possible extensions of kinetic estimations of various metal ion oxidants and other organic compounds particularly pharmaceutical samples. These studies have the potential to develop a simple, inexpensive but accurate laboratory procedure for kinetic

estimations using various electron transfer indicator reactions involving metal ions and organic/inorganic substrates.

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