

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Rejection of Chromate Anion

The removal efficiency of the chromate is represented by the rejection percentage, R (%), as defined by

$$\% \text{ Rejection (R)} = (1 - (C_p/C_r)) \times 100$$

where C_p is permeate concentration of solute (M) and C_r is retentate concentration of solute (M).

The QUAT concentrations are based on the moles per liter of the repeating units and not on the total molecular weight. (Tangvijitsri *et al.*, 2002) Since the repeating unit has a charge of +1, the stoichiometric ratio of [QUAT]:[CrO₄²⁻] and [QUAT]:[SO₄²⁻] are two to one.

Figure 4.1 shows a semi-logarithmic plot of the rejection percentage of chromate as a function of QUAT concentration in retentate at various ratios of [QUAT]:[CrO₄²⁻]:[SO₄²⁻]. These PEUF experiments were performed at [QUAT]:[CrO₄²⁻]:[SO₄²⁻] of 5:1:1, 10:1:1 and 20:1:1. Higher chromate rejection occurred at lower concentrations of QUAT in retentate where the chromate rejection greater than 90% can be obtained at the concentration ratios of [QUAT]:[CrO₄²⁻]:[SO₄²⁻] of 10:1:1 and 20:1:1. In previous PEUF studies on the removal of chromate from aqueous stream using poly(diallyldimethyl ammonium chloride), the chromate rejection at the concentration ratios of QUAT to chromate of 5:1 and 10:1 (Tangvijitsri *et al.*, 2002) are in the same level as the concentration ratios of [QUAT]:[CrO₄²⁻]:[SO₄²⁻] of 10:1:1 and 20:1:1 or the concentration ratios of QUAT to total anions of 5:1 and 10:1, respectively. In this present PEUF studies, the rejection of chromate tended to decrease when QUAT concentration was higher than 100 mM. The lower the ratios of QUAT to total anions, the higher reduction in chromate rejection. For QUAT concentration in the retentate of 300 mM, the chromate rejections are approximately 67%, 89% and 97% for the ratios of

[QUAT]:[CrO₄²⁻]:[SO₄²⁻] equal to 5:1:1, 10:1:1 and 20:1:1, respectively. The high QUAT concentrations in retentate caused decrease in the chromate rejection (Figure 4.1) due to the increase in concentration polarization near the membrane surface (Juang and Chen, 1996). However, the concentration ratio of [QUAT]:[CrO₄²⁻]:[SO₄²⁻] equal to 5:1:1 has low chromate rejection due to decrease in the availability of the positively charged sites on the poly(diallyldimethyl ammonium chloride), which provides more binding sites for the target anions.

Figure 4.2 shows a semi-logarithmic plot of the chromate rejection as a function of QUAT concentration in retentate at different initial chromate concentrations at constant [QUAT]:[SO₄²⁻] of 20:1. The higher the concentration of the chromate anion, the lower the rejection of chromate caused by reducing the availability of positively charged sites on the poly(diallyldimethyl ammonium chloride) to bind with target anions.

Figure 4.3 shows a semi-logarithmic plot of the chromate rejection as a function of QUAT concentration in retentate at different initial sulfate concentrations at constant ratio of [QUAT]:[CrO₄²⁻] equal to 20:1. When sulfate anion was increased, the lower chromate rejection was obtained. Sulfate anion has the same number of electrical charges of -2 as chromate anion. Therefore, chromate anions and sulfate anions can be simultaneously bound with the positively charged sites of poly(diallyldimethyl ammonium chloride).

4.2 Effect of Concentration Polarization on relative flux

Figures 4.4-4.6 show semi-logarithmic plots between the relative flux of PEUF during the removal of chromate and sulfate from water and polyelectrolyte concentration in retentate at various ratios of [QUAT]:[CrO₄²⁻]:[SO₄²⁻] equal to 5:1:1, 10:1:1 and 20:1:1, respectively. The results indicated that the flux declined when the concentration of QUAT in retentate increased due to the gel formation over the surface of an ultrafiltration membrane (Sriratana *et al.*, 1996 and Tangvijitsri *et al.*, 2002). This is the concentration polarization behavior which generally occurs in ultrafiltration process as described by equation (2.1). According to this equation, when gel concentration (C_g) and bulk concentration (C_b) are equal, the solvent flux

passed through the membrane is zero or no solvent can permeate. Therefore, gel concentration (C_g) can be determined from the intercept of the line and slope of the graph is a mass-transfer coefficient (K_T). At [QUAT]:[CrO₄²⁻]:[SO₄²⁻] equal to 5:1:1, 10:1:1 and 20:1:1, the gel concentrations (zero flux) were approximately 840, 1220 and 1600 mM, respectively.

Figures 4.7-4.11 show the relative flux as a function of QUAT concentration in retentate at various chromate concentrations by fixing [QUAT] to [SO₄²⁻] equal to 20. At ratios of [QUAT]:[CrO₄²⁻]:[SO₄²⁻] equal to 20:2:1, 20:4:1, 20:6:1, 20:8:1 and 20:10:1, the gel concentration could be extrapolated from these figures and were approximately 1100, 1200, 700, 640 and 690 mM, respectively.

Figures 4.11-4.16 show the relative flux as a function of QUAT concentration in retentate at different sulfate concentrations by fixing [QUAT] to [CrO₄²⁻] equal to 20. At ratios of [QUAT]:[CrO₄²⁻]:[SO₄²⁻] equal to 20:1:2, 20:1:4, 20:1:6, 20:1:8 and 20:1:10, the gel concentration could be extrapolated from these figures and were approximately 460, 450, 540, 550 and 660 mM, respectively.

The flux data obtained from PEUF experiments are essentially valuable for scaling-up the PEUF process. Whether the relative flux of chromate-sulfate mixture are significantly different from the relative flux from previous work (Tangvijitsri *et al.*, 2002), these PEUF experiments for chromate-sulfate mixture show that concentration polarization is not a severe problem in PEUF if the polyelectrolyte concentration of retentate is much lower than the gel concentration. The gel concentration is practical for limiting the maximum concentration of polyelectrolyte used in PEUF.

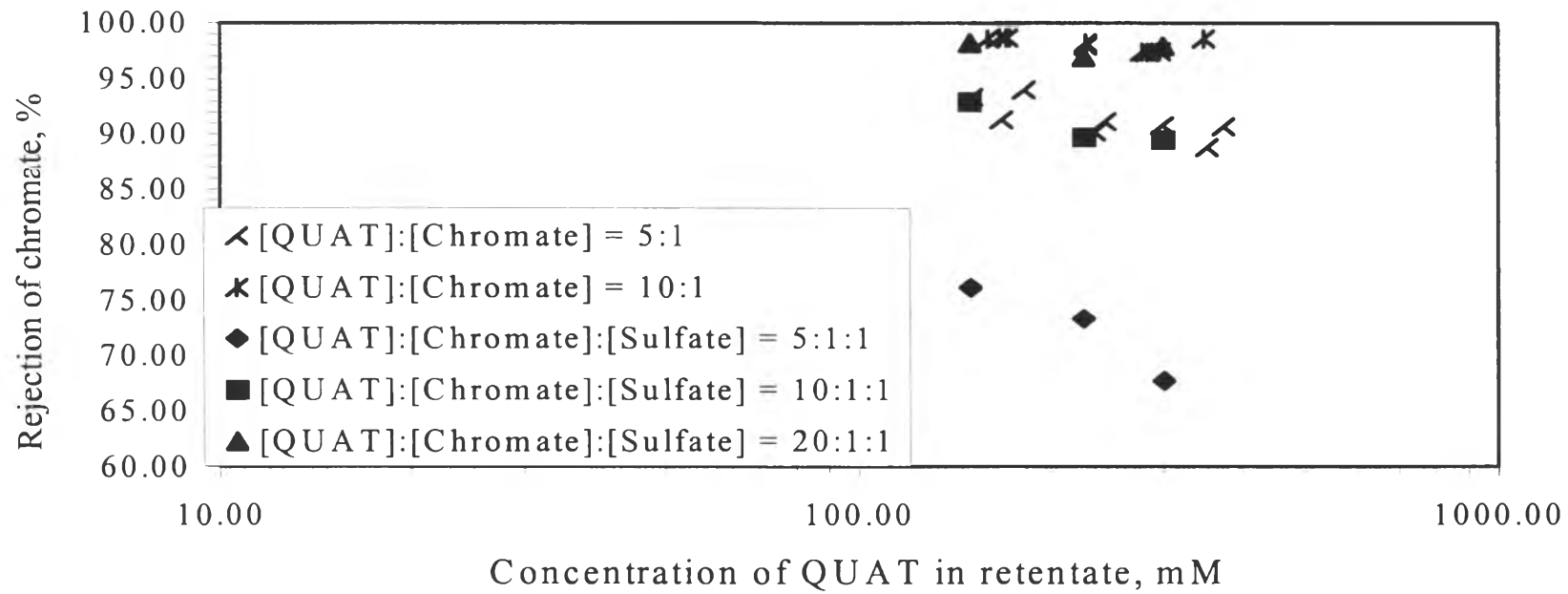


Figure 4.1 Chromate rejection as a function of QUAT concentration in retentate.

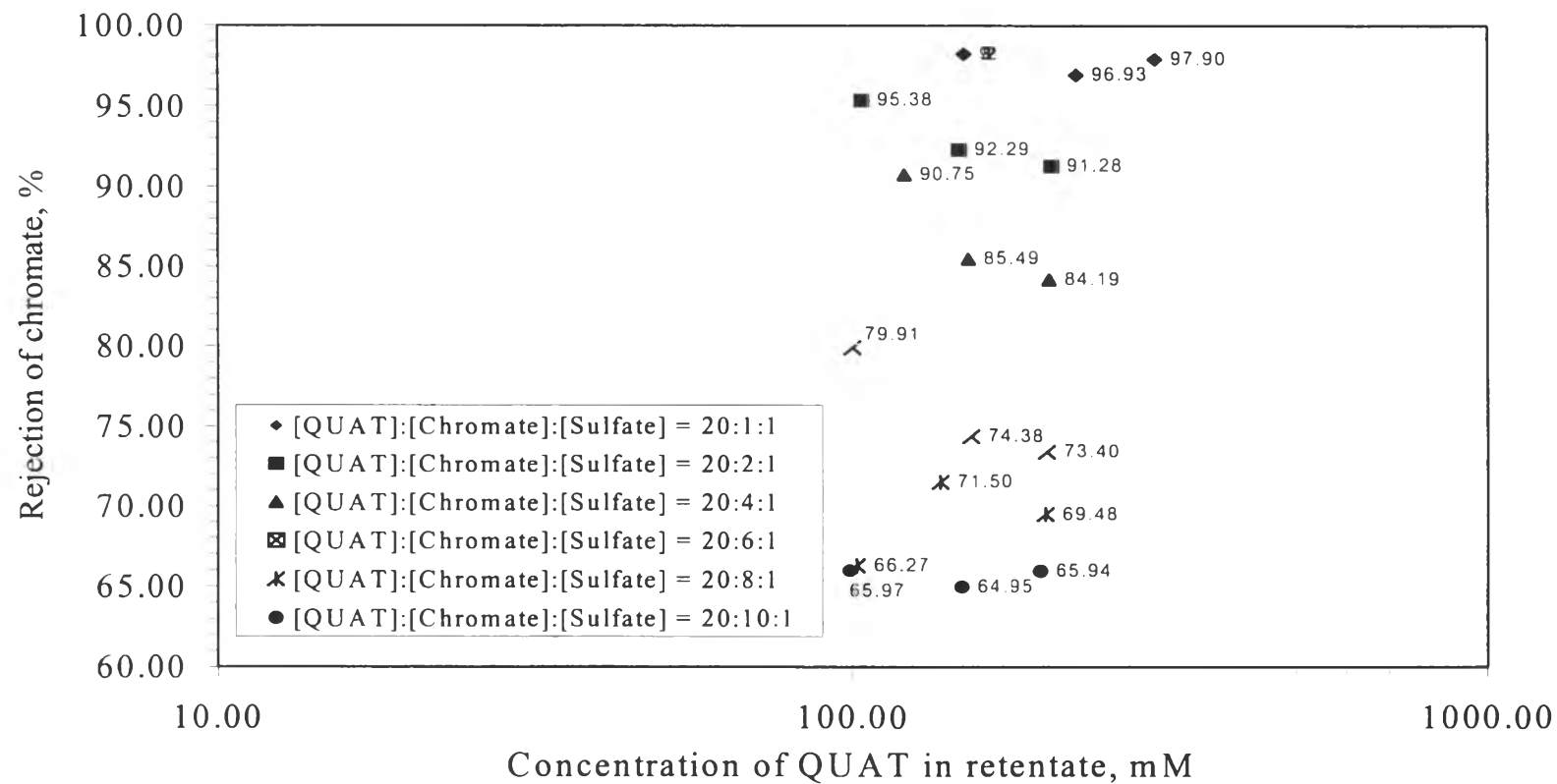


Figure 4.2 Effect of initial [Chromate] at a [QUAT]/[Sulfate] of 20.

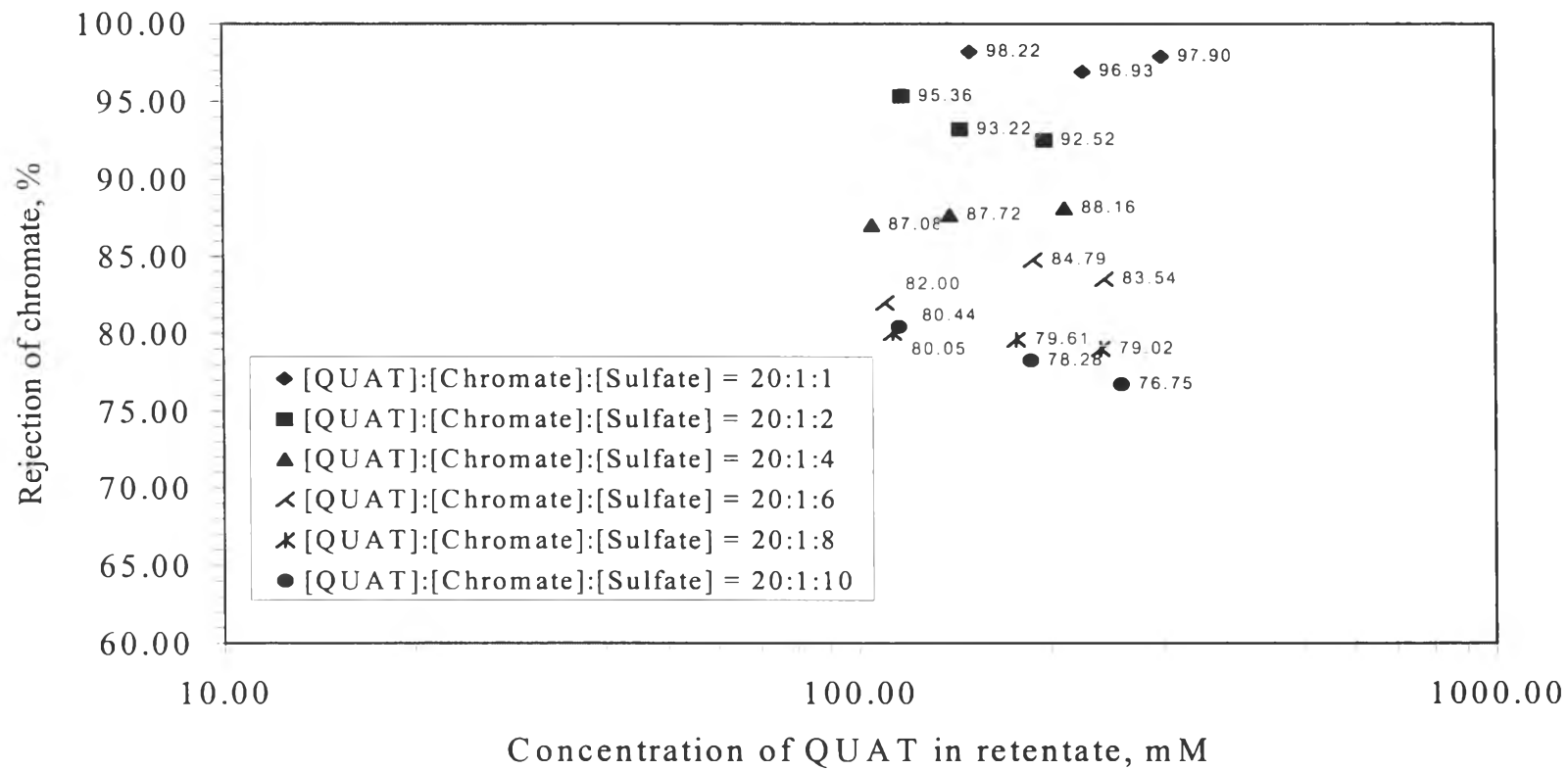


Figure 4.3 Effect of initial [Sulfate] at a [QUAT]/[Chromate] of 20.

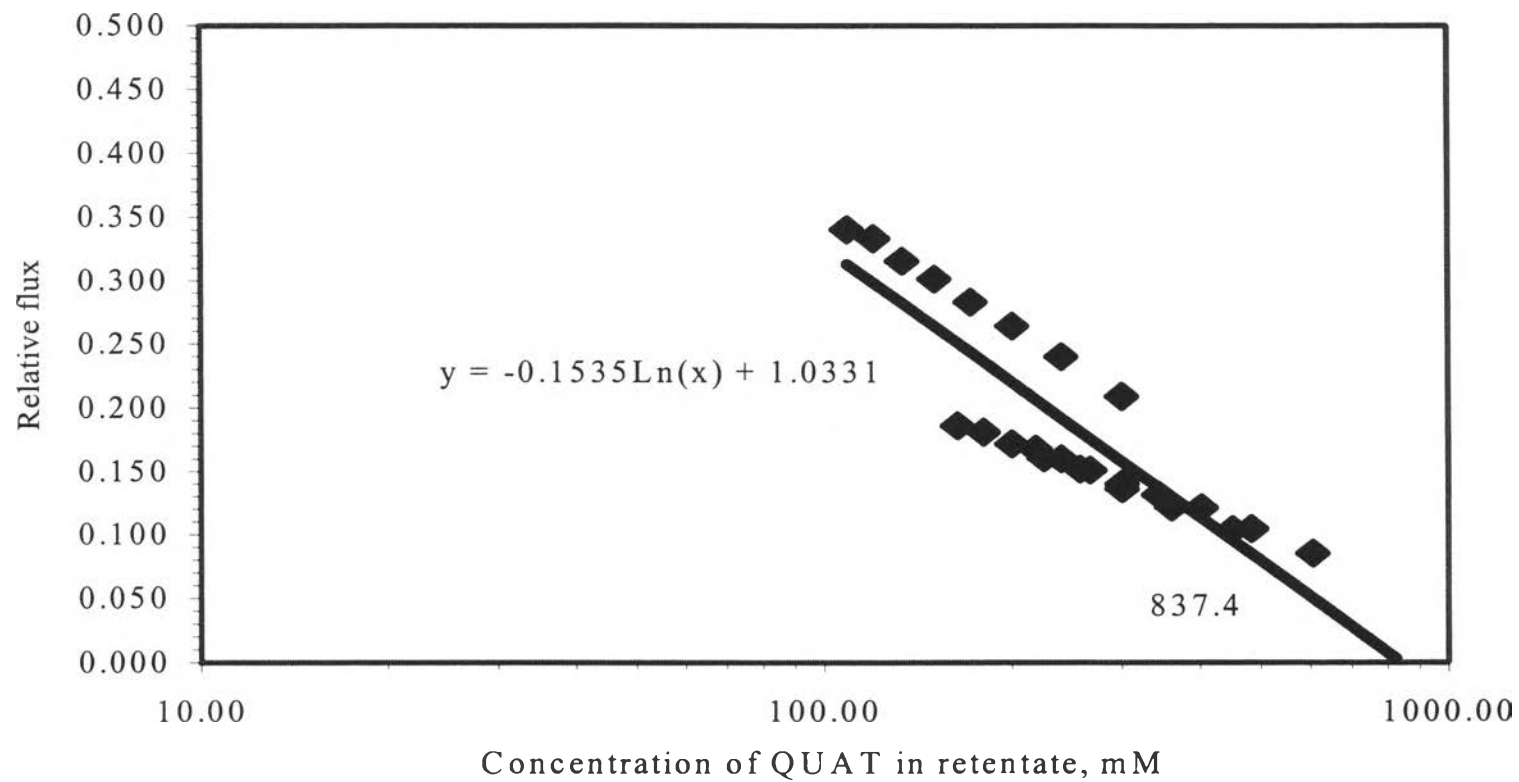


Figure 4.4 Relative flux as a function of QUAT concentration in retentate at ratio [QUAT]:[Chromate]:[Sulfate] = 5:1:1.

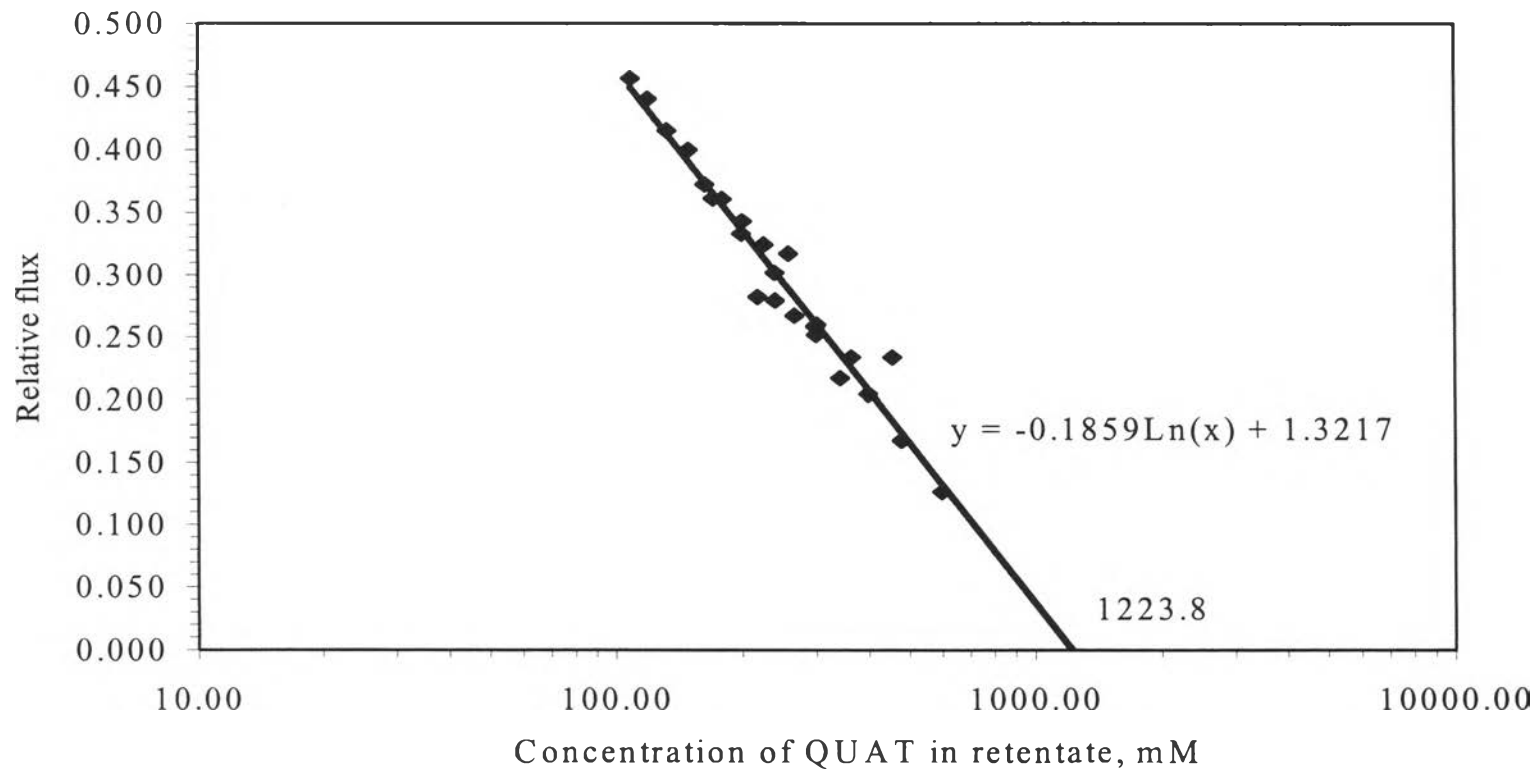


Figure 4.5 Relative flux as a function of QUAT concentration in retentate at ratio [QUAT]:[Chromate]:[Sulfate] = 10:1:1.

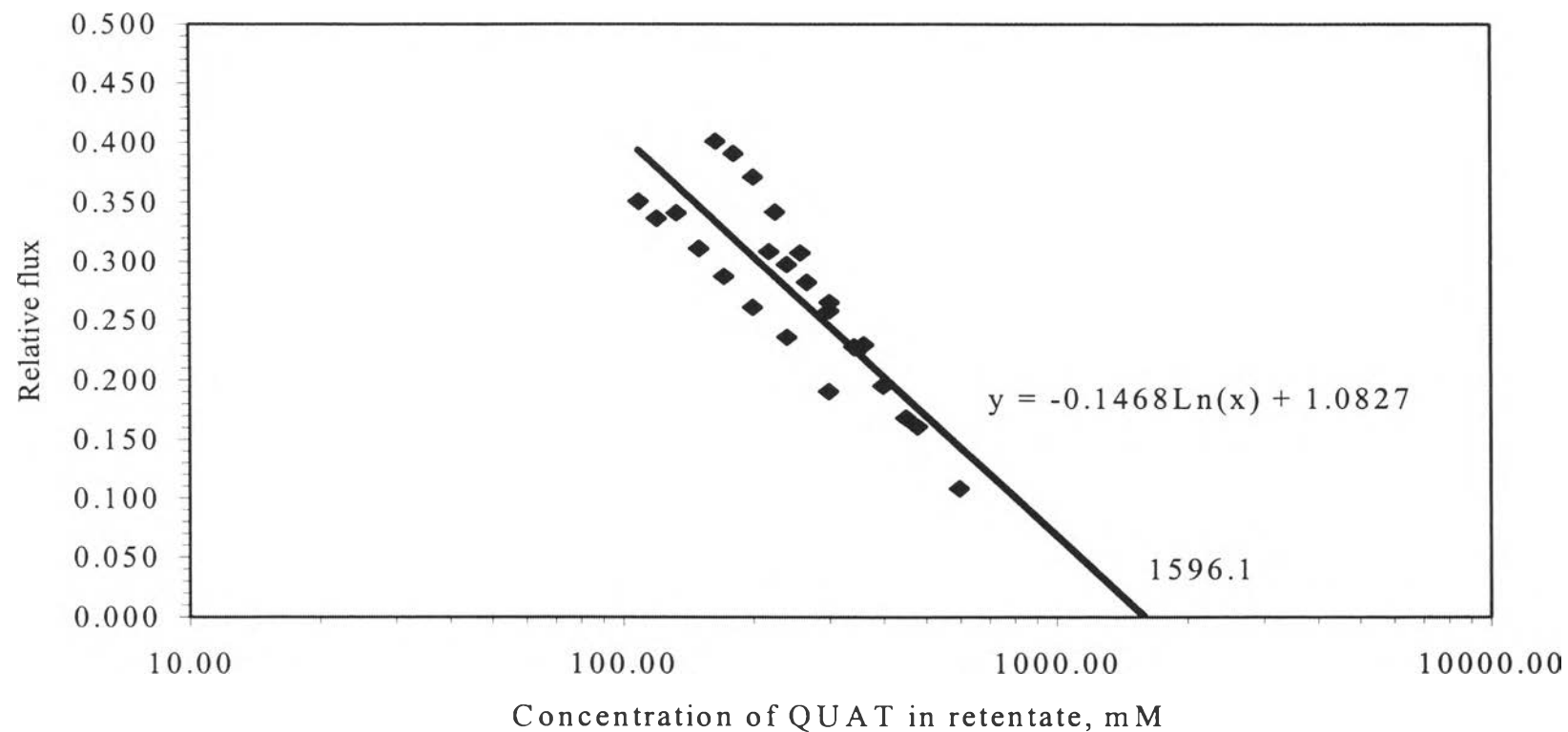


Figure 4.6 Relative flux as a function of QUAT concentration in retentate at ratio [QUAT]:[Chromate]:[Sulfate] = 20:1:1.

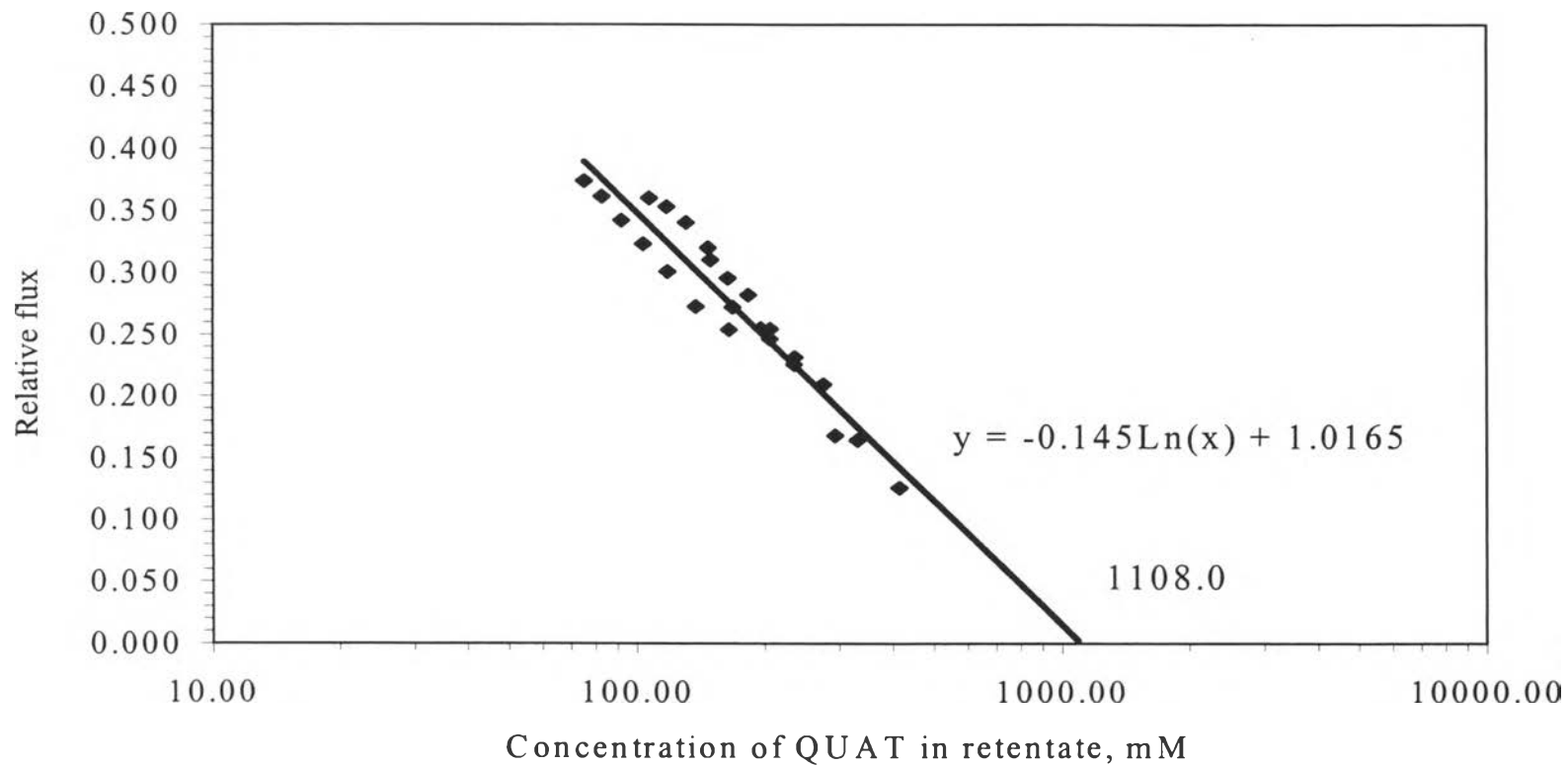
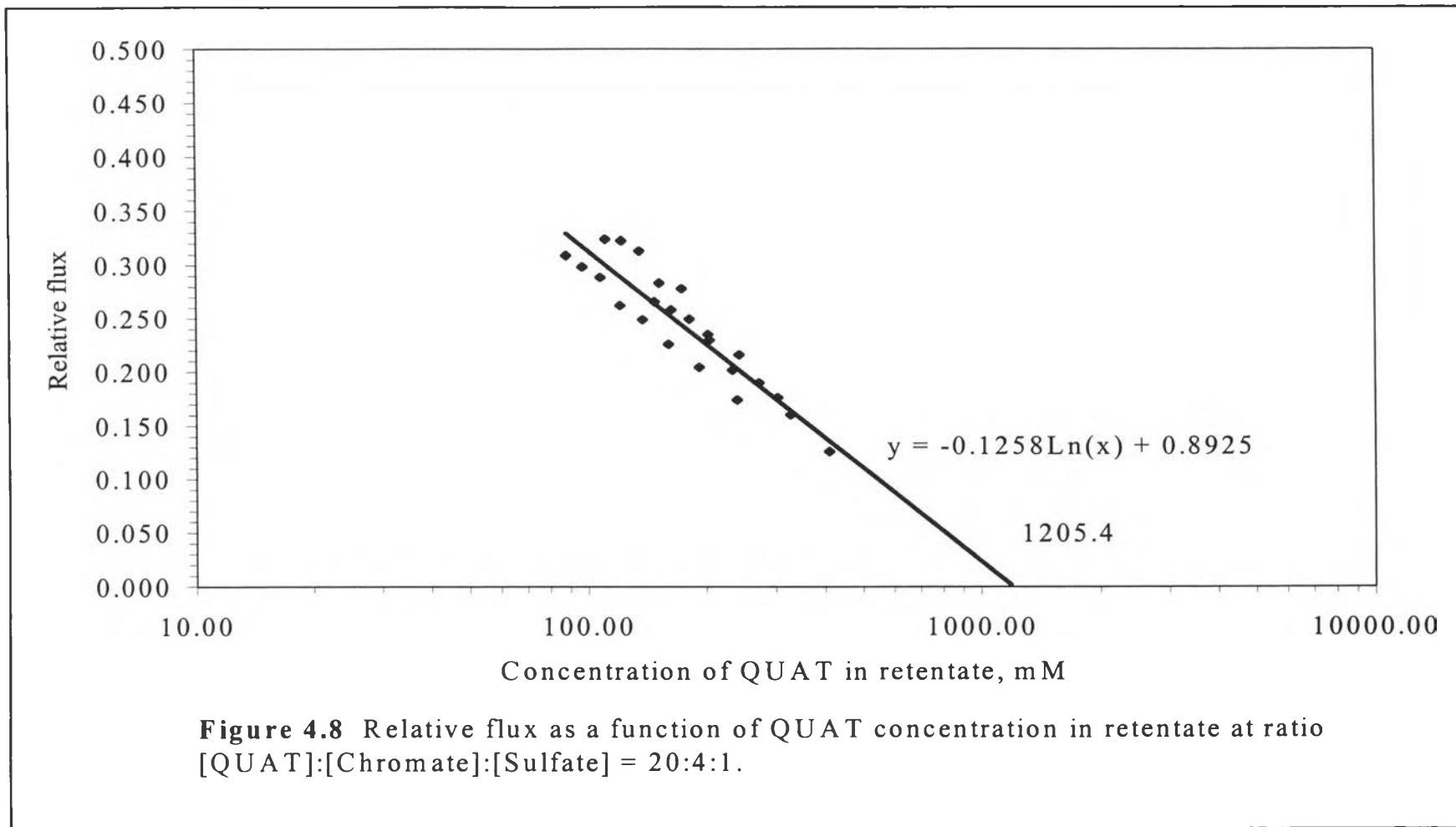


Figure 4.7 Relative flux as a function of QUAT concentration in retentate at ratio [QUAT]:[Chromate]:[Sulfate] = 20:2:1.



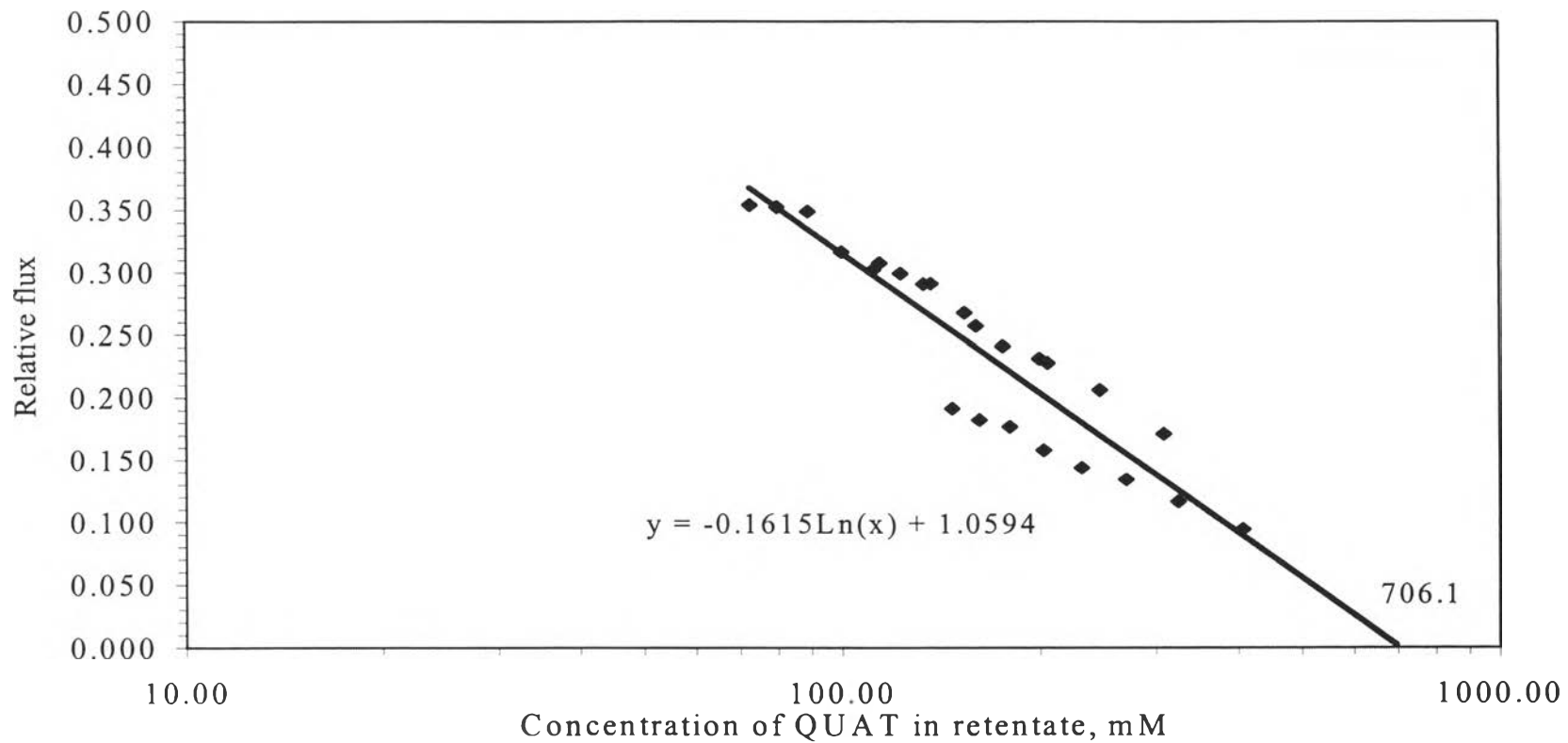


Figure 4.9 Relative flux as a function of QUAT concentration in retentate at ratio [QUAT]:[Chromate]:[Sulfate] = 20:6:1.

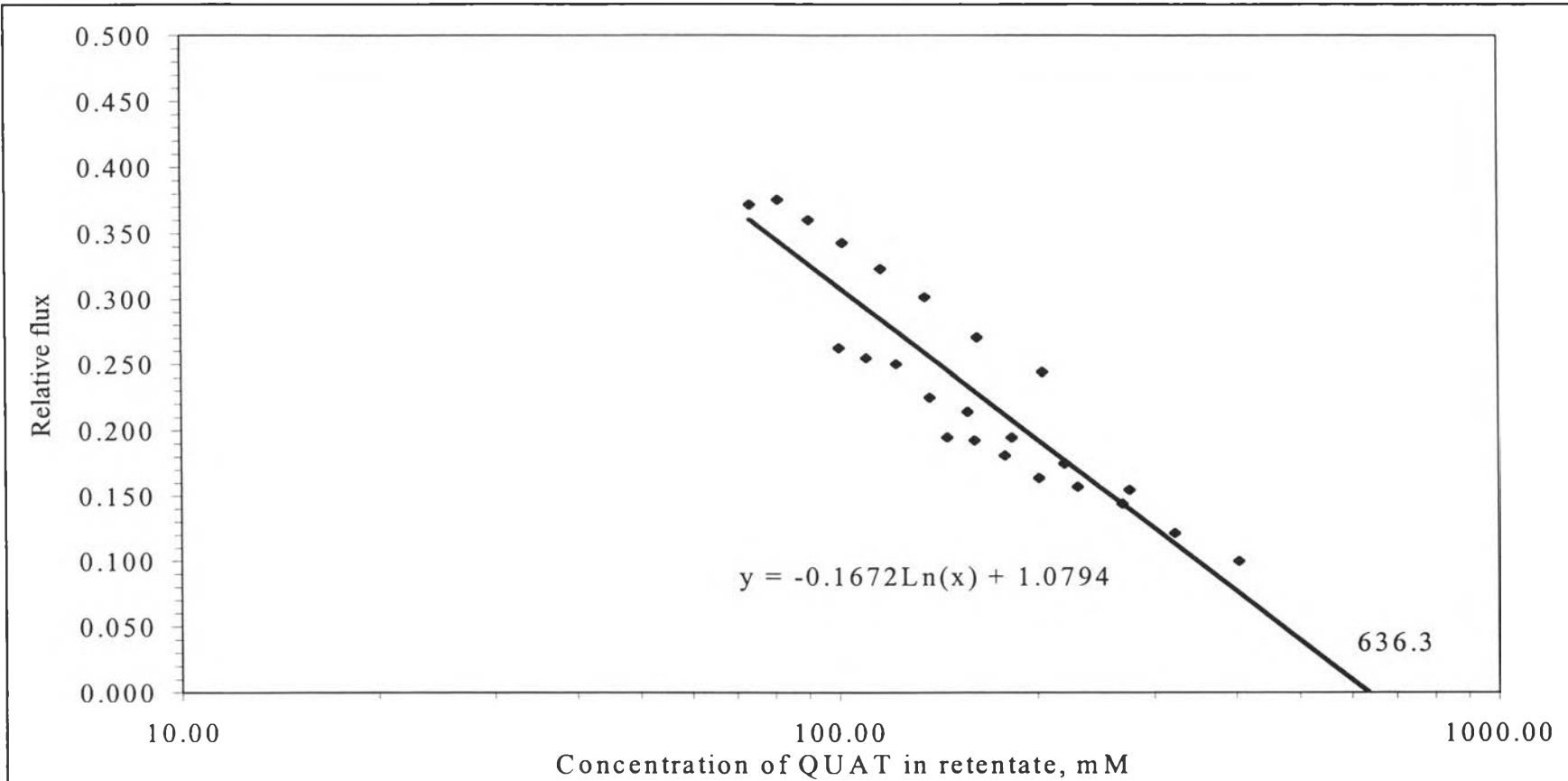
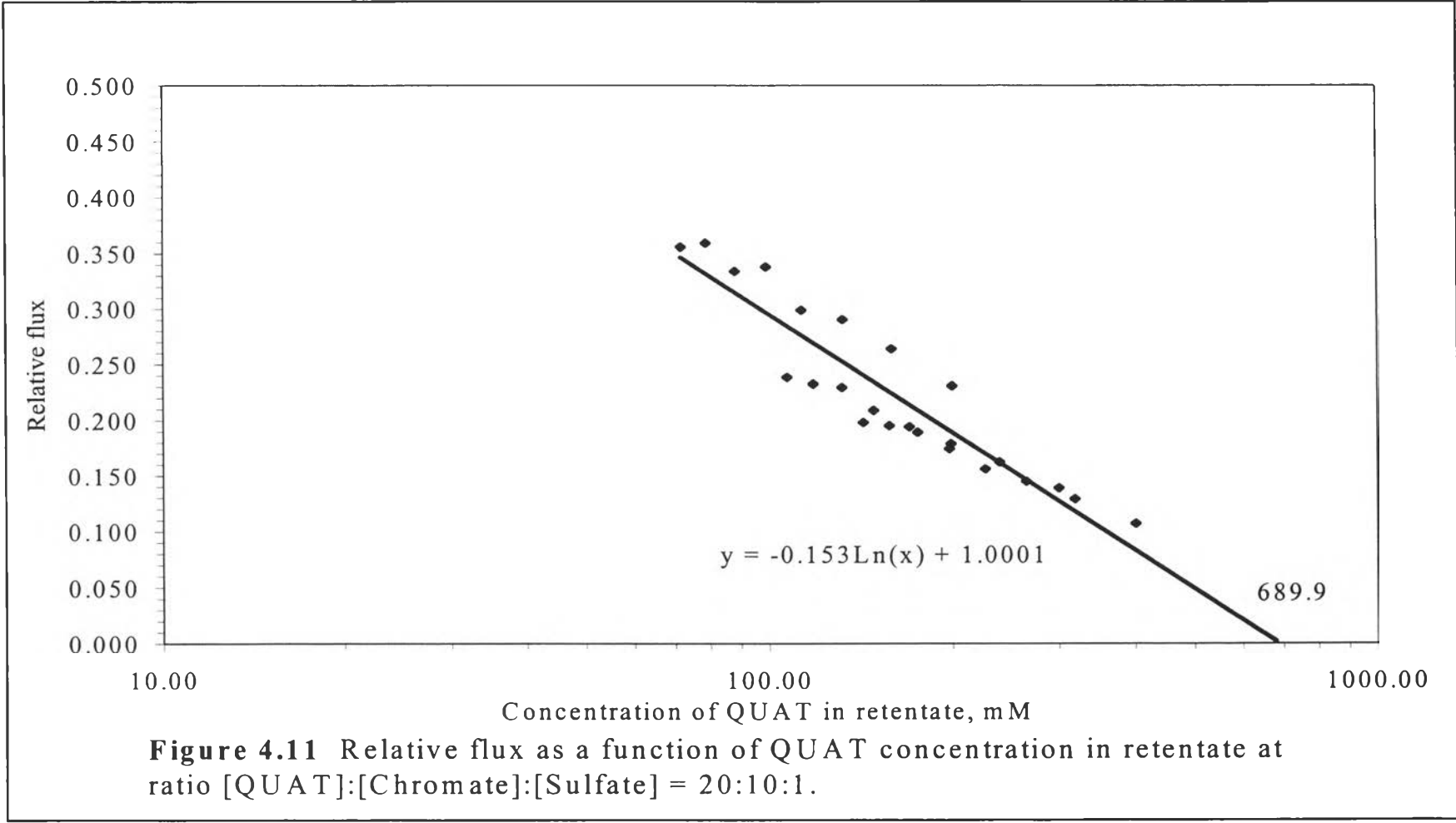


Figure 4.10 Relative flux as a function of QUAT concentration in retentate at ratio [QUAT]:[Chromate]:[Sulfate] = 20:8:1.



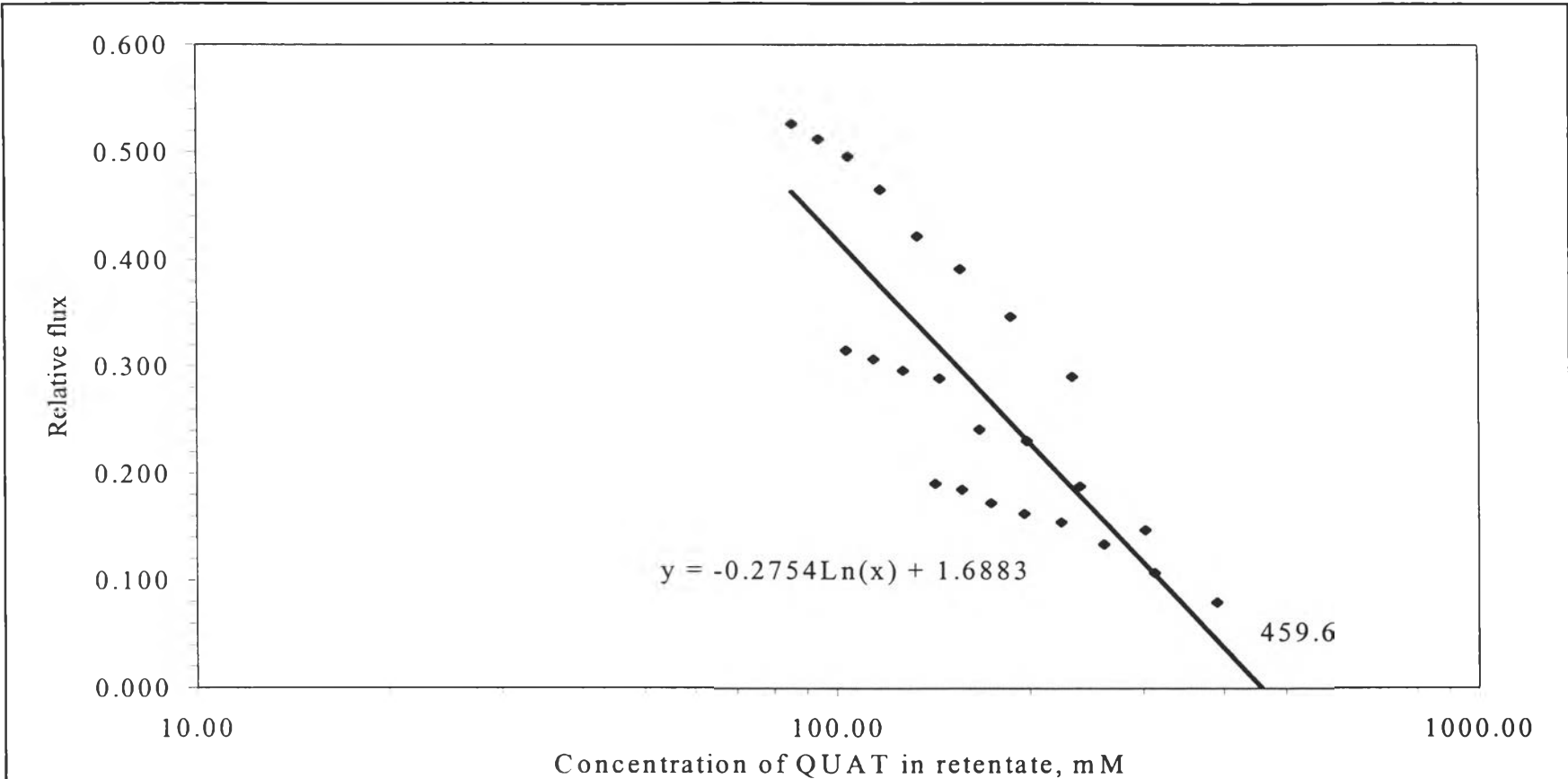
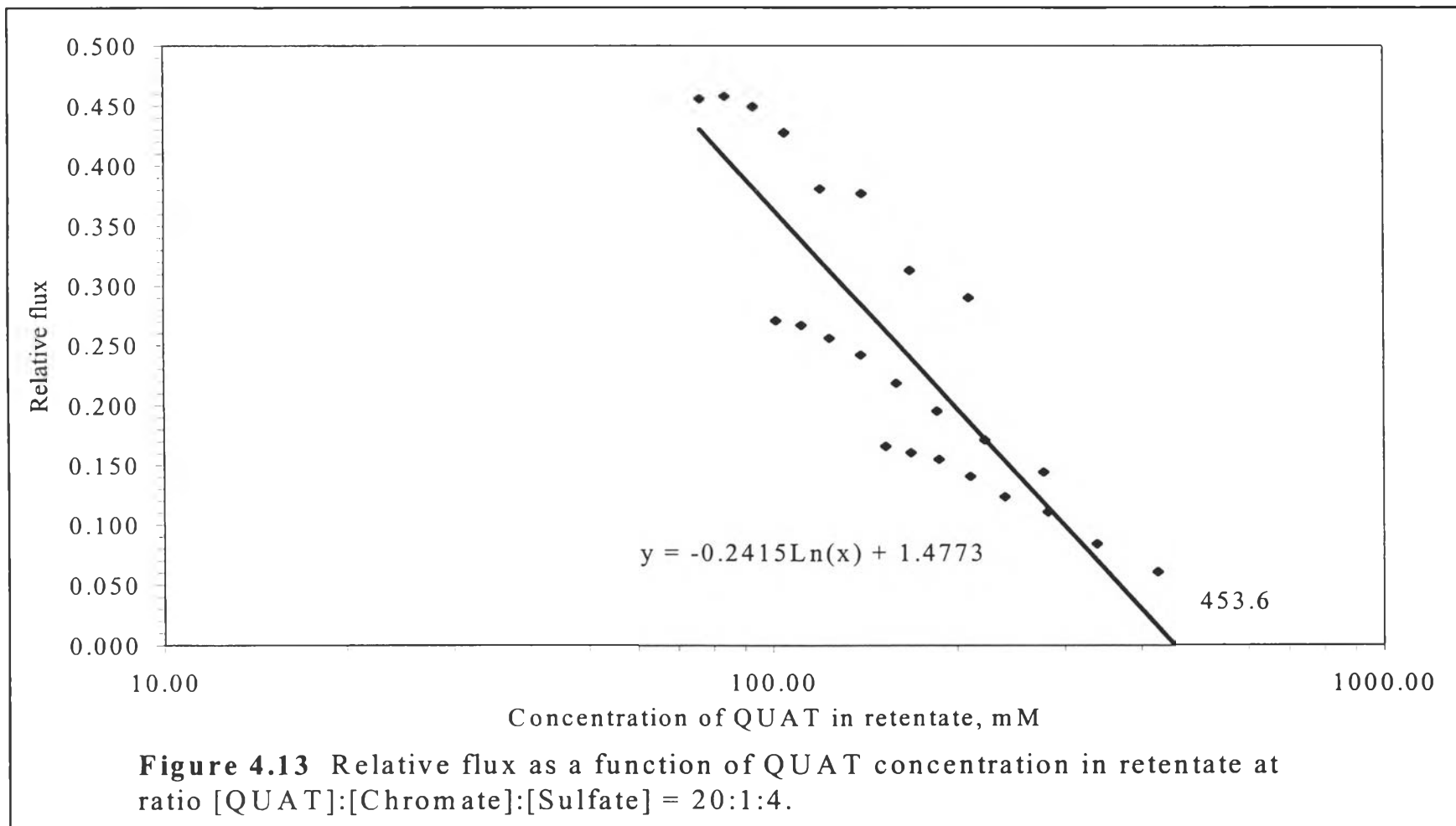


Figure 4.12 Relative flux as a function of QUAT concentration in retentate at ratio [QUAT]:[Chromate]:[Sulfate] = 20:1:2.



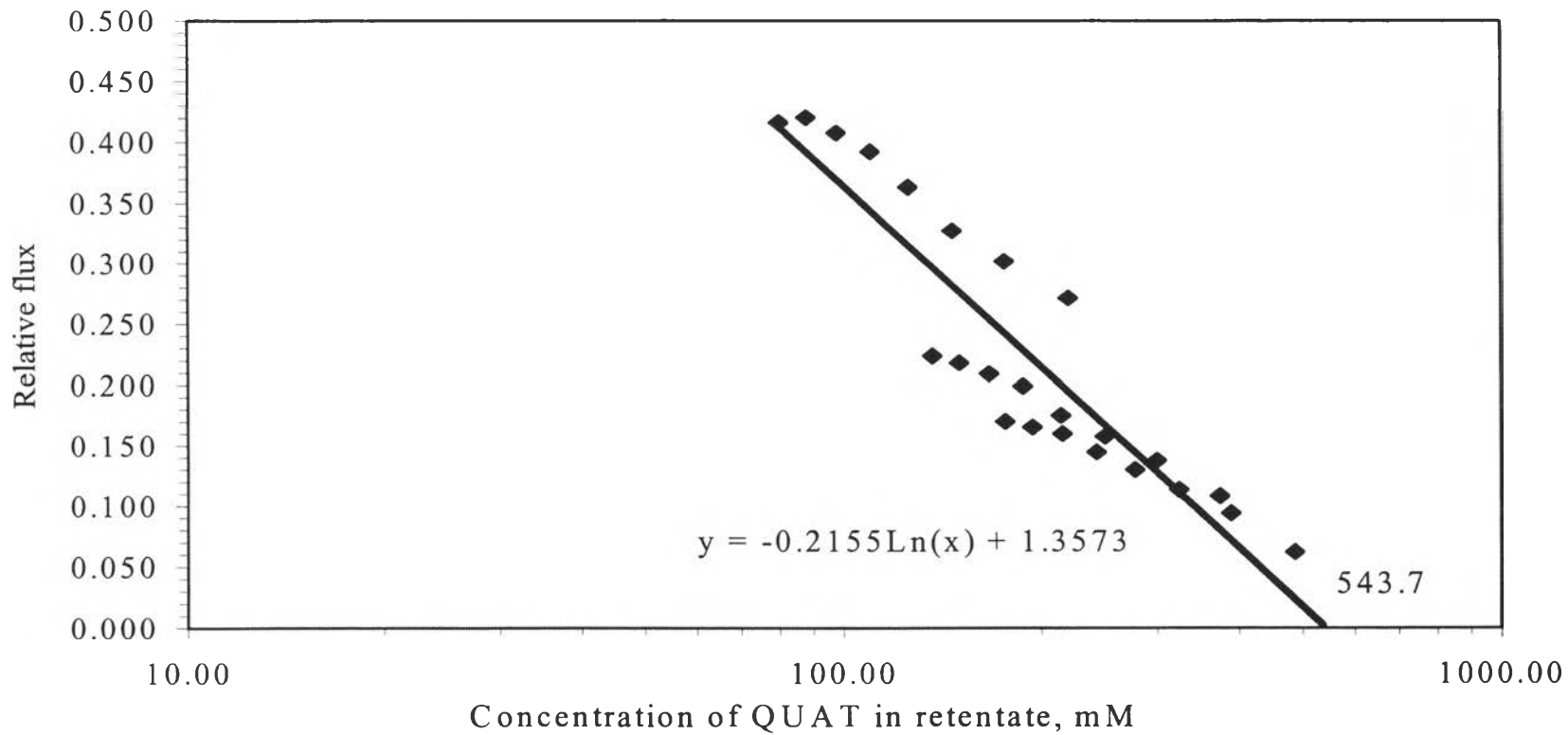


Figure 4.14 Relative flux as a function of QUAT concentration in retentate at ratio [QUAT]:[Chromate]:[Sulfate] = 20:1:6.

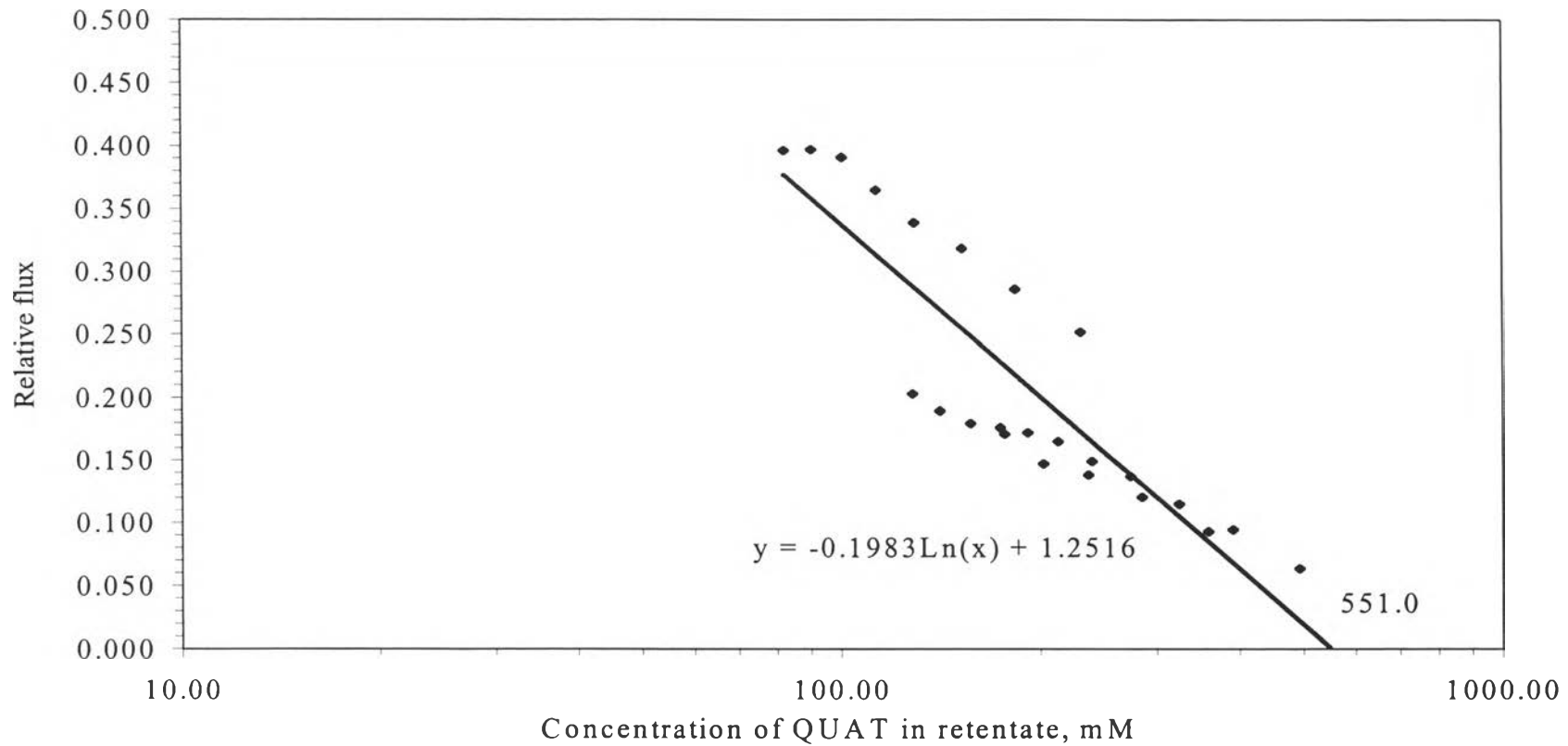


Figure 4.15 Relative flux as a function of QUAT concentration in retentate at ratio [QUAT]:[Chromate]:[Sulfate] = 20:1:8.

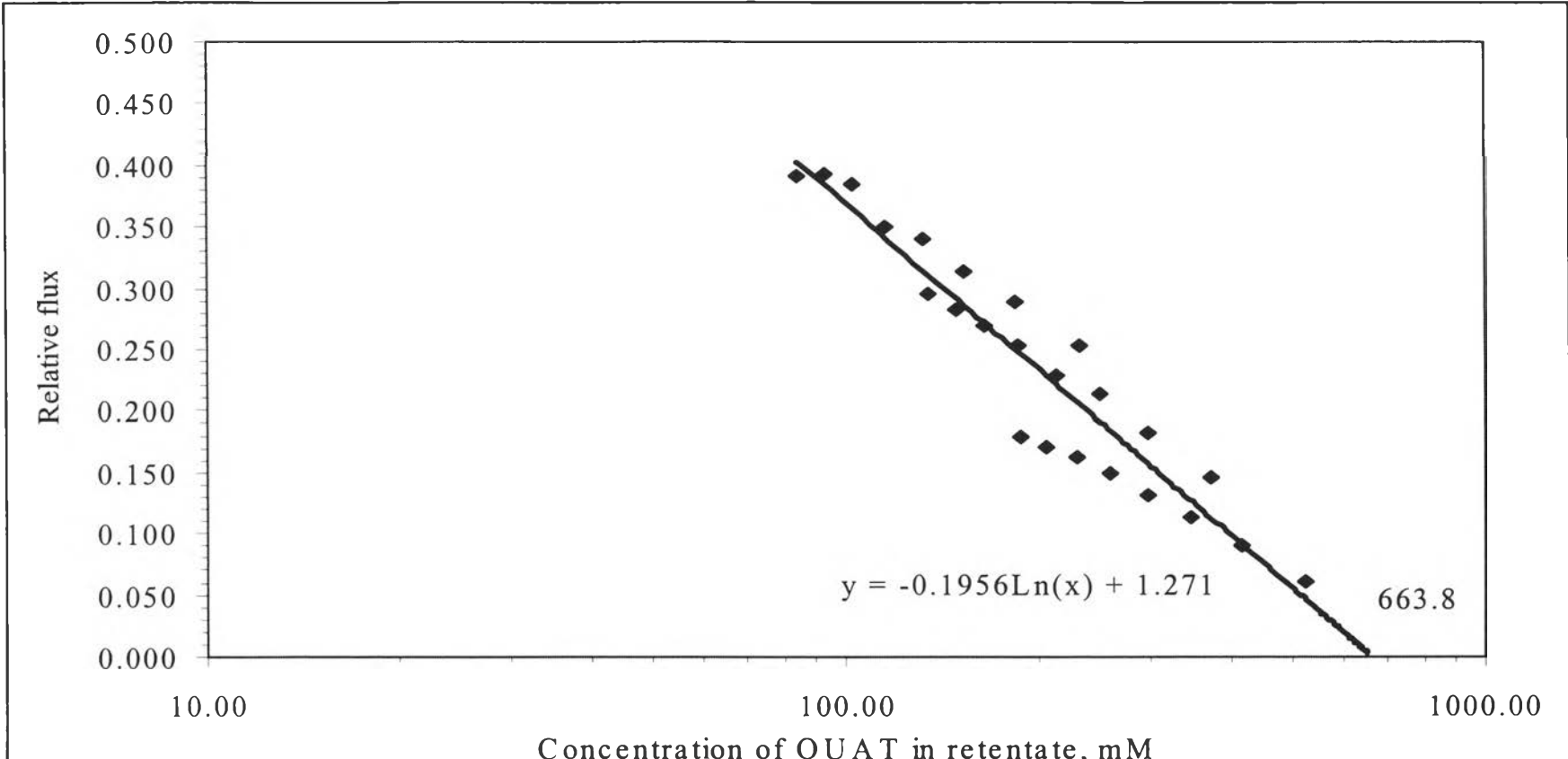


Figure 4.16 Relative flux as a function of QUAT concentration in retentate at ratio [QUAT]:[Chromate]:[Sulfate] = 20:1:10.

4.3 Equilibrium Precipitation

4.3.1 Effect of barium(II) ion on equilibrium precipitation

Figure 4.17 shows the effect of barium(II) ion on the precipitation of barium chromate and barium sulfate as a function of fraction of chromate precipitated at differently initial QUAT concentrations (0.1, 0.2 and 0.3 M). When barium(II) ion or $[\text{Barium}]:[\text{Chromate} + \text{Sulfate}]$ was increased, the higher fraction of chromate precipitated. For example, at the concentration ratio of barium to total anions (equimolar of chromate and sulfate) equals to 2, the fraction of chromate precipitated almost reach 100% due to the excess-stoichiometric usage of barium(II) ion for equilibrium precipitation with divalent anions. This condition means that the polyelectrolyte was recovered almost 100%. Whereas the higher QUAT concentration, the slightly higher reduction in the fraction of chromate precipitated.

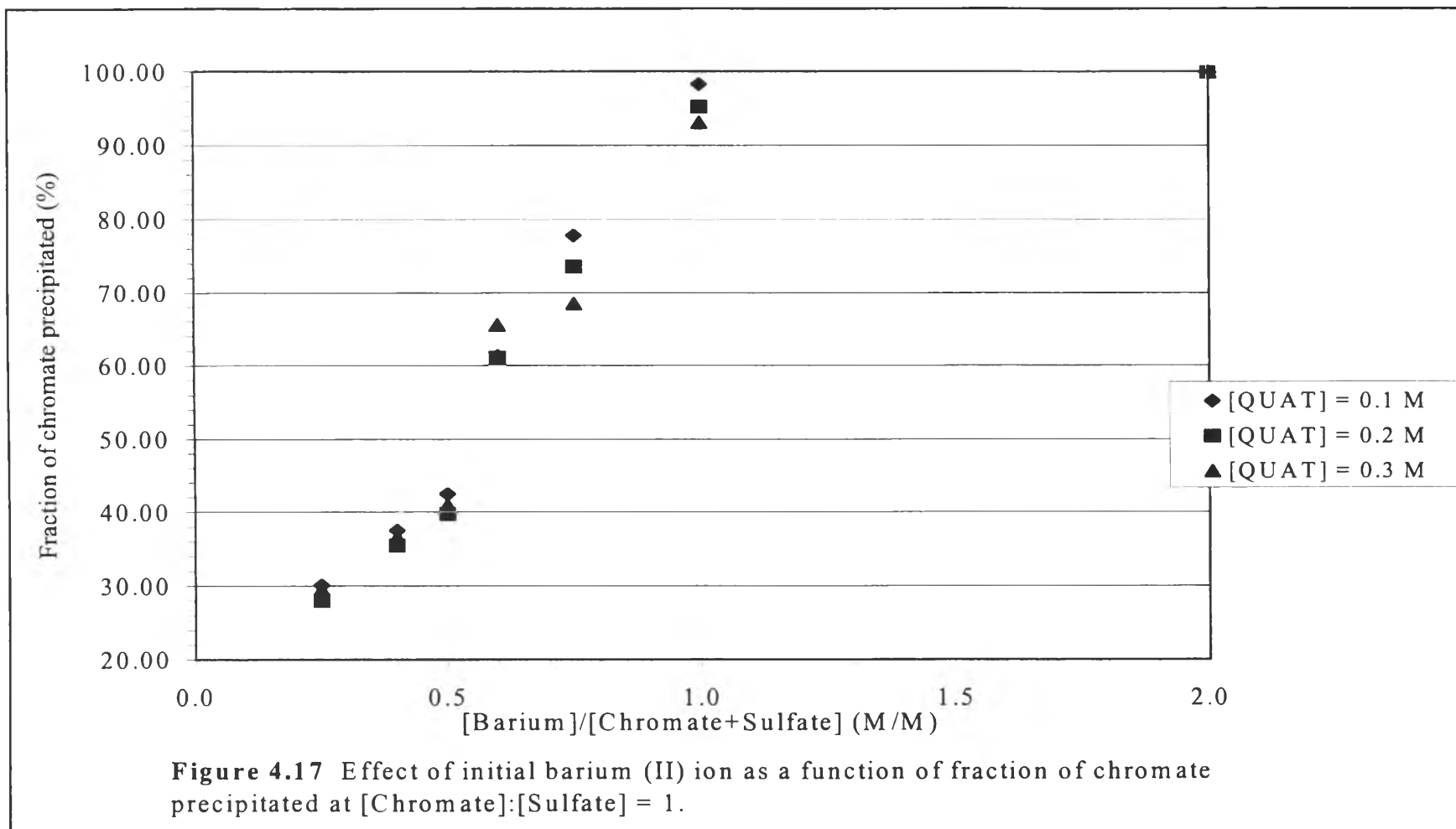
4.3.2 Effect of chromate on equilibrium precipitation

Figure 4.18 shows the effect of initial chromate on the precipitation of barium chromate and barium sulfate as a function of fraction of chromate precipitated at different initial QUAT concentrations (0.1, 0.2 and 0.3 M). When concentration of chromate was increased or $[\text{Barium}]:[\text{Chromate}]$ was decreased, a lower fraction of chromate precipitated. At the concentration ratio of barium to chromate and barium to sulfate equal to 2, $[\text{Barium}]:[\text{Chromate}]:[\text{Sulfate}] = 2:1:1$ or stoichiometric ratio, the fraction of chromate precipitated was approximately 98%, 95% and 93% for different initial QUAT concentrations (0.1, 0.2 and 0.3 M, respectively). It cannot reach the fraction of chromate precipitated of 100% caused by polymer-binding with free anions. The higher QUAT concentration, the more difficult to precipitate barium chromate and barium sulfate than the lower QUAT concentration.

4.3.3 Effect of sulfate on equilibrium precipitation

Figure 4.19 shows the effect of initial sulfate on the precipitation of barium chromate and barium sulfate as a function of fraction of chromate precipitated at different initial QUAT concentrations (0.1, 0.2 and 0.3 M). When

sulfate concentration was increased or [Barium]:[Sulfate] was decreased, the lower fraction of chromate precipitated. At [Barium]:[Chromate]:[Sulfate] = 2:1:1 or stoichiometric ratio, the fraction of chromate precipitated was approximately 98%, 95% and 93% for different initial QUAT concentration (0.1, 0.2 and 0.3 M, respectively). It cannot reach the fraction of chromate precipitated of 100% due to positively charged site of polymer bound with free chromate and sulfate. Therefore, the higher QUAT concentration is more difficult to precipitate barium chromate and barium sulfate than the lower QUAT concentration.



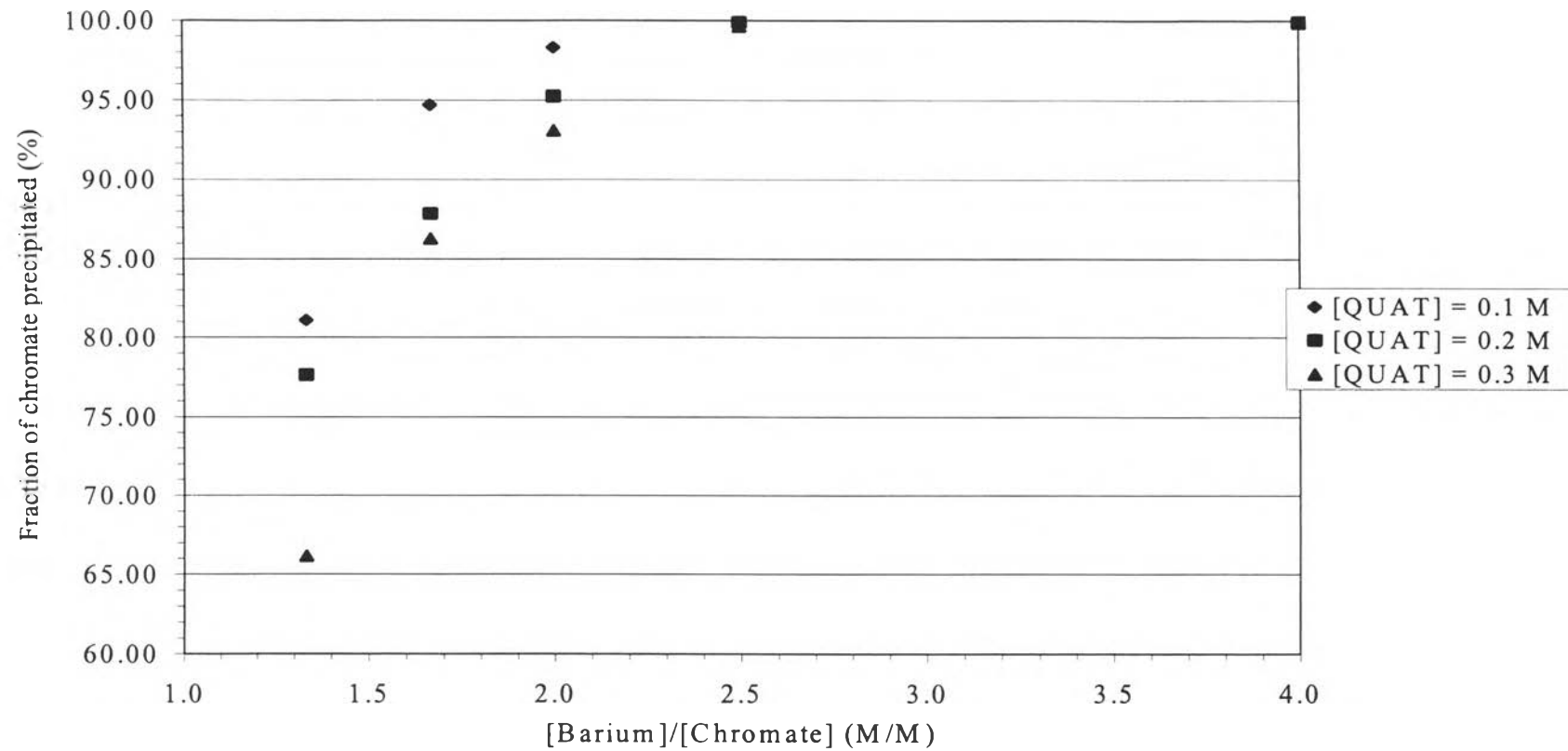


Figure 4.18 Effect of initial chromate as a function of fraction of chromate precipitated at [Barium]:[Sulfate] = 2.

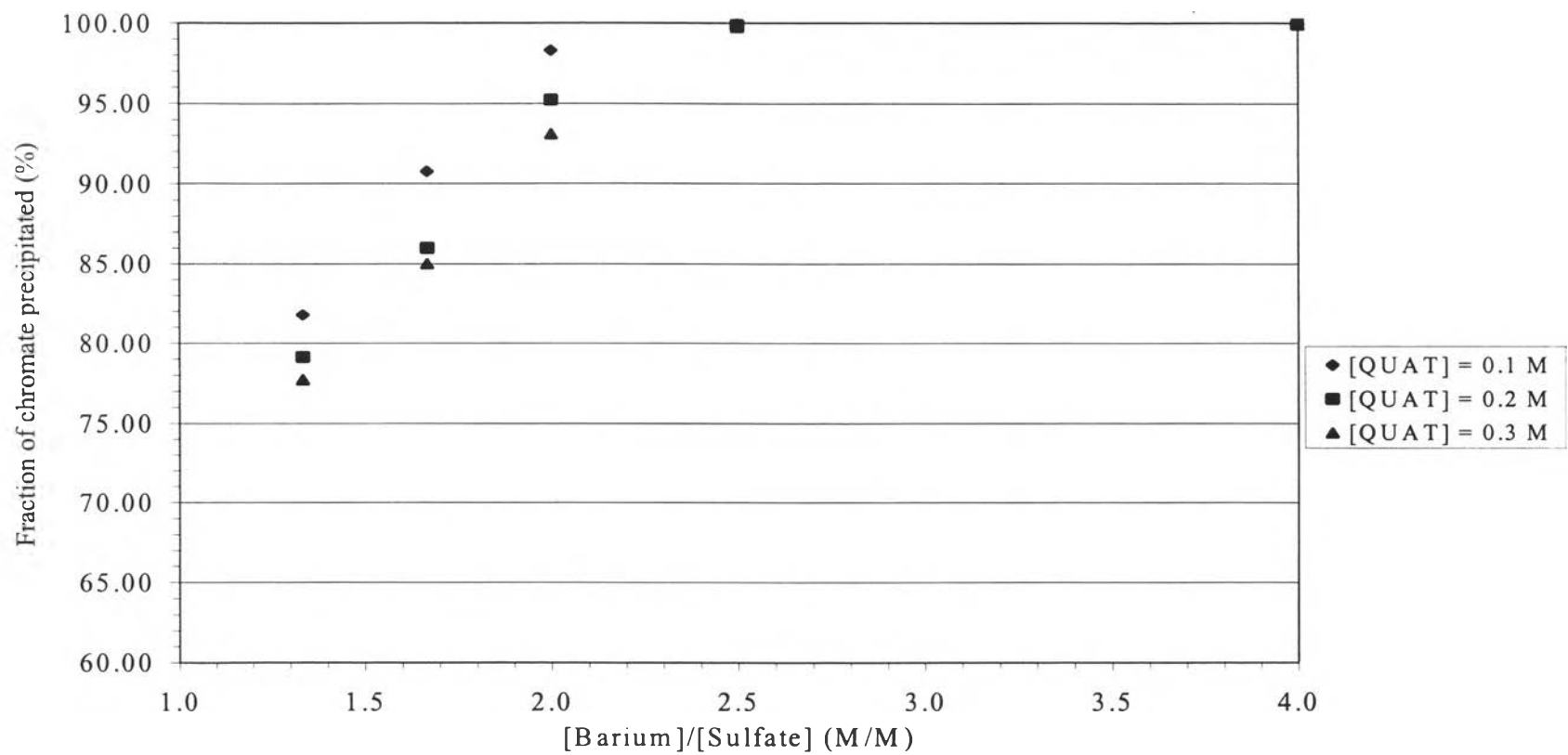


Figure 4.19 Effect of initial sulfate as a function of fraction of chromate precipitated at [Barium]:[Chromate] of 2.