

## CHAPTER IV

### RESULTS AND DISCUSSION

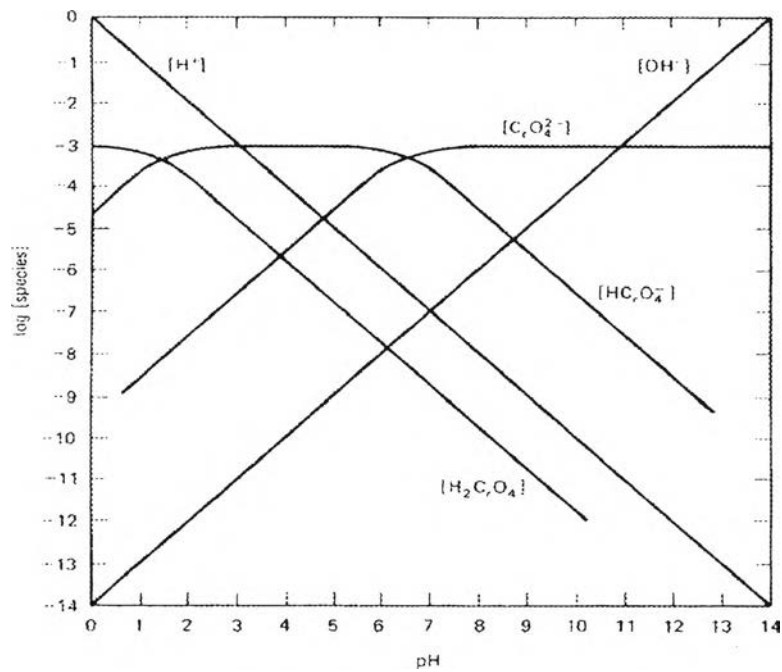
#### 4.1 Rejection of Anions

Generally, chromate and other anions (such as  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ) do not exist alone, but some accompanying cations also present in aqueous stream. The extent to which these ions occur in the ionic forms is strongly effected by a solution pH. Figure 4.1 indicates that the predominant species between pH 1.5 and 4.0 is  $\text{HCrO}_4^-$ . At pH 6.5,  $\text{HCrO}_4^-$  and  $\text{CrO}_4^{2-}$  exist in equal amount and at higher pH,  $\text{CrO}_4^{2-}$  predominates. Figure 4.2 indicates that the only the sulphate ion,  $\text{SO}_4^{2-}$  predominates at pH level above 3.0. The sulphate and bisulphate ions exist about equal amount at pH 2.0 and the bisulphate ion predominates at pH 1.0 (Benefield, 1982). Nitrate ions from most metal nitrate salts or strong nitric acid are in  $\text{NO}_3^-$  form at both low and high pH. The pH conditions at which the PEUF was operated were about 8.0 in most cases. Therefore, the ions species present mainly would be  $\text{CrO}_4^{2-}$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  and there is insignificant pH effect involved throughout this study.

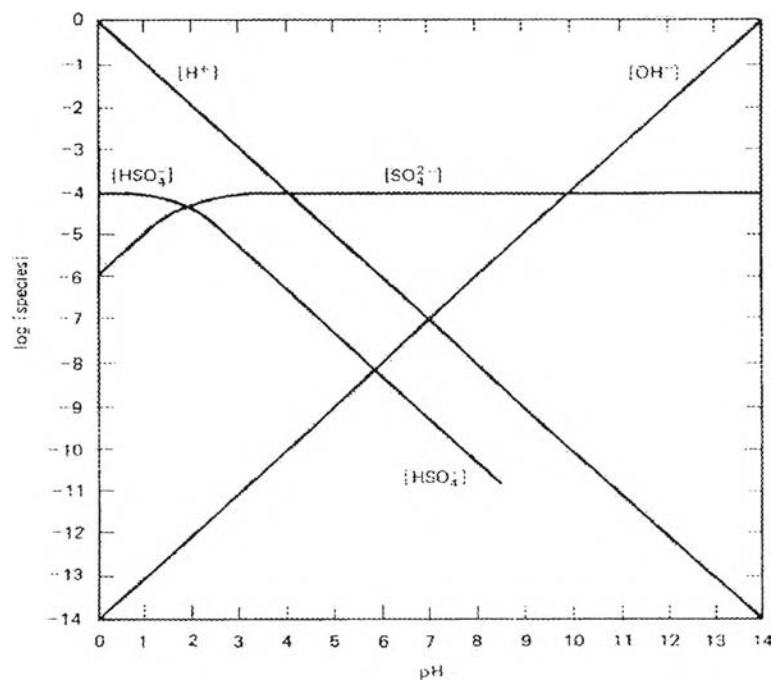
The results of the PEUF runs were shown as the removal efficiency of the chromate, sulphate, and nitrate which was represented by the rejection percentage, R (%), as defined by

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

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



**Figure 4.1** Logarithmic concentration diagram for  $10^{-3}$  M  $\text{H}_2\text{CrO}_4$  solution at various pH values (Benfield *et al.*, 1982).



**Figure 4.2** Logarithmic concentration diagram for  $10^{-3}$  M  $\text{H}_2\text{SO}_4$  solution at various pH values (Benfield *et al.*, 1982).

Figure 4.3 shows a semilog plot of the rejection percentage of chromate as a function of QUAT concentration in retentate at various ratios of [QUAT] to  $[\text{CrO}_4^{2-}]$ . These PEUF runs were performed at the [QUAT] to [anion] ratios of 5, 10 and 20, respectively. High rejection percentage of chromate occurred at low concentrations of QUAT in retentate (less than 150 mM) where the rejection percentage greater than 99% can be obtained at various ratios studied. In previous PEUF studies on the removal of chromate ( $\text{CrO}_4^{2-}$ ) from water using poly(dimethyldiallyl ammonium chloride), the rejection reached as high as 99.60% for low QUAT concentrations in retentate (less than 150 mM) (Sriratana *et al.*, 1994). In the present PEUF studies, when QUAT concentration was higher than 150 mM, the rejection percentage of chromate started to decrease. The lower the ratio of [QUAT] to  $[\text{CrO}_4^{2-}]$ , the higher reduction in rejection percentage. When QUAT concentration in retentate reached to 400 mM, the rejection percentage are approximately 89%, 97%, and 98% for ratio of [QUAT] to  $[\text{CrO}_4^{2-}]$  equal to 5, 10, and 20, respectively. The high QUAT concentrations in retentate (as high as 400 mM) have caused decrease in the chromate rejection (Figure 4.3) due to the increase in polarization phenomena near the membrane surface (Juang and Chen, 1996). Only ratio of [QUAT] to  $[\text{CrO}_4^{2-}]$  equal to 20 that could maintain high rejection percentage due to increase in the availability of the positively charged sites on the poly(diallyldimethyl ammonium chloride) which increased the magnitude of the poly(diallyldimethyl ammonium chloride) surface electrical potential and thus enhancing the binding of the negatively charge ions.

Figure 4.4 shows the rejection percentage of chromate at various chromate concentrations in retentate. When ratio of [QUAT] to  $[\text{CrO}_4^{2-}]$  was equal to 5, the rejection percentage was the lowest (less than 92%). Again only the high ratios of [QUAT] to  $[\text{CrO}_4^{2-}]$  (10 and 20) could maintain high rejection percentage (more than 97%). High rejection percentage of chromate

(nearly 100%) was obtained at concentration of chromate in retentate less than 10 mM. When chromate concentration in retentate was more than 10 mM, the rejection percentage decreased due to the fact that excess chromate ion could pass through the membrane.

Figures 4.5-4.7 show the rejection percentages of anions ( $\text{CrO}_4^{2-}$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$ ) as a function of QUAT concentration in retentate at various ratios of [QUAT] to [anion] of 5, 10, and 20. The rejection percentages of anions increased with increasing the concentration ratio of QUAT to anion. The rejection greater than 99.5% can be obtained for  $\text{CrO}_4^{2-}$  as well as for  $\text{SO}_4^{2-}$  at high concentration ratio of QUAT to anion (20:1) and about 96.3% for  $\text{NO}_3^-$ . As QUAT concentration increased beyond 150 mM, the rejection percentages of anions decreased, when the concentration of QUAT was considered only. At a given ratio, the PEUF showed the rejection of  $\text{CrO}_4^{2-}$  and  $\text{SO}_4^{2-}$  approximately the same value and higher than rejection percentage of  $\text{NO}_3^-$  differs from  $\text{CrO}_4^{2-}$  and  $\text{SO}_4^{2-}$ . The divalent anions ( $\text{CrO}_4^{2-}$  and  $\text{SO}_4^{2-}$ ) which have higher electrostatic affinity to polymer, must be stronger competitor for the reagent than monovalent anion ( $\text{NO}_3^-$ ) (Juang and Chen, 1996). The nitrate ion is the most oxidizing form of nitrogen and chemically unreactive in dilute aqueous solution. All common metal nitrate salts are soluble and nitric acid is a strong acid. In this work, nitrate ion has little tendency to form complexes with cationic polyelectrolyte, therefore the nitrate rejection is low. The results also show that at the same concentration ratios of QUAT to anion, the rejection percentages of  $\text{CrO}_4^{2-}$  are approximately the same as  $\text{SO}_4^{2-}$  and differ from  $\text{NO}_3^-$ , reinforcing the conclusion that ion charge is the main factor in separation efficiency using PEUF, and that the metal species type and complexing characteristics are secondary effects (Scamehorn *et al.*, 1994).

Figures 4.8-4.10 show the rejection percentages of anions as a function of anion concentration in retentate at various ratios of [QUAT] to

[anion] (5, 10, and 20, respectively). The results showed that when concentration ratio of QUAT to anion increased, the rejection percentage decreased. These results were similar to those observed in Figures 4.5-4.7. As concentration of anion increased, the rejection percentage decreased due to the fact that excess anion could pass through the membrane.

#### 4.2 Effect of Concentration Polarization on Flux

Figures 4.11-4.13 show semilog plots between the relative flux of PEUF during the removal of chromate from water and polyelectrolyte concentration in retentate at various ratios of [QUAT] to  $[\text{CrO}_4^{2-}]$  (5, 10, and 20, respectively). The results indicated that the flux declined linearly with logarithm of retentate concentrations. This is a traditional concentration polarization behavior normally observed with ultrafiltration process as described by equation (2.2). According to this equation, when gel concentration ( $C_g$ ) and bulk concentration ( $C_b$ ) are equal, the solvent flux through the membrane is zero. Thus, 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 the ratios of [QUAT] to  $[\text{CrO}_4^{2-}] = 5, 10$  and 20, the gel formation concentrations (where flux decreases to 0) were approximately 750, 670, and 520 mM, respectively.

Figures 4.14-4.16 show the relative flux of sulphate as a function of polyelectrolyte concentration in retentate at various the ratios of [QUAT] to  $[\text{SO}_4^{2-}]$  (5, 10 and 20). The gel formation at the respective ratios of [QUAT] to  $[\text{SO}_4^{2-}]$  were determined and the gel concentrations were approximately 1000, 740, and 590 mM, respectively.

Figures 4.17-4.19 show relative flux during PEUF removal of nitrate at the ratios of [QUAT] to  $[\text{NO}_3^-]$  equal to 5, 10 and 20 and the gel formation concentrations were approximately 700, 550, and 550 mM, respectively.

The flux data obtained from the stirred cell ultrafiltration experiments are potentially valuable in planning a scale-up of the PEUF process. Information about the dependence of the relative flux on colloid concentration can be used to calculate the gel layer formation concentration, where flux decreases to zero. This relationship is still valid at high retentate polyelectrolyte concentrations (approximately 200, 300, and 400 mM) as shown in Figure 4.11-4.19. For all anions, the relative flux decreased with increasing polyelectrolyte concentrations in retentate to a high level and with increasing the concentration ratios of QUAT to anion as well. When the gel polarization concentrations were compared to other polyelectrolyte and surfactant systems, the gel formation concentrations were found to be 708 mM for anionic surfactant in previous study of MEUF (Scamehorn *et al.*, 1994), 530 mM for cationic surfactant (Dunn *et al.*, 1987) and 1,000 mM for MEUF of anionic polyelectrolyte (Scamehorn *et al.*, 1994). Our results agreed reasonably well with these studies.

It was reported that these gel concentrations did not depend on molecular-weight cutoffs (MWCO) of the membrane (Scamehorn *et al.*, 1990) which was consistent with the results observed here. It can be seen from this study that concentration polarization is not a severe problem in PEUF if the retentate concentration of polyelectrolyte is much lower than the gel polarization concentration. The gel formation concentration is very useful for setting a limit for operating concentration of the feed solution while running PEUF so that high flux can be obtained.

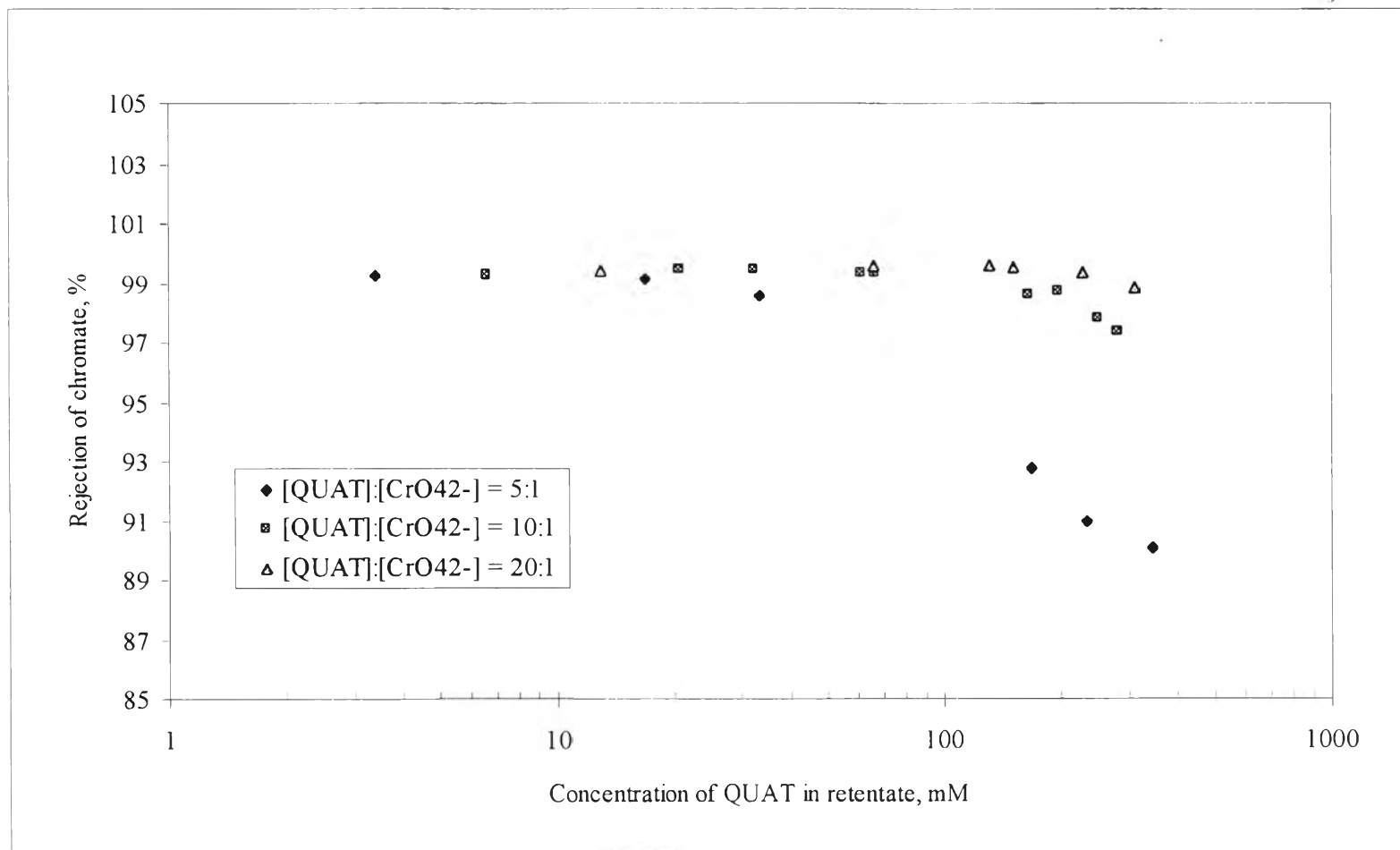
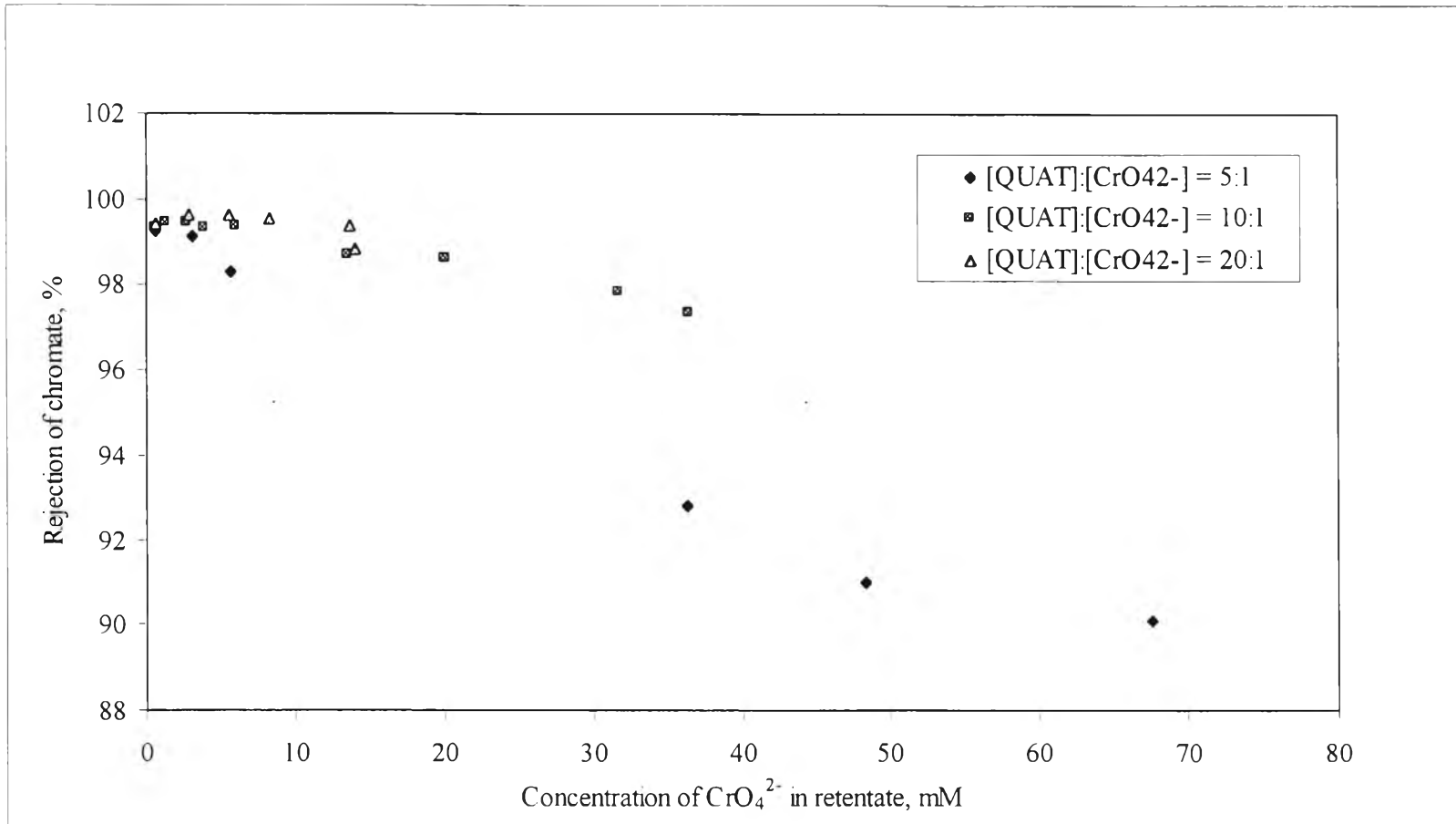
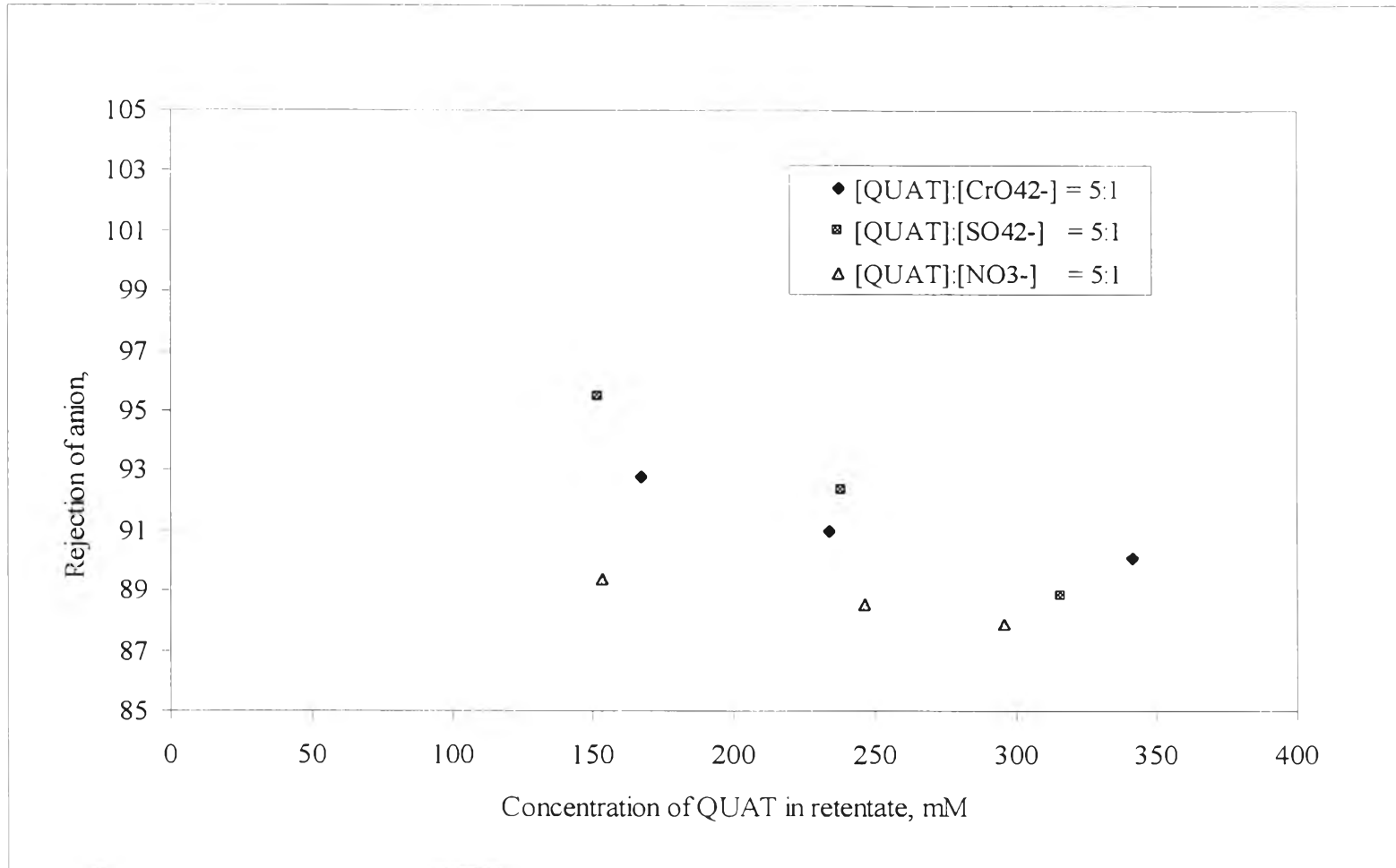


Figure 4.3 Chromate rejection as a function of QUAT concentration in retentate.

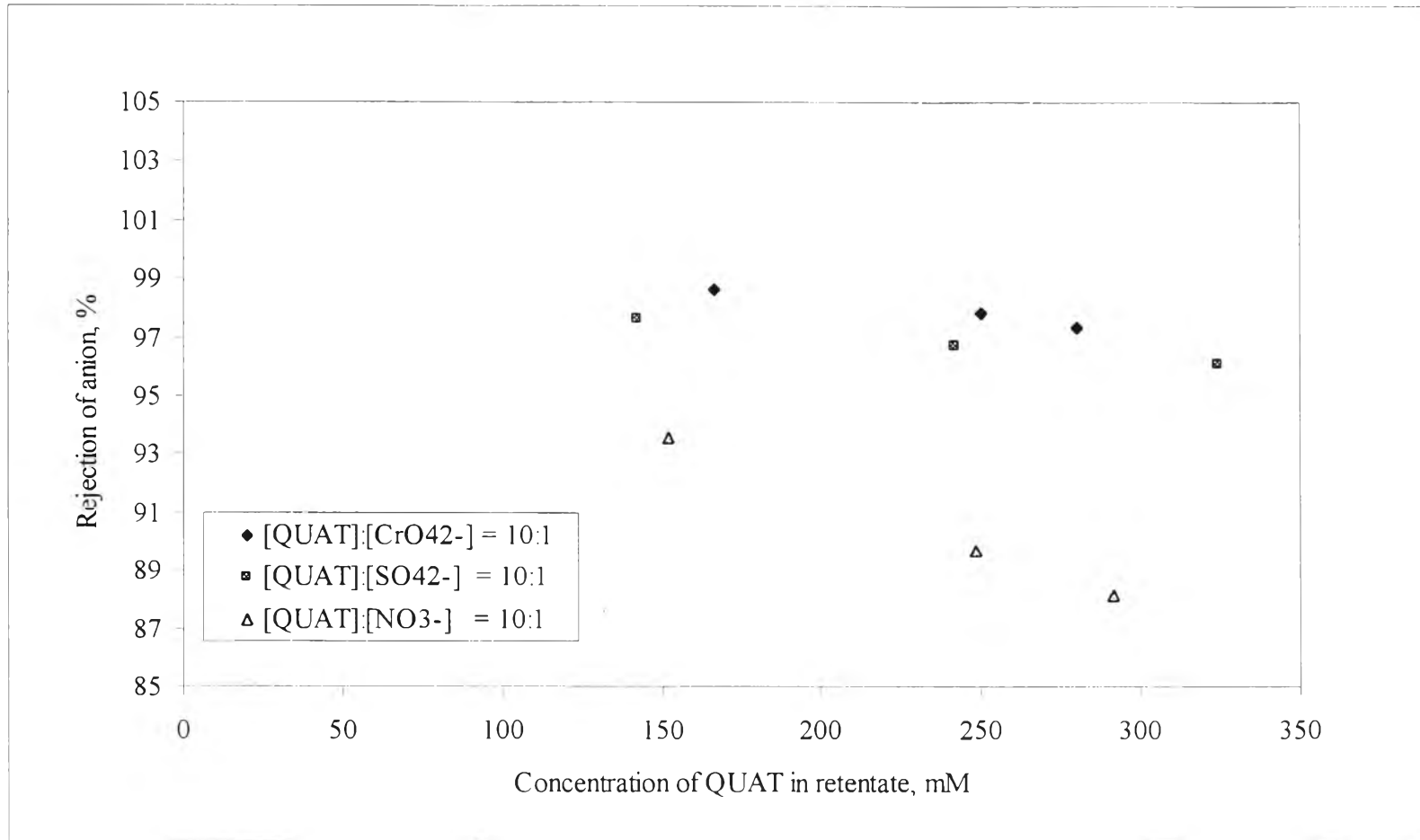


**Figure 4.4** Chromate rejection as a function of chromate concentration in retentate.

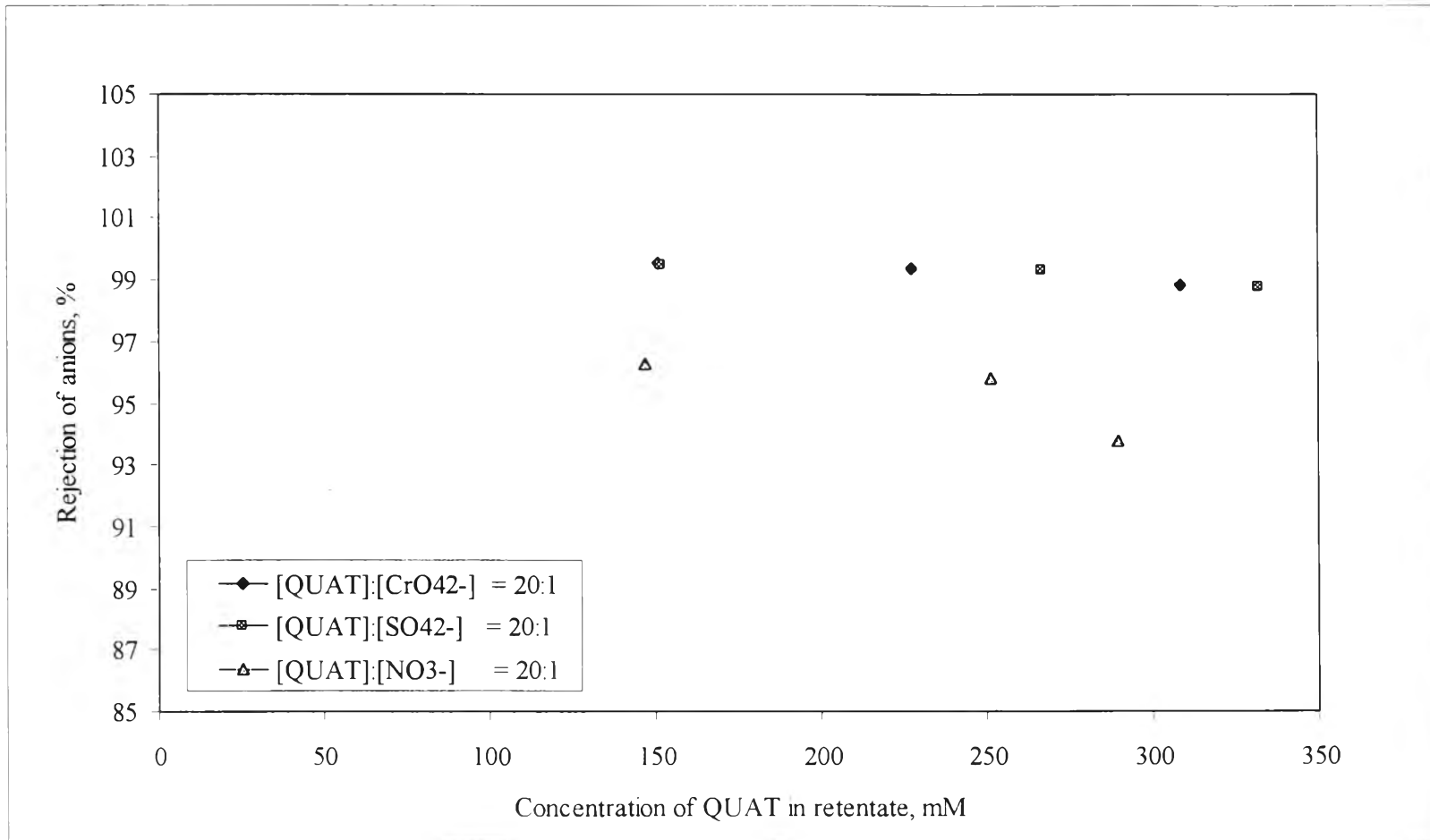




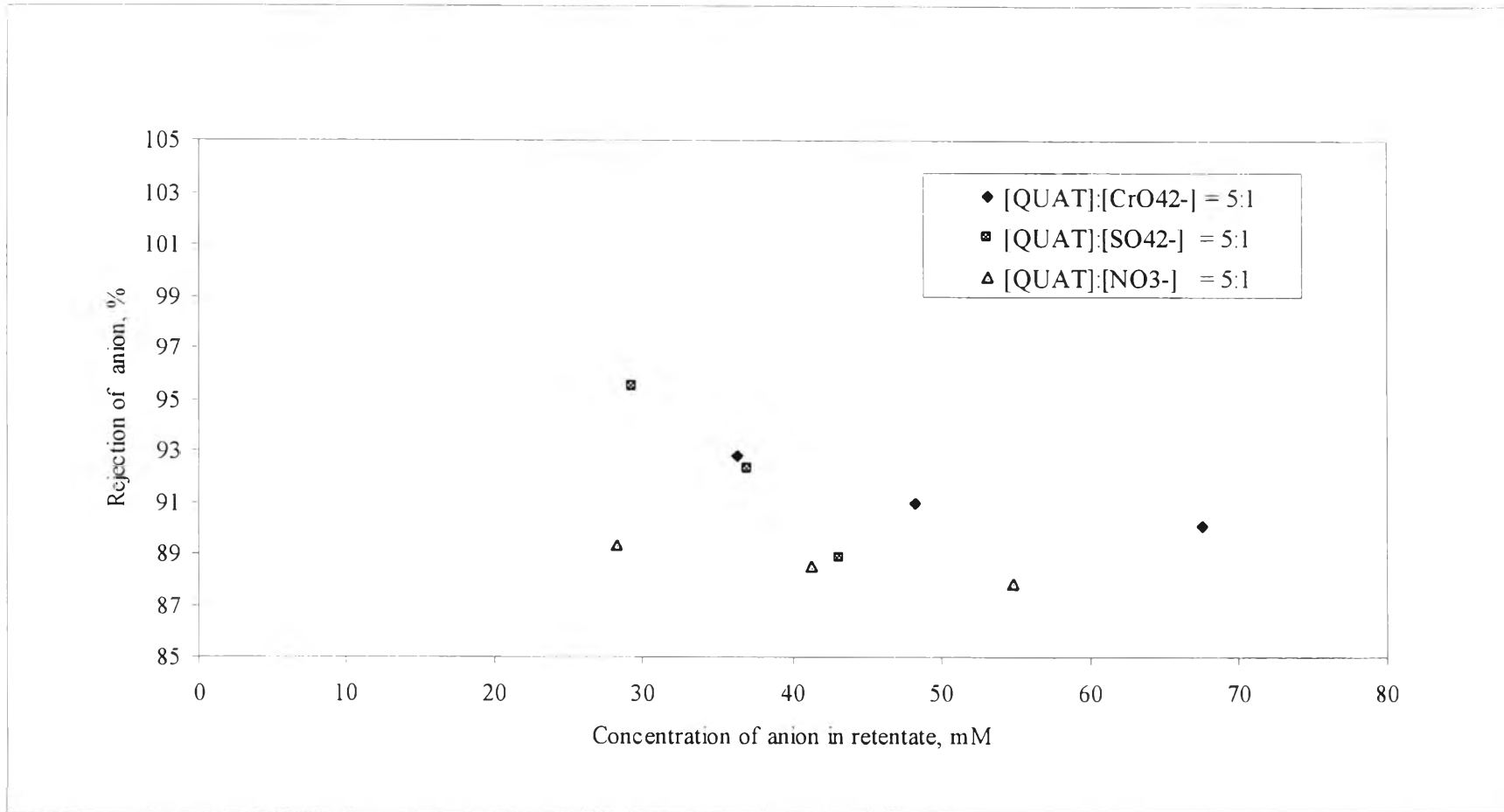
**Figure 4.5** Chromate, sulphate, and nitrate rejections as a function of QUAT concentration in retentate at ratio [QUAT]:[anion] = 5:1.



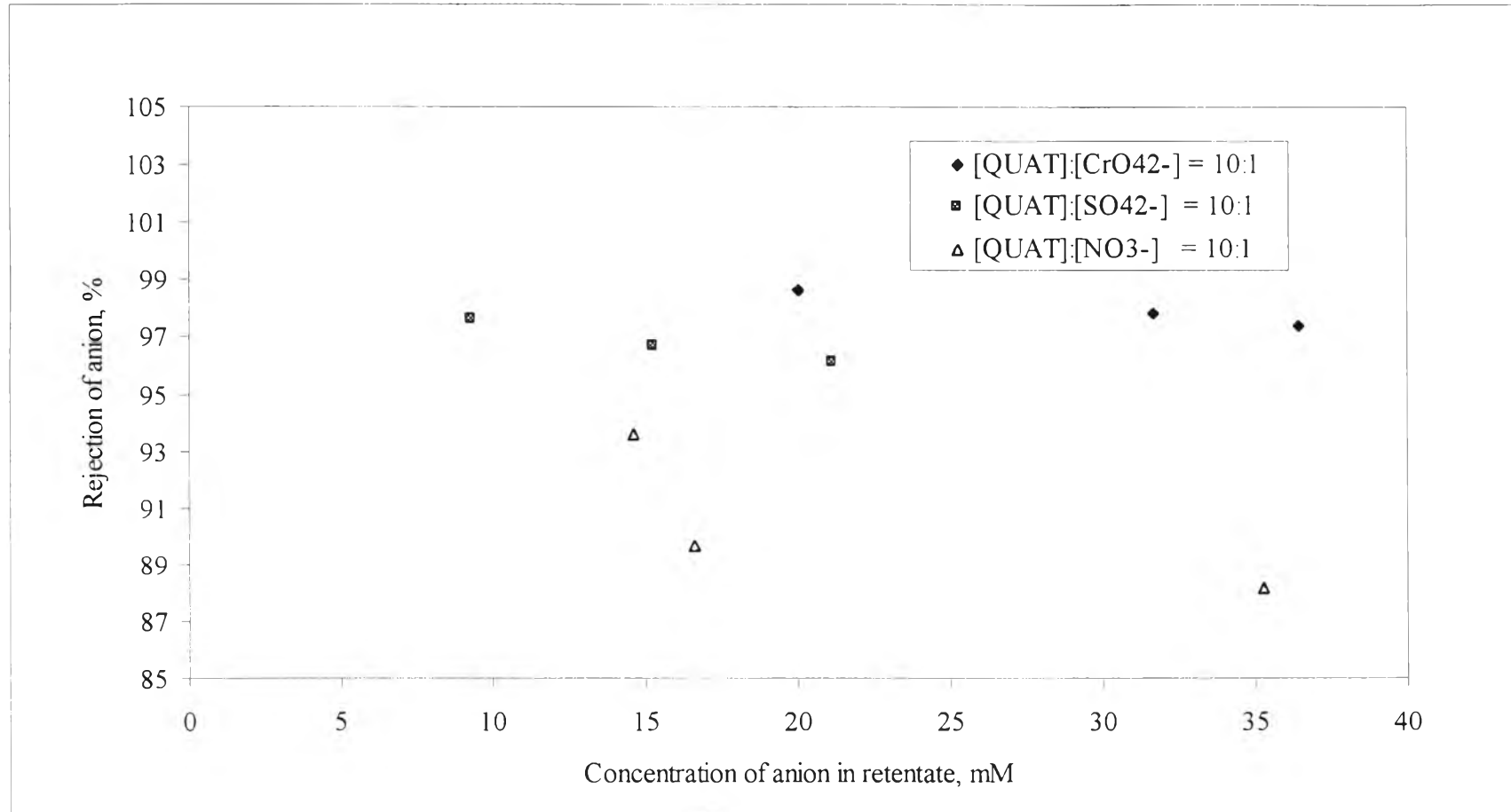
**Figure 4.6** Chromate, sulphate, and nitrate rejections as a function of QUAT concentration in retentate at ratio [QUAT]:[anion] = 10:1.



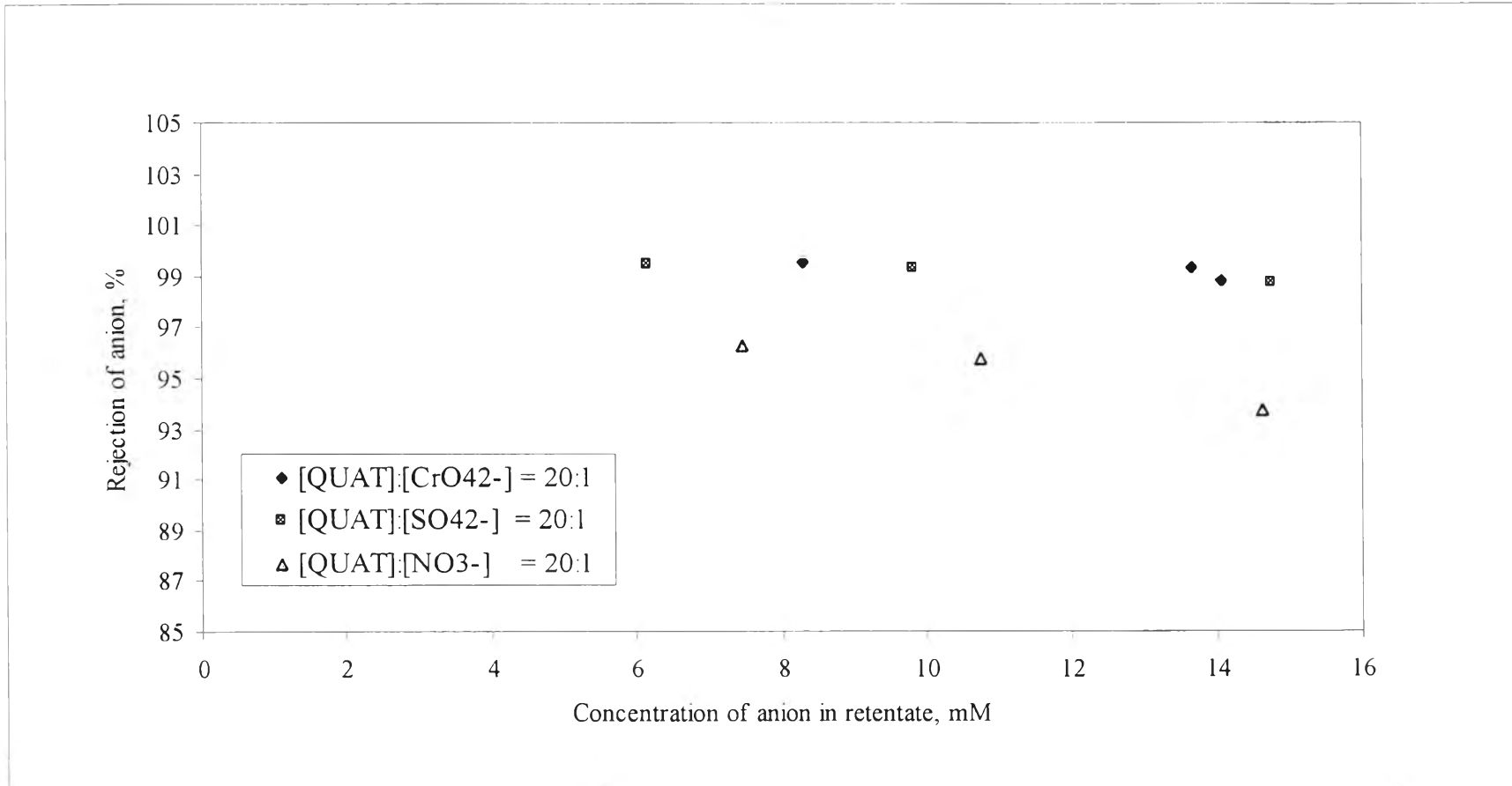
**Figure 4.7** Chromate, sulphate, and nitrate rejections as a function of QUAT concentration in retentate at ratio [QUAT]:[anion] = 20:1.



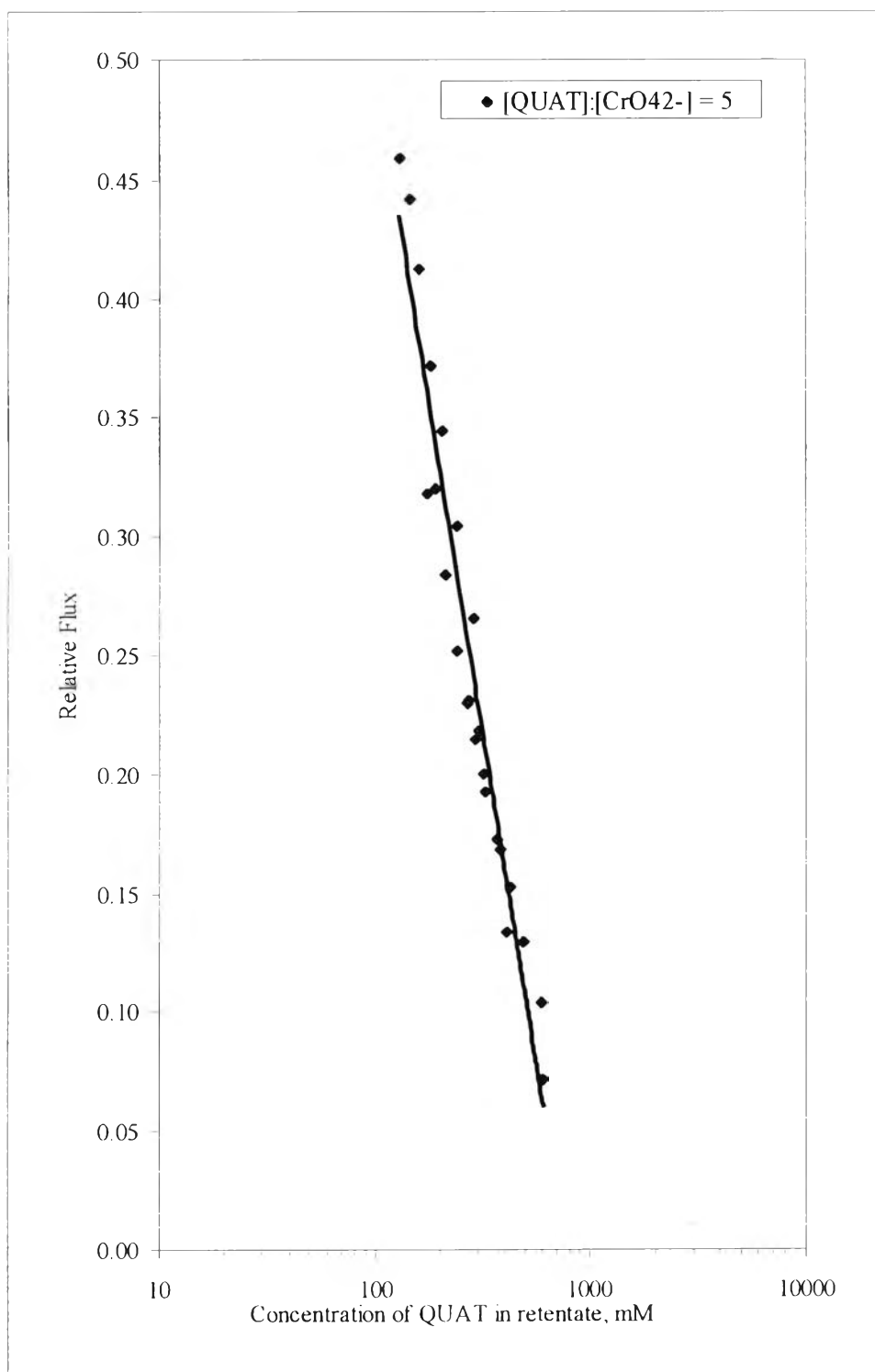
**Figure 4.8** Chromate, sulphate, and nitrate rejections as a function of anions concentration in retentate at ratio [QUAT]:[anion] = 5:1.



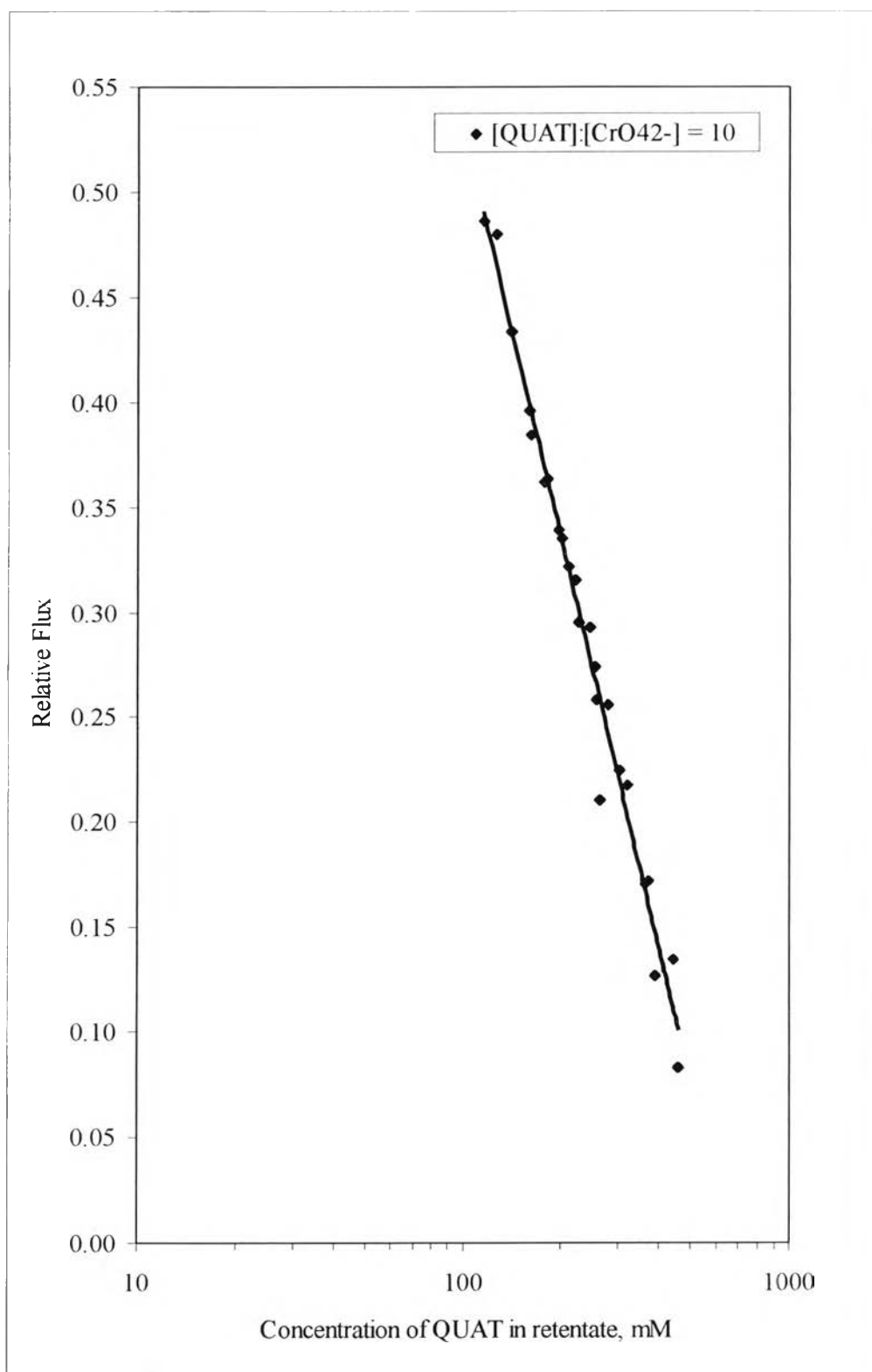
**Figure 4.9** Chromate, sulphate, and nitrate rejections as a function of anions concentration in retentate at ratio [QUAT]: [anion] = 10:1.



**Figure 4.10** Chromate, sulphate, and nitrate rejections as a function of anion concentration in retentate at ratio [QUAT]:[anion] = 20:1.

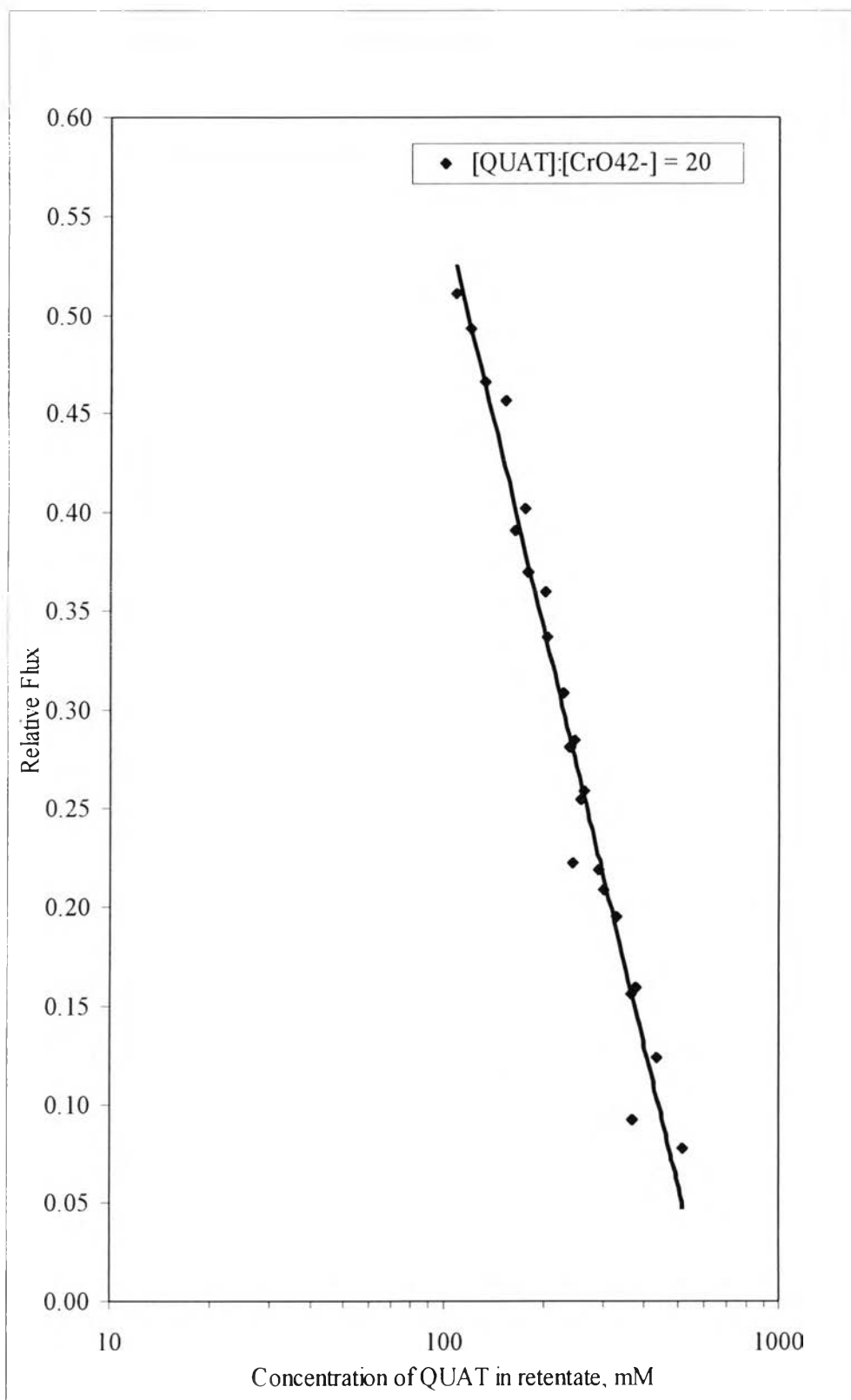


**Figure 4.11** Relative flux as a function of QUAT concentration in retentate at ratio  $[QUAT]:[CrO_4^{2-}] = 5$ .

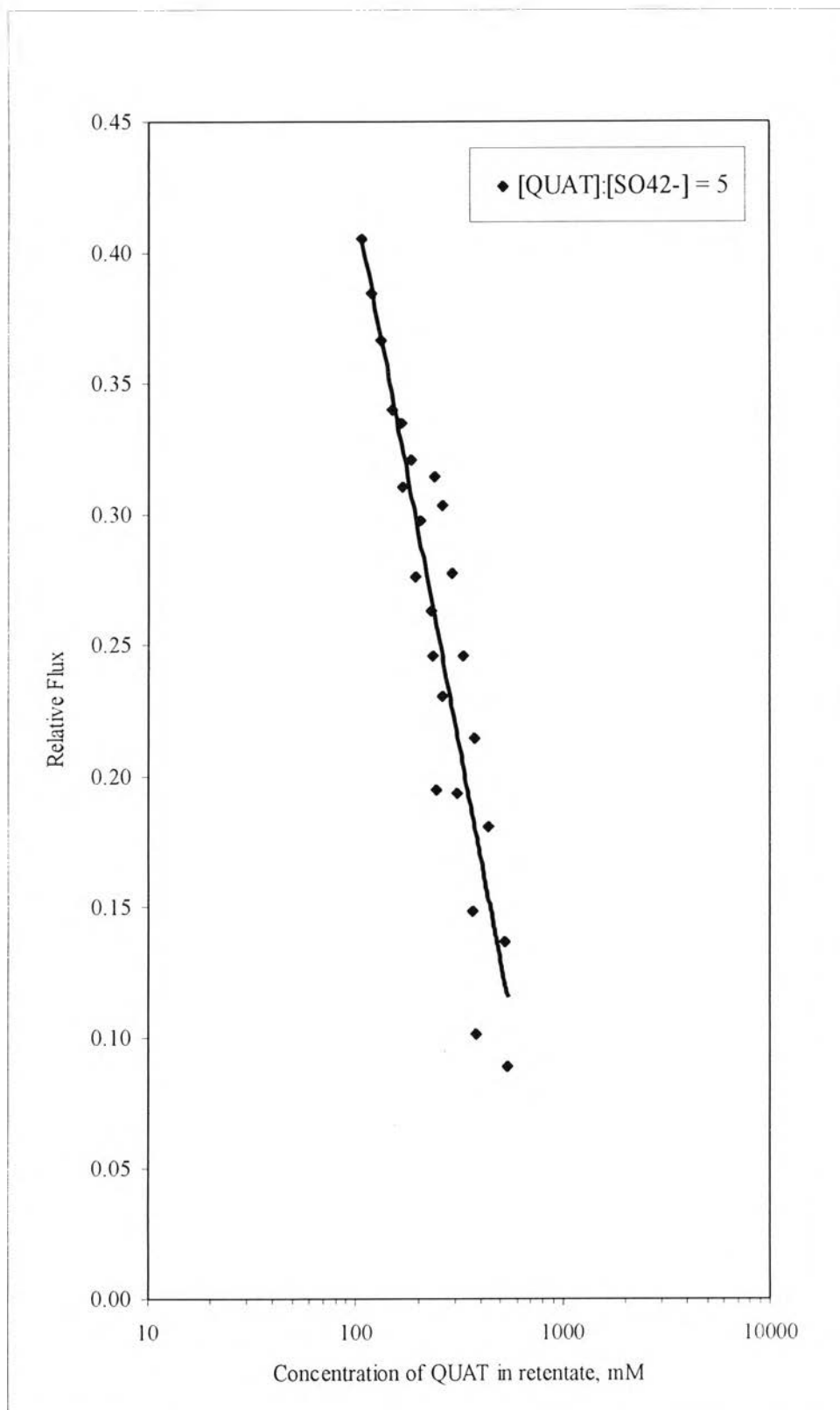


**Figure 4.12** Relative flux as a function of QUAT concentration in retentate at ratio  $[\text{QUAT}]:[\text{CrO}_4^{2-}] = 10$ .

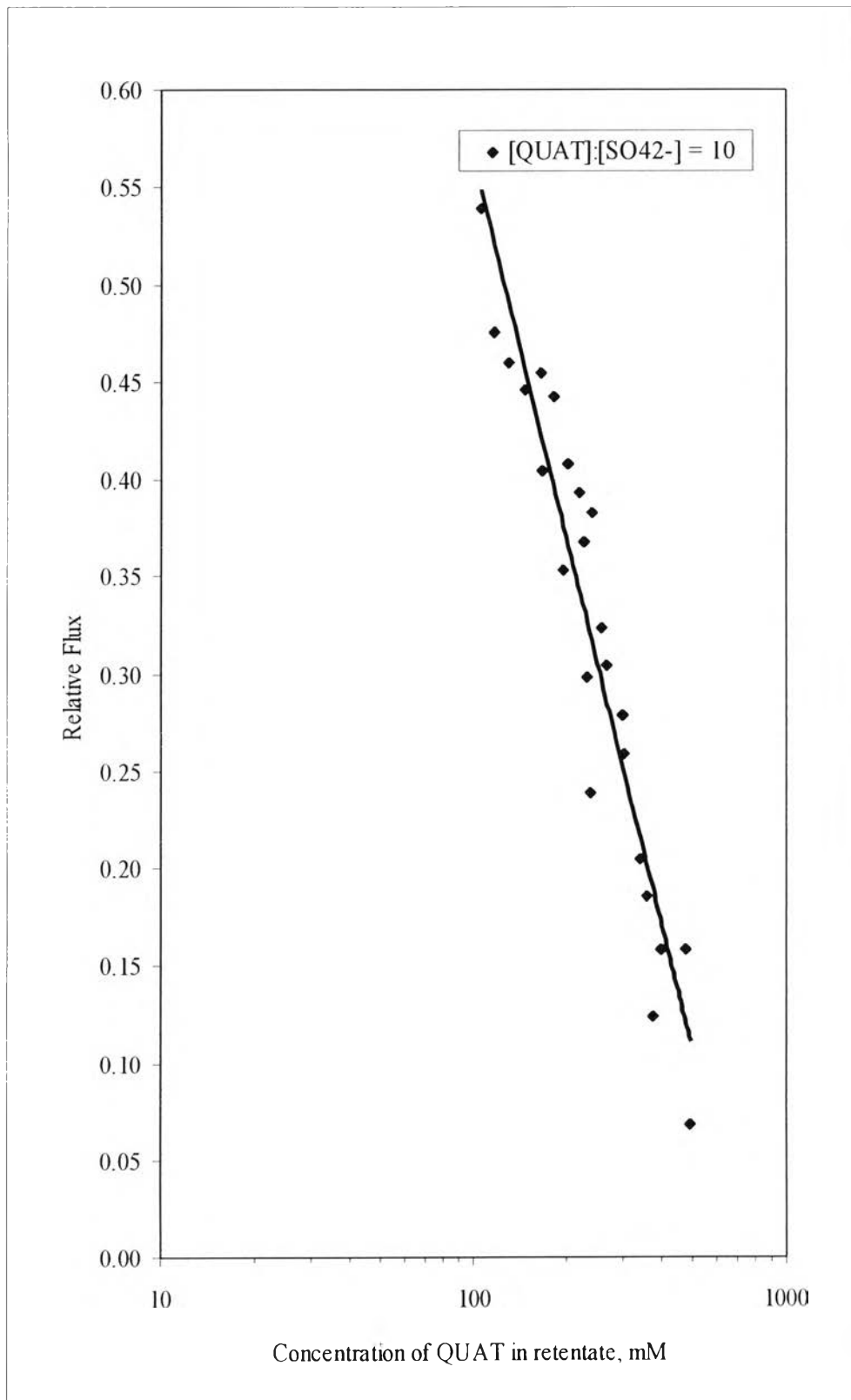




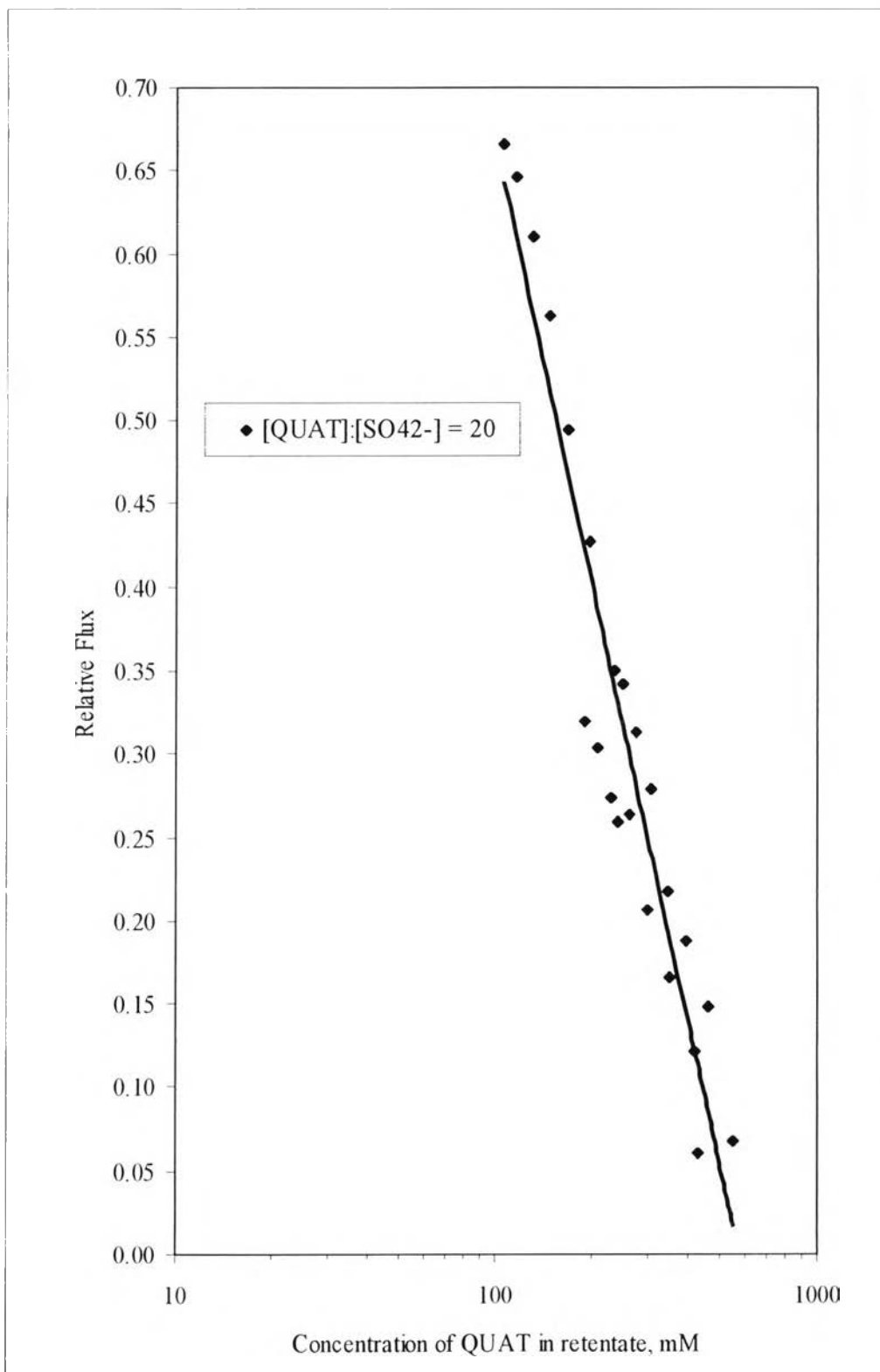
**Figure 4.13** Relative flux as a function of QUAT concentration in retentate at ratio  $[QUAT]:[CrO_4^{2-}] = 20$ .



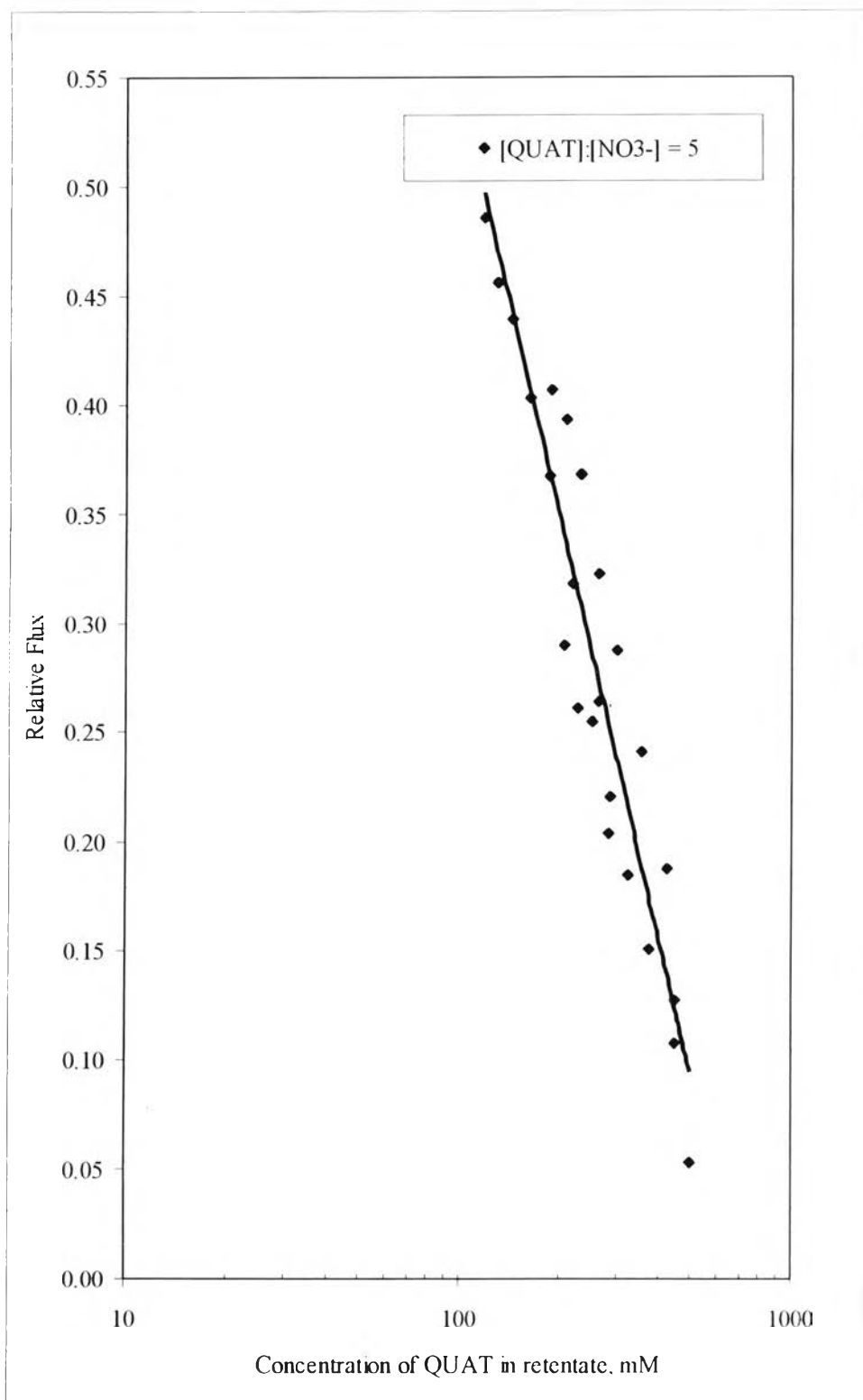
**Figure 4.14** Relative flux as a function of QUAT concentration in retentate at ratio  $[\text{QUAT}]:[\text{SO}_4^{2-}] = 5$ .



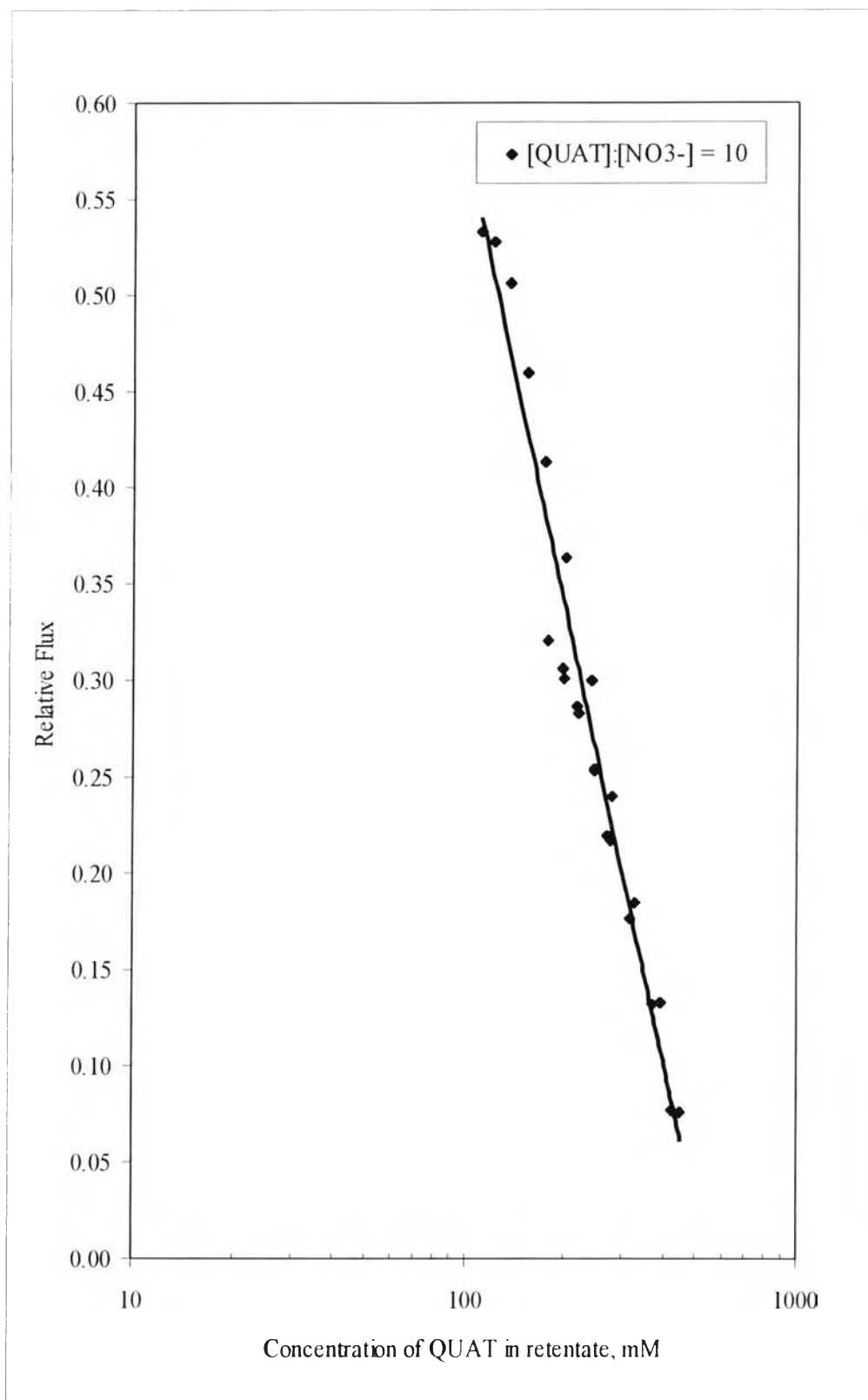
**Figure 4.15** Relative flux as a function of QUAT concentration in retentate at ratio  $[\text{QUAT}]:[\text{SO}_4^{2-}] = 10$ .



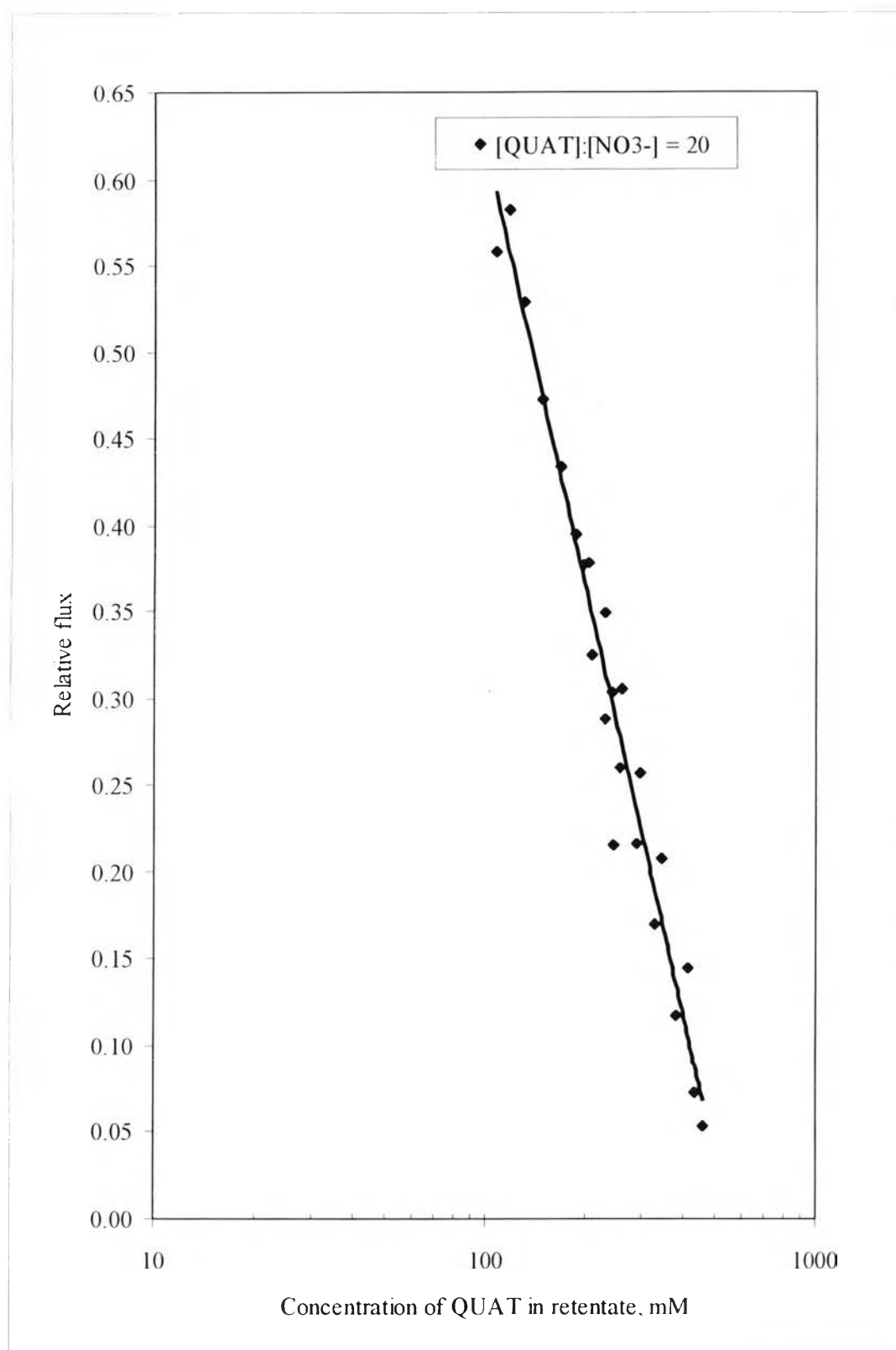
**Figure 4.16** Relative flux as a function of QUAT concentration in retentate at ratio  $[\text{QUAT}]:[\text{SO}_4^{2-}] = 20$ .



**Figure 4.17** Relative flux as a function of QUAT concentration in retentate at ratio  $[\text{QUAT}]:[\text{NO}_3^-] = 5$ .



**Figure 4.18** Relative flux as a function of QUAT concentration at ratio [QUAT]:[NO<sub>3</sub><sup>-</sup>] = 10.



**Figure 4.19** Relative as a function of QUAT concentration in retentate at ratio [QUAT]:[NO<sub>3</sub><sup>-</sup>] = 20.