CHAPTER IV

RESULTS

4.1 Glycine-Nitrate Ions System

Concentrations ranging from 5×10^{-4}M to 5×10^{-3}M of nitrate ions were chosen to observe the kinetic behavior. Glycine concentrations were varied from 0.1 M to 2.0 M according to the fixed concentration of nitrate in each system. $G(NO_2^-)$ values were measured, $G_0(NO_2^-)$ values and their reciprocals were calculated. The data is presented in Table 4.1.

The competition kinetic graphs are shown in Figures 4.1, 4.2 and 4.3 respectively. The first graph with the most dilute concentration of nitrate (5×10^{-4}M) observed is linear through the observed values of (glycine)/(NO_3^-) ratio. The other two are linear from the beginning until the ratio of glycine to nitrate exceeds a certain value, then they show curvature.

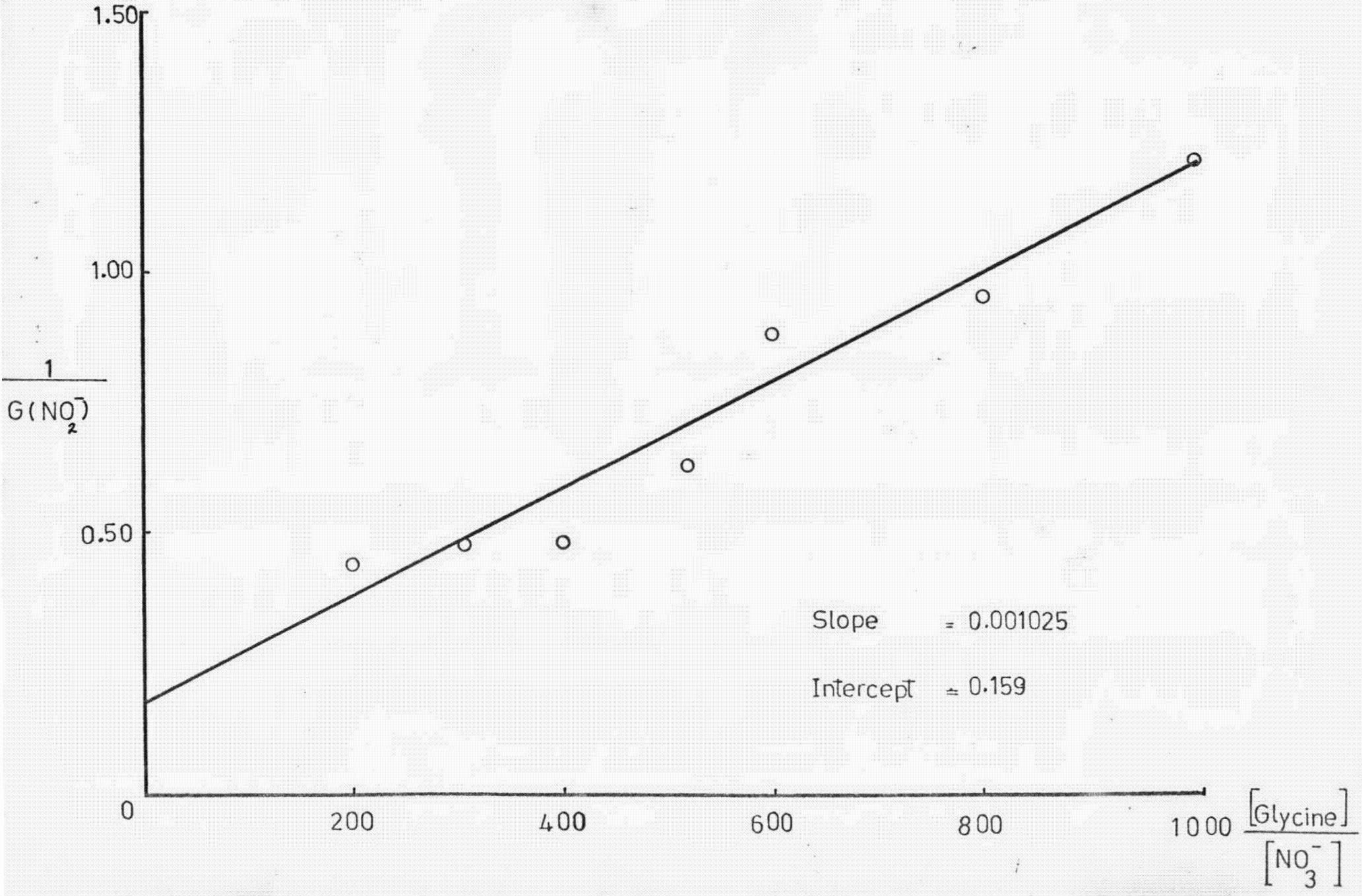
The slopes of the linear part of the graphs were determined by the method of least squares on an IBM 360 computer. From the slopes and the intercepts the rate constants (k) of glycine and $G_{e_{aq}^-}$ were calculated. The data is shown in Table 4.2.

TABLE 4.1

Yields of Nitrite in Aqueous Solutions of Glycine

[glycine] M	$[NO_3^-]$ M	$\frac{[\text{glycine}]}{[NO_3^-]}$	$G_0(NO_2^-)$	$\frac{1}{G_0(NO_2^-)}$
0.10	5×10^{-4}	200	2.275	0.44
0.15	5×10^{-4}	300	2.125	0.47
0.20	5×10^{-4}	400	2.075	0.48
0.25	5×10^{-4}	500	1.725	0.58
0.30	5×10^{-4}	600	1.130	0.88
0.40	5×10^{-4}	800	1.050	0.95
0.50	5×10^{-4}	1000	0.825	1.21
0.10	1×10^{-3}	100	1.850	0.54
0.25	1×10^{-3}	250	0.950	1.05
0.50	1×10^{-3}	500	0.900	1.11
0.75	1×10^{-3}	750	0.500	2.00
1.00	1×10^{-3}	1000	0.312	3.21
1.50	1×10^{-3}	1500	0.230	4.35
2.00	1×10^{-3}	2000	0.000	∞
0.25	5×10^{-3}	50	1.750	0.57
0.50	5×10^{-3}	100	1.700	0.59
0.75	5×10^{-3}	150	1.650	0.61
0.875	5×10^{-3}	175	1.325	0.75
1.00	5×10^{-3}	200	1.000	1.00
1.50	5×10^{-3}	300	0.400	2.50
2.00	5×10^{-3}	400	0.080	12.50

Fig. 4.1 Competition Plot for Glycine and Nitrate Ions 5×10^{-4} M



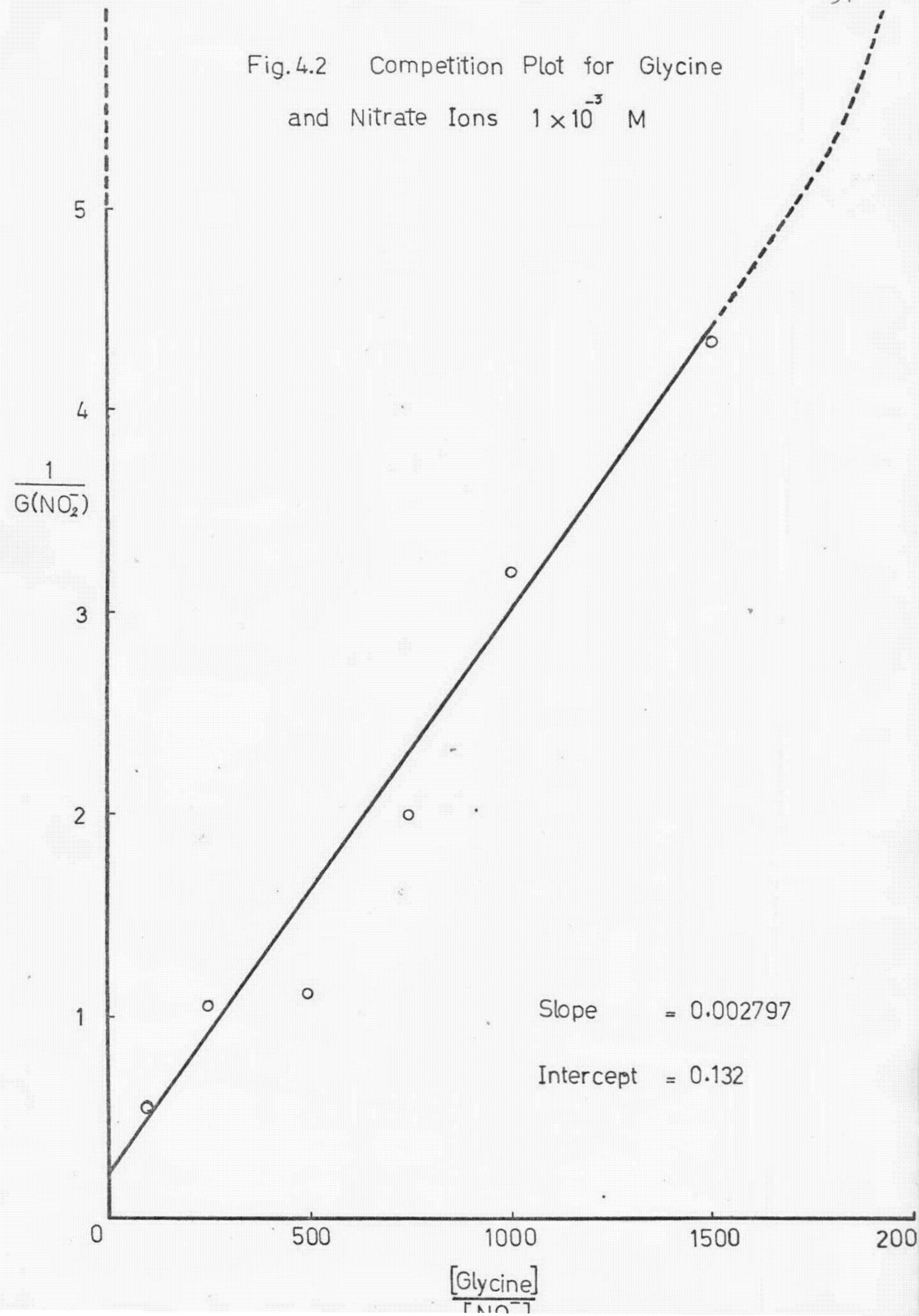


Fig. 4.2 Competition Plot for Glycine
and Nitrate Ions 1 × 10^{-3} M
$\frac{1}{G(NO_2^-)}$
5
4
3
2
1
0
500
1000
1500
200
Slope = 0.002797
Intercept = 0.132
$\frac{[Glycine]}{[NO_3^-]}$

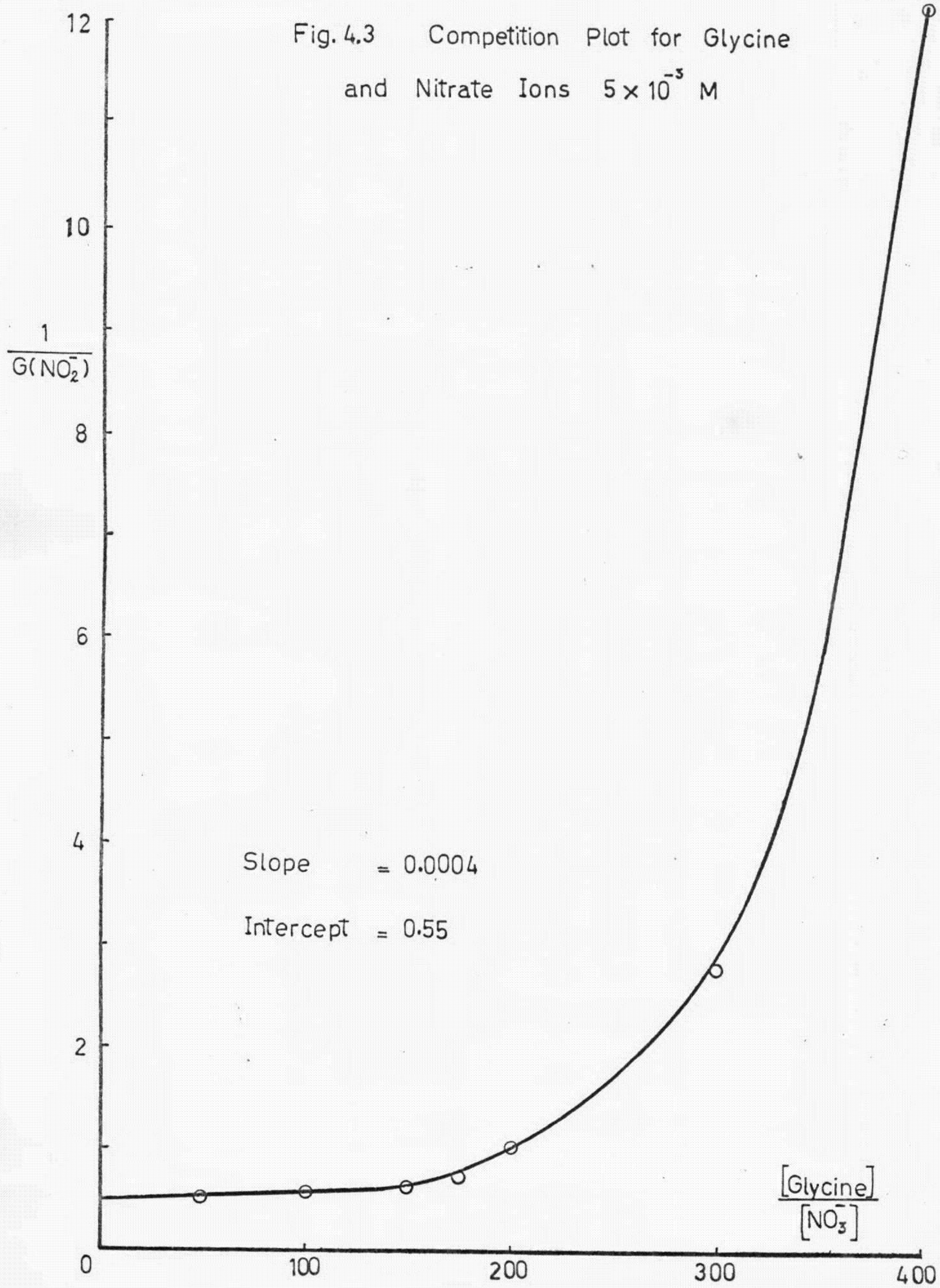


Fig. 4.3 Competition Plot for Glycine and Nitrate Ions 5×10^{-3} M
$\frac{1}{G(NO_2^-)}$
12
10
8
6
4
2
0
Slope = 0.0004
Intercept = 0.55
$\frac{[Glycine]}{[NO_3^-]}$
100
200
300
400

TABLE 4.2

Yields of e^-_{aq} and the Rate Constants of Glycine

$[NO_3^-]$	glycine conc$^{\underline{n}}$ range	$\frac{[glycine]}{[NO_3^-]}$	$k_{(glycine)}$ M^{-1} sec^{-1}	$G_{0e^-_{aq}}$
5×10^{-4}	0.10 - 0.50	200 - 1000	7.09×10^{7}	6.29
1×10^{-3}	0.10 - 2.00	100 - 2000	2.33×10^{8}	7.58
5×10^{-3}	0.25 - 2.00	50 - 400	8.00×10^{6}	1.82

4.2 Alanine-Nitrate Ions System

The same concentration range of nitrate ion was used in the case of alanine but different concentration ranges of alanine were used; the limits were imposed by the lower solubility of alanine. The data is presented in Table 4.3.

The three competition kinetic graphs obtained are shown in Figure 4.4, 4.5 and 4.6. They are linear for smaller ratios of alanine to nitrate and show curvature at higher concentration ratios.

The slopes of the linear part and the intercepts were determined as in the case of glycine. The rate constants of alanine and $G_{e^-_{aq}}$ are shown in Table 4.4.

TABLE 4.3

Yields of Nitrite in Aqueous Solutions of Alanine

[alanine] M	$[NO_3^-]$ M	[alanine]/$[NO_3^-]$	$G_0(NO_2^-)$	$\frac{1}{G_0(NO_2^-)}$
0.10	5×10^{-4}	200	1.960	0.51
0.20	5×10^{-4}	400	1.715	0.58
0.30	5×10^{-4}	600	1.055	0.95
0.40	5×10^{-4}	800	0.510	1.96
0.50	5×10^{-4}	1000	0.050	20.00
0.10	1×10^{-3}	100	2.800	0.36
0.25	1×10^{-3}	250	1.650	0.61
0.50	1×10^{-3}	500	0.942	1.06
0.75	1×10^{-3}	750	0.525	1.90
1.00	1×10^{-3}	1000	0.125	8.00
0.10	5×10^{-3}	20	2.80	0.36
0.25	5×10^{-3}	50	2.30	0.43
0.50	5×10^{-3}	100	1.75	0.57
0.75	5×10^{-3}	150	0.73	1.37
1.00	5×10^{-3}	200	0.15	6.67

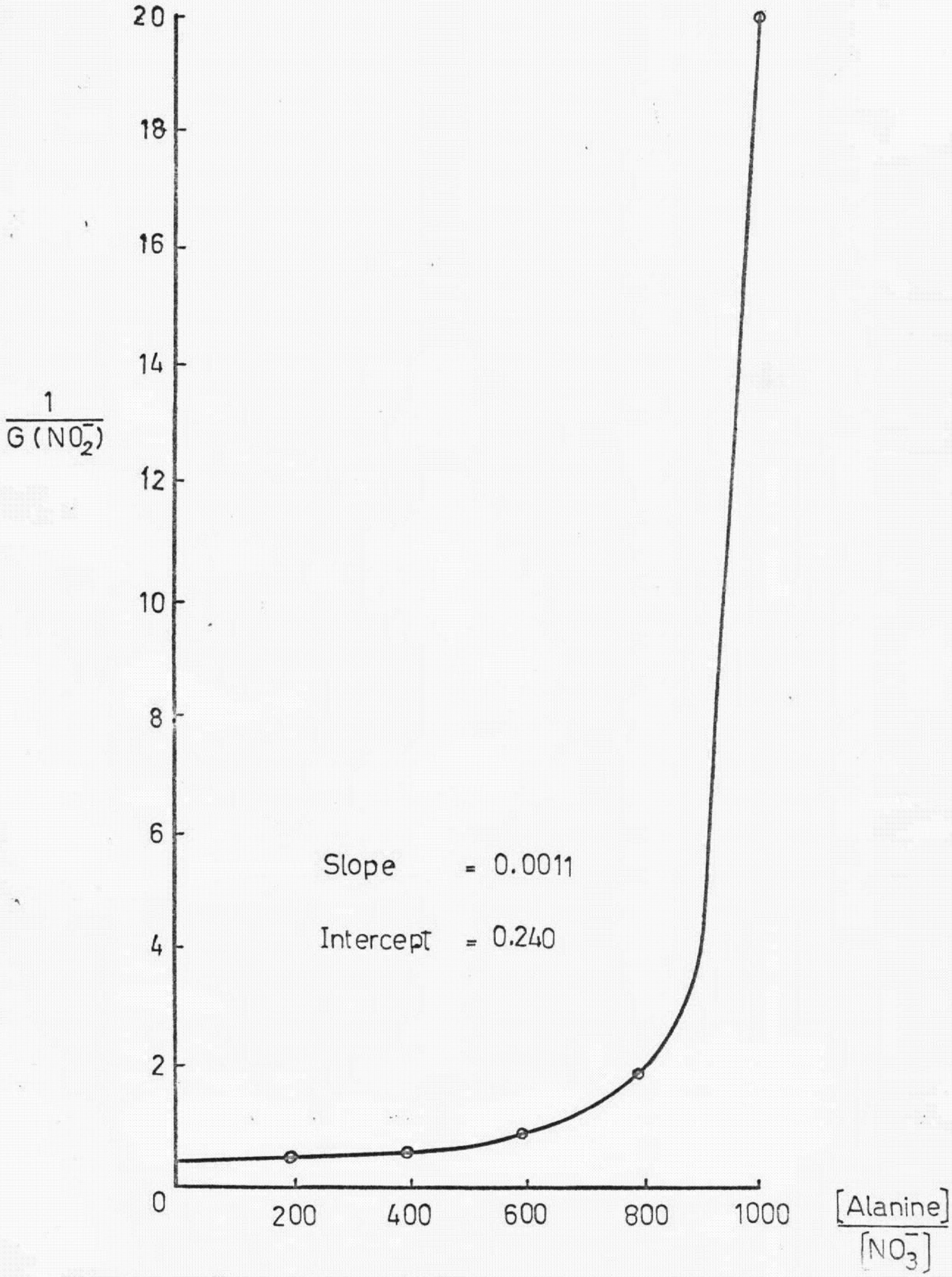


Fig.4.4 Competition Plot for Alanine and Nitrat[illegible] 5×10^{-4} M

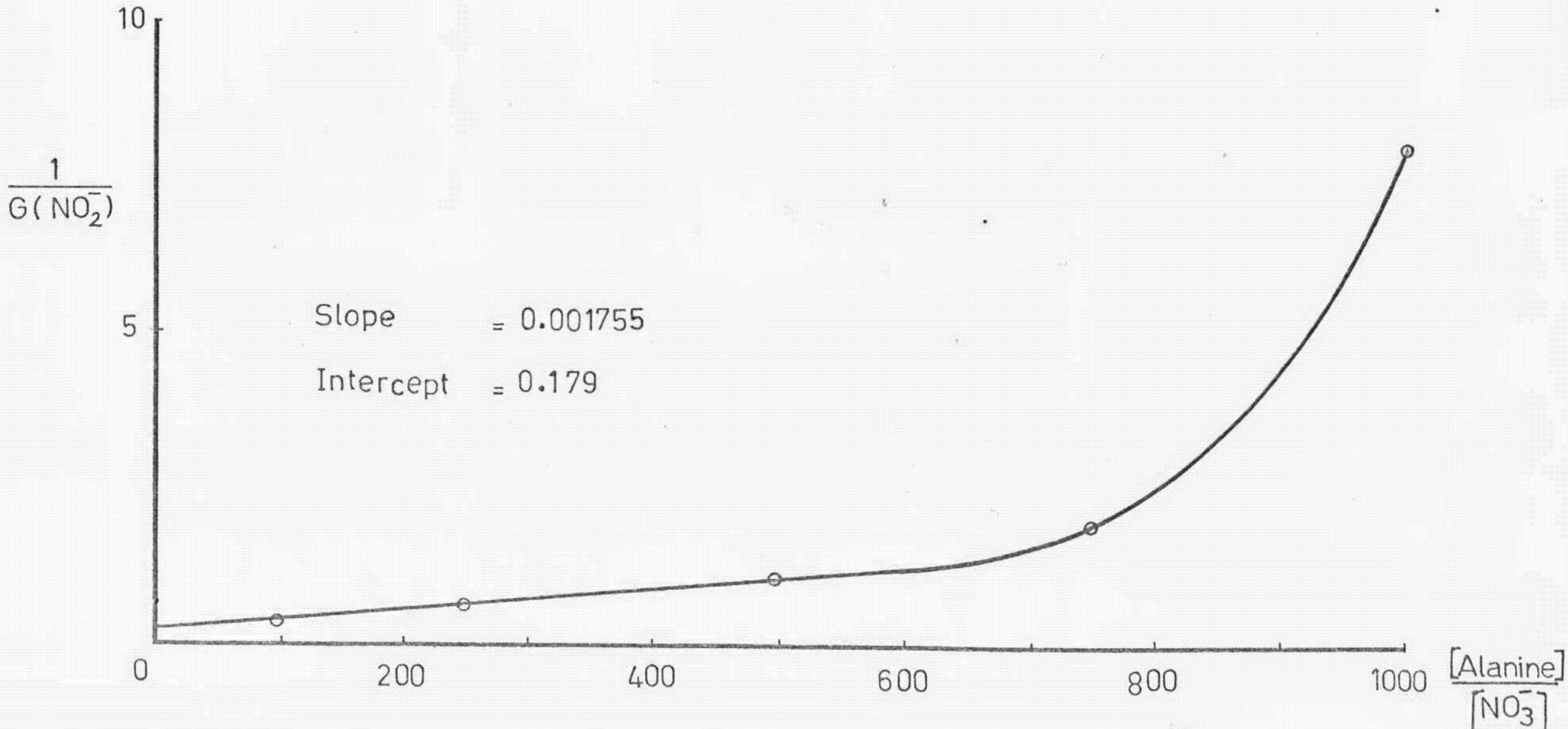


Fig. 4.5 Competition Plot for Alanine and Nitrate Ions 1×10^{-3} M

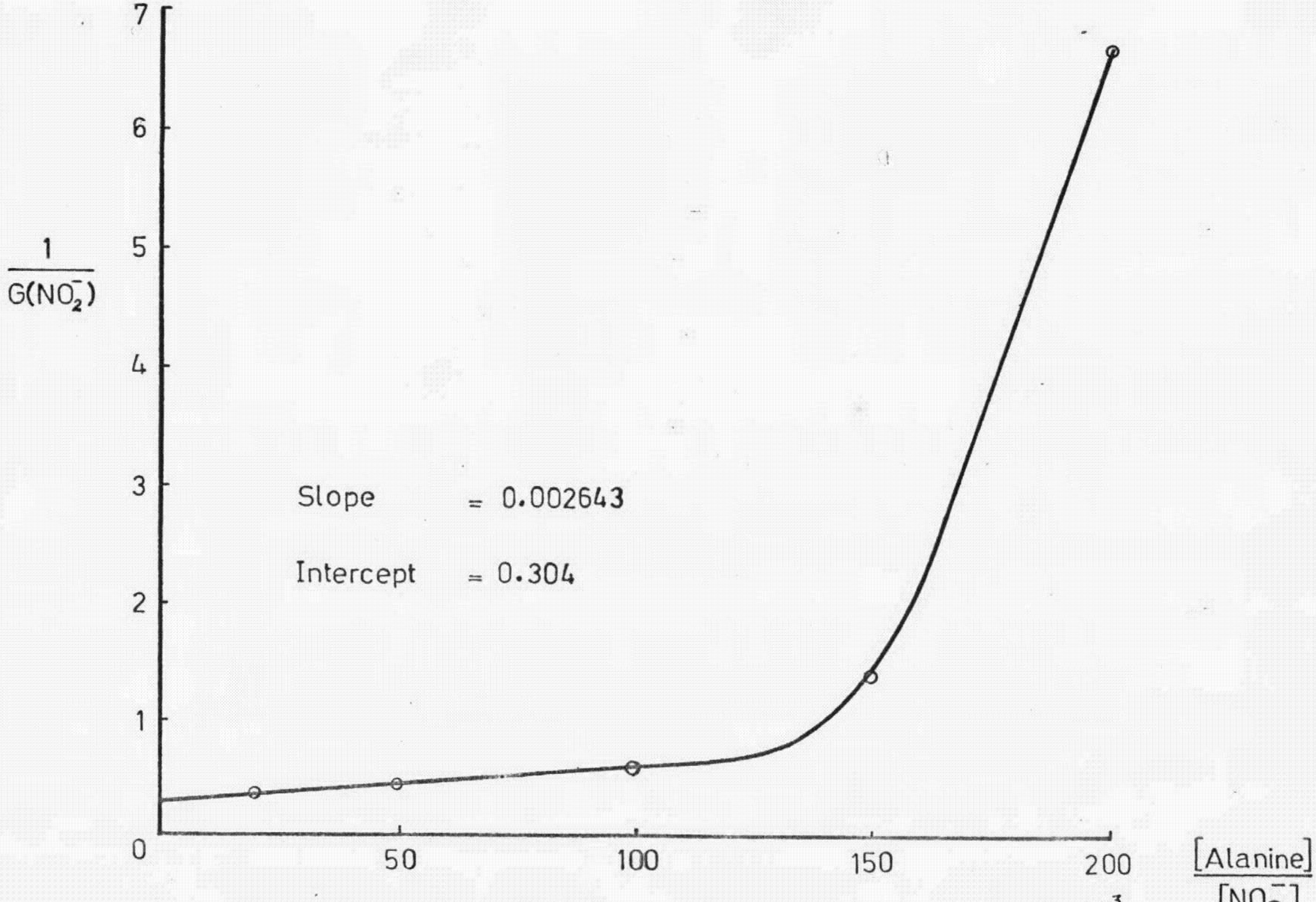


Fig.4.6 Competition Plot for Alanine and Nitrate Ions 5×10^{-3} M

TABLE 4.4

Yields of e^-_{aq} and the Rate Constants of Alanine

$[NO_3^-]$	alanine conc$^{\underline{n}}$ range	$\frac{[\text{alanine}]}{[NO_3^-]}$	$k_{(\text{alanine})}$ M^{-1} sec^{-1}	$G_{Oe^-_{aq}}$
5×10^{-4}	0.10 - 0.50	200 - 1000	5.04×10^{7}	4.17
1×10^{-3}	0.10 - 1.00	100 - 1000	1.08×10^{8}	5.59
5×10^{-3}	0.10 - 1.00	20 - 200	9.56×10^{7}	3.29

4.3 Kinetics Plots and Calculation for Rate Constants

The competition kinetics equations and the relative rate constant determinations discussed in chapter II were used as the methods of plotting the data and calculating the rate constants and G_O values obtained in these experiments.

The working equation is as follows (1):

$$\frac{1}{G(P_A)} = \frac{1}{G_R}\,\frac{k_A[A] + k_B[B]}{k_A[A]}$$

$$= \frac{1}{G_R} + \frac{1}{G_R}\,\frac{k_B[B]}{k_A[A]}$$

which is of linear type. The slope is tan α , which is equal to $\frac{1}{G_R} \cdot \frac{k_B}{K_A}$ and the intercept is $\frac{1}{G_R}$.

From this the relative rate constant $\frac{k_B}{K_A}$ can be calculated. If one of the rate constants is known the other can also be determined.

In this specific work, R stands for e^-_{aq}, A for NO_3^- and B for amino acid (glycine or alanine). The value of rate constants of nitrate (k_A) has been determined and is equal to 1.1 X $10^{10} M^{-1} sec^{-1}$ (1). Therefore the rate constant of amino acid (k_B) and the reacting radical yield ($G_{e^-_{aq}}$) are calculated for each system from the slopes and intercepts of competition plots. The data is given in Table 4.2 and 4.4.