# A CHRONOCOULOMETRIC STUDY OF THE ADSORPTION OF CADMIUM (II) ON MERCURY FROM BROMIDE SOLUTIONS

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# A Chronocoulometric Study of the Adsorption of Cadmium (II) on Mercury from Bromide Solutions

## Introduction:

The double step chronocoulometric method of determining the amount of adsorbed species onto a mercury electrode was used in studying the adsorption of cadmium (II) bromide complexes on mercury. The technique of adsorption determination has been previously discussed theoritically[1] and was used in study of adsorption of cadmium (II) on mercury from thiocyanate solutions.[2] This paper attempts to achieve results with bromide that would be comparable to the thiocyanate experiment and thus be able to speculate on the method of adsorption. The result that the adsorption reaches a maximum as the initial potential is increased from -0.10 volts to -0.50 volts with the final potential of -1.00 volts. for most bromide experiments indicates a different mechanism for adsorption than that for thiocyanate since thiocyanate has been reported as having uniform potential dependence for adsorption.[2]

By varying the concentration of cadmium (II) from zero to 1.2 milliformal, the concentration of bromide from zero to 1.0 formal with enough potassium nitrate to maintain unity ionic strength, and the initial potential, the effect of cadmium adsorption with bromide can be compared to that achieved with other anions, such as iodide[3], chloride and thiocyanate[2].

Theory:

The double potential step chronocoulometric method allows a reasonably accurate determination of small amounts of adsorbed species by internally correcting for double-layer charging when adsorption occurs. Christie, Osteryoung and Anson[1] treat the theory as follows. In general, the redox couple is:

$$Ox + ne^- \rightleftharpoons R$$

with a standard potential $E^o$. When the solution has Ox but no R, the initial electrode potential, $E_i$, is always anodic of $E^o$ to allow no current to flow. At t=0, the potential is jumped to the final electrode potential, $E_f$, cathodic of $E^o$ to reduce the concentration of Ox at the electrode to zero. Species R is then formed, limited by the diffusion of Ox through the solution. At $t=\tau$, the potential is stepped back to $E_i$. Hence the concentration of R at the electrode surface becomes zero and the current is then dependent on the diffusion rate of R back through the surface. The assumption is made that the potential is either $E_i$ or $E_f$ so that at the electrode surface only Ox or only R exist. Also assumed is the double-layer charges instantaneously, and that the adsorbed species reacts whenever the potential is stepped to a value that the unadsorbed would react.

Therefore the measured parameter of the total charge as a function of time can be broken up as the charge from the reaction of the species by diffusion at the electrode, the charge of the double-layer and the charge needed for the adsorbed material.

Using the analogs of the integral equations of linear diffusion problems with Neumann boundary conditions, the chronocoulometric total charge dependence on time when the double potential step is applied can be approximated as:

$$Q(t\leq\tau) = \frac{nFA\sqrt{D_r}}{\sqrt{\pi}} \int \frac{C_r(0,\theta)}{\sqrt{t-\theta}}\, d\theta + nFA\Gamma_o + Q_{dl}$$

$$Q_r = Q(\tau) - Q(t\geq\tau) = -\frac{nFA\sqrt{D_r}}{\sqrt{\pi}} \int \frac{C_r(0,\theta)}{t-\theta}\, d\theta + 2nFA\sqrt{\frac{D_r}{\pi}}\, C_r(0,t)\sqrt{\tau}$$

$$+ nFA\Gamma_o \left[1 - \frac{2}{\pi}\sin^{-1}\sqrt{\frac{\tau}{t}}\right] + Q_{dl}$$

with A the electrode surface area, $D_r$ the diffusion constant for R, $C_r$ the concentration of R, $\Gamma_o$ the amount of adsorbed reactant, $Q_{dl}$ the charge taken by the double-layer capacitance and n and F the usual symbols. However, when $t<\tau$,

$$C_r(0,t) = \sqrt{\frac{D_o}{D_r}}\, {}^*C_o$$

where $D_o$ is the diffusion constant for Ox and ${}^*C_o$ is the initial concentration of the species; thus making:

$$Q(t\leq\tau) = \frac{2nFA\sqrt{D_o}\ {}^*C_o\sqrt{t}}{\sqrt{\pi}} + nFA\Gamma_o + Q_{dl}$$

and

$$Q_r = \frac{2nFA\sqrt{D_o}\ {}^*C_o}{\sqrt{\pi}}\left[1 + a_1\frac{nFA\Gamma_o}{Q_c}\right]\Theta + a_o nFA\Gamma_o + Q_{dl}$$

where $\Theta = (\sqrt{t-\tau} + \sqrt{\tau} - \sqrt{t}\ )$ and $Q_c = 2nFA{}^*C_o\sqrt{\frac{D_o}{\pi}}$, the Cottrell diffusing

charge. $a_o$ and $a_1$ are the intercept and slope, respectively, of the plot of $\left[1 - \frac{2}{\pi}\sin^{-1}\sqrt{\frac{\tau}{t}}\right]$ versus $\frac{\theta}{\sqrt{\tau}}$. $a_o$ is usually close to zero and $a_1$ is close to unity.

The true double-layer charge is calculated from:

$$Q_{dl} = \frac{{}^{o}Q(t\geq\tau) - a_o\ {}^{o}Q(t\leq\tau)}{1-a_o}$$

where ${}^{o}Q(t\geq\tau)$ and ${}^{o}Q(t\leq\tau)$ are the Q-axis intercepts of the $Q(t\geq\tau)$ versus $\theta$ and $Q(t\leq\tau)$ versus $t^{1/2}$ plots, respectively. Thus the double-layer charge is determined for each experiment, and separate runs to find the charge "blanks" are not needed except to act as a check.

Because of the arithmetic complexity involved in the above equations, the formulas are programmed into a small digital computer. The reaction cell is directly connected to the computer through the mercury drop, the auxiliary and the reference electrodes. The number of forward and reverse potential step data points was usually 100 each way with the time base for each point set at $4.0 \times 10^{-4}$ seconds. Usually four and two data points were dropped at the beginning and the end, respectively, of each potential step to insure incorrect data points were not used in calculating results. The correction terms $a_o$ and $a_1$, using the above number of points, were -0.0646 and 0.953, respectively.

Experimental:

The electronic apparatus and the multichannel analyzer data acquisition system are the same equipment described and used in previous work.[4] The small computer greatly eased the volume of calculations and

increased the accuracy to the level of solution variations from the previous method[4] of reading photographs taken from charge-time traces on the oscilloscope. Output from the data acquisition system gave directly the amount of adsorbed species (microcoulombs/$cm^2$), the true double-layer charge (microcoulombs/$cm^2$), the slope of the charge versus time$^{1/2}$ graph (microcoulombs/root second-$cm^2$), the intercepts of the graph (microcoulombs/$cm^2$) and the corrected slopes with the constants $a_o$ and $a_1$ determined internally from the number of points taken. All data was printed on computer paper for later direct reference.

Solutions were made from stock solutions of reagent grade cadmium nitrate, potassium nitrate, potassium bromide, potassium chloride and potassium thiocyanate, using triply distilled water. No further purification was done on the solid chemicals.

The hanging mercury drop electrode used was the commercial Brinkman Instruments electrode with very extreme care maintained in keeping the electrodes co-sistent. Many methods of cleaning and filling the electrode were tried with the best results achieved by cleaning the capillary of the electrode with dilute hydrofloric acid several times, followed by thorough rinsing with triply distilled water, then by acetone and a fresh thick coat of Desecote. The electrode was used until inconsistent results from run to run appeared or the mercury column retracted, and the above procedure was then repeated. This method of cleaning by etching aws thought to have provided enough resistance in the capillary to avoid variation in the drop size due to the movement

of the mercury column. Extreme care was aslso taken in avoiding air gaps within the instrument when filling.

The mercury drop size was identical to the size used in previously reported experiments.[4] The value for the drop area was 0.032 $cm^2$.

All experiments were "air-free" by bubbling very dry nitrogen gas through the solution. Several trials showed no difference in measured values if the solution was stirred by bubbling nitrogen during the experiment. However, each experiment was "degassed" before performing to insure even concentration throughout the cell and that no air existed in the solution. During the experiment, nitrogen gas flowed just over the surface of the solution.

All potentials are expressed in volts versus the saturated calomel electrode (S.C.E.). The temperature of the solutions remained constantly around 20°C due to the air conditioning in the laboratory.

Data Summary for Adsorption of Cadmium (II) from Bromide, Chloride, Nitrate and Thiocyanate Solutions:

Tables I, II, III, IV, V, VI, AND VII of the appendix show the experimental data for adsorption. Data were taken for most 50 millivolt jumps and were used in the plots discussed later. However, to avoid complicated plots, some only recorded 100 millivolt jumps in initial potential. All final potentials ($E_f$) were set at -1.00 volts versus S.C.E.

Adsorption as a Function of Cadmium Concentration:

Figure 1, 2 and 3 show plots of adsorption versus cadmium (II) concentration for four different potentials. The expected result

is that more species will be adsorbed as cadmium is increased. And as more adsorption sites are taken, the amount of adsorption for higher concentrations will be proportionally less. Thus the curves level out as $[Cd^{+2}]$ increases.

The corrected slope value from the computer output should be proportional to the cadmium concentration.[2] For Figure 1, these ratios are:

640 microcoul/$sec^{1/2}cm^2$ mF for 0.2 mF $Cd^{+2}$
630 microcoul/$sec^{1/2}cm^2$ mF for 0.4 mF $Cd^{+2}$
639 microcoul/$sec^{1/2}cm^2$ mF for 0.8 mF $Cd^{+2}$
618 microcoul/$sec^{1/2}cm^2$ mF for 1.2 mF $Cd^{+2}$

No data is given for cadmium greater than 1.2 milliformal because the uncompensated resistance in the solution produces errors. This can be overcome by compensating to a certain extent,[5] but four concentrations are enough to give satisfactory data on this topic.

Adsorption as a Function of Bromide Concentration:

Figure 4 shows a plot of adsorption versus bromide for seven different initial potentials, keeping cadmium concentration constant. As with thiocyanate[2], bromide complex adsorption reaches a maximum. As the potential becomes more negative with respect to S.C.E., the maximum will move to higher bromide concentration, as clearly shown in Fig. 4. Also with the potential more negative, the peak widens to the point of almost disappearing for a potential step of -0.50 volts to -1.00 volts.

Adsorption as a Function of Initial Potential:

Figure 5 shows the dependence of adsorption on potential for cadmium (II) thiocyanate complexes. These values differ from the previously reported data[2] by approximately the same fraction.

For -0.20 volts the ratio is 0.674; for -0.30 volts the ratio is 0.728; and for -0.40 volts the ratio is 0.695. As the potential becomes less negative, the adsorption of mercury increases. [No attempt was made to carry the initial potential across zero (vs. S.C.E.) to detect any decrease in adsorption as the potential step is increase further]. F. C. Anson, et al, agree that the adsorption for thiocyanate increases as the potential becomes more positive.[2] This dependence undoubtedly means that the larger the voltage step, the more the specie is adsorbed with no hinderance ocurring from a large amount of adsorption.

However, Figures 6, 7, and 8, clearly show this dependence for cadmium bromide complex on the initial potential reaching a maximum for three bromide concentrations of 0.1 F, 0.3 F, 0.5 F, 0.7 F and 1.0 F. This peak is dependent on bromide concentration, but relatively independent of cadmium. As bromide is increased the peak moves toward the shorter potential step. This same phenomenon ocurred with iodide ion, as well.[3] This maximum adsorption tends to indicate a limit on the number of available sites for adsorption.

Adsorption as a Function of Initial Double-layer Charge:

Figures 9 and 9(cont.) indicate the dependence of adsorption on the initial double-layer charge. The initial double-layer charge was determined by subtracting 11.4 microcoul/$cm^2$, the charge on the double-layer of 1.0 M $NO_3^-$ at -1.00 volts from the corrected double-layer charging from the computer output. By using the transparency of Fig. 9, the graphs show a slight dependence of the location of the peak on the bromide concentration.

Figures 10 and 11 indicate the dependence of adsorption on the initial charge for several concentrations of cadmium (II). The maximums have relatively the same abscissa when the bromide concentration is constant.

Possibility of a Study of Cadmium (II) Chloride Complex Adsorption:

Experimental results (Table IIIc) show that the amount of cadmium-chloride adsorbed is too small (and even negative!) to analyze and compare as was done with the data for cadmium bromide.

Conclusions:

The fact that a maximum adsorption is obtained both for an intermediate bromide concentration and for an intermediate initial potential indicates a different mechanism for adsorption than that for cadmium thiocyanate which has a maximum adsorption for an intermediate thiocyanate concentration, but does not have the maximum for initial potential plots. The mechanism for adsorption of cadmium bromide must satisfactorily explain the maximum adsorptions. F. C. Anson, et al,[2] suggested that the mechanism for cadmium(II) adsorption with thiocyanate is the bonding of cadmium to the already specifically adsorbed thiocyanate, with the cadmium sitting on the end of the linear molecule away from the mercury. Their reasoning involved the increasing adsorption with increasing potential step. However, in the case of cadmium with bromide ions on the surface of the mercury, the cation would more likely fit in between the bromides on the surface. This would require more space per cadmium on the mercury and would likely fill up the surface to the point that cadmium ions would repel other cadmium and thus bring a decrease in the absorbed species. As was the case with F. C. Anson, et al,[2]

calculations of cadmium bromide complex concentrations by complex-ion equilibrium constants can not be corresponded with the amount of adsorbed cadmium (II) due to the inaccuracies of the constants. Thus the exact formula of the adsorbed cadmium bromide complex is not presently determined.

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Summary:

The double-step chronocoulometric analysis was used to study cadmium bromide complex adsorption on mercury. The amount of cadmium adsorbed was studied as a function of cadmium and bromide concentrations and of the initial potential. Experimental evidence shows that cadmium bromide complex does not have the same mechanism for adsorption as does cadmium thiocyanate complex. The study of cadmium chloride complex proved to be impossible due to the very small amount of complex adsorbed.

## References


1. J. H. Christie, R. A. Osteryoung and F. C. Anson, J. Electroanal. Chem., 13 (1967), 236-244.

2. F. C. Anson, J. H. Christie and R. A. Osteryoung, J. Electroanal. Chem., 13 (1967), 343-353.

3. F. C. Anson, data as yet unpublished.

4. F. C. Anson and D. A. Payne, J. Electroanal. Chem., 13 (1967),35-43.

5. G. Taver and D. A. Osteryoung, Anal. Chem., 38 (1966), 1137.

Table I

Data Summary for Adsorption of Cadmium (II)
from Bromide Solutions

Potential steps from -0.20 to -0.50 (in steps of 0.05 volts) to -1.00 volts vs. SCE.

Ionic strength is balanced by $KNO_3$ to unity.

$[Br^-]$ = 0.10 F

| $[Cd^{+2}]$ \ $E_i$ (volts) | -0.20 | -0.25 | -0.30 | -0.35 | -0.40 | -0.45 | -0.50 |
|---|---|---|---|---|---|---|---|
| 0.20 mF | 2.89 | 2.53 | 2.05 | 1.57 | 1.28 | 0.70 | 0.54 |
| 0.40 mF | 5.82 | 5.52 | 4.55 | 3.94 | 3.16 | 2.50 | 1.90 |
| 0.80 mF | 8.29 | 7.72 | 6.83 | 5.78 | 4.80 | 4.13 | 3.25 |
| 1.20 mF | 9.57 | 9.50 | 8.51 | 7.34 | 6.12 | 4.64 | 3.63 |

$[Br^-]$ = 0.30 F

| $[Cd^{+2}]$ \ $E_i$ (volts) | -0.20 | -0.25 | -0.30 | -0.35 | -0.40 | -0.45 | -0.50 |
|---|---|---|---|---|---|---|---|
| 0.20 mF | 4.93 | 5.61 | 5.65 | 5.60 | 4.96 | 4.02 | 3.05 |
| 0.40 mF | 7.98 | 8.72 | 8.80 | 8.29 | 7.61 | 6.41 | 4.72 |
| 0.80 mF | 12.00 | 13.31 | 13.27 | 12.43 | 11.50 | 10.22 | 8.43 |
| 1.20 mF | 13.99 | 15.49 | 15.35 | 14.59 | 13.25 | 11.91 | 9.83 |

$[Br^-]$ = 0.40 F

| $[Cd^{+2}]$ \ $E_i$ (volts) | -0.20 | -0.25 | -0.30 | -0.35 | -0.40 | -0.45 | -0.50 |
|---|---|---|---|---|---|---|---|
| 0.40 mF | 7.86 | 9.19 | 9.40 | 9.28 | 8.58 | 7.50 | 6.33 |

$[Br^-]$ = 0.50 F

| $[Cd^{+2}]$ \ $E_i$ (volts) | -0.20 | -0.25 | -0.30 | -0.35 | -0.40 | -0.45 | -0.50 |
|---|---|---|---|---|---|---|---|
| 0.20 mF | 4.64 | 5.90 | 6.32 | 6.32 | 6.16 | 5.26 | 4.46 |
| 0.40 mF | 7.22 | 9.03 | 9.52 | 9.50 | 8.72 | 7.85 | 6.39 |
| 0.80 mF | 10.96 | 13.10 | 13.88 | 13.87 | 13.20 | 12.04 | 10.47 |
| 1.20 mF | 12.29 | 14.06 | 15.09 | 15.05 | 13.90 | 13.51 | 10.75 |

$[Br^-]$ = 0.60 F

| $[Cd^{+2}]$ \ $E_i$ (volts) | -0.20 | -0.25 | -0.30 | -0.35 | -0.40 | -0.45 | -0.50 |
|---|---|---|---|---|---|---|---|
| 0.40 mF | - | 7.95 | 8.78 | 9.24 | 8.79 | 8.17 | - |

Table I (cont.)

| $[Br^-]$ = 0.70 F; $[Cd^{+2}]$ \ $E_i$ (volts) | -0.20 | -0.25 | -0.30 | -0.35 | -0.40 | -0.45 | -0.50 |
|---|---|---|---|---|---|---|---|
| 0.20 mF | 2.84 | 4.26 | 4.98 | 5.56 | 5.47 | 4.97 | 4.50 |
| 0.40 mF | 5.61 | 7.43 | 8.30 | 8.56 | 8.39 | 7.93 | 7.32 |
| 0.80 mF | 8.18 | 10.65 | 12.30 | 12.75 | 12.68 | 12.00 | 9.42 |
| 1.20 mF | - | 13.18 | 15.26 | 15.54 | 15.35 | 14.05 | 12.58 |

| $[Br^-]$ = 1.00 F; $[Cd^{+2}]$ \ $E_i$ (volts) | -0.20 | -0.25 | -0.30 | -0.35 | -0.40 | -0.45 | -0.50 |
|---|---|---|---|---|---|---|---|
| 0.20 mF | - | 3.28 | 3.90 | 4.38 | 4.75 | 4.52 | 4.29 |
| 0.40 mF | - | 5.66 | 6.12 | 6.80 | 7.01 | 6.74 | 6.23 |
| 0.80 mF | - | 7.31 | 9.52 | 10.24 | 10.44 | 10.77 | 9.87 |
| 1.20 mF | - | 8.20 | 10.12 | 11.16 | 11.73 | 12.65 | 11.83 |

Table II

Data Summary for Adsorption of Cadmium (II)
from Bromide Solutions

(Data taken form Ch 188b, 1967)

Potential steps from -0.10 to -0.50 (in steps of 0.05 volts) to -1.00 volts vs. SCE.

Ionic strength is balanced by $KNO_3$ to unity.

| $[Br^-]$ = 0.10 F<br>$[Cd^{+2}]$ \ $E_i$ (volts) | -0.10 | -0.15 | -0.20 | -0.25 | -0.30 | -0.35 | -0.40 |
|---|---|---|---|---|---|---|---|
| 0.20 mF | 2.29 | 2.71 | 3.18 | 3.02 | 2.43 | 1.99 | 1.56 |
| 0.40 mF | 3.91 | 5.32 | 6.01 | 5.50 | 4.76 | 4.00 | 3.28 |
| 0.80 mF | - | 6.45 | 7.09 | 7.10 | 6.42 | 6.04 | 5.23 |

| $[Br^-]$ = 0.50 F<br>$[Cd^{+2}]$ \ $E_i$ (volts) | -0.25 | -0.30 | -0.35 | -0.40 | -0.45 | -0.50 |
|---|---|---|---|---|---|---|
| 0.20 mF | 6.26 | 6.96 | 7.55 | 6.94 | 6.21 | 5.41 |
| 0.40 mF | 8.94 | 9.93 | 10.55 | 10.73 | 10.00 | 8.79 |
| 0.80 mF | 12.75 | 13.84 | 14.18 | 14.44 | 12.81 | 11.65 |
| 1.20 mF | 12.44 | 15.02 | 15.58 | 16.34 | 14.92 | 14.01 |

| $[Br^-]$ = 1.00 F<br>$[Cd^{+2}]$ \ $E_i$ (volts) | -0.25 | -0.30 | -0.35 | -0.40 | -0.45 | -0.50 |
|---|---|---|---|---|---|---|
| 0.20 mF | 4.59 | 5.57 | 6.11 | 6.60 | 6.32 | 4.82 |
| 0.40 mF | 7.12 | 8.50 | 9.56 | 9.29 | 9.30 | 8.44 |
| 0.80 mF | 9.44 | 12.40 | 13.79 | 14.19 | 13.54 | 13.02 |
| 1.20 mF | 9.39 | 13.60 | 15.76 | 16.91 | 16.20 | 15.13 |

Table III

Data Summary for Adsoption of Cadmium (II) from

A) Bromide Solution with no $KNO_3$ to balance ionic strength
B) Chloride Solutions with $KNO_3$ to balance ionic strength to unity
C) Thiocyanate Solutions with $KNO_3$ to balance ionic strength to unity

A)

$[Br^-]$ = 0.40 F

| $[Cd^{+2}]$ \ $E_i$ (volts) | -0.25 | -0.30 | -0.35 | -0.40 | -0.45 |
|---|---|---|---|---|---|
| 0.40 mF | 9.40 | 9.65 | 9.40 | 8.75 | 7.99 |

B)

$[Cl^-]$ = 0.10 F

| $[Cd^{+2}]$ \ $E_i$ (volts) | -0.15 | -0.20 | -0.25 | -0.30 |
|---|---|---|---|---|
| 0.40 mF | 0.156 | - | - | -0.256 |

$[Cl^-]$ = 0.50 F

| $[Cd^{+2}]$ \ $E_i$ (volts) | -0.05 | -0.10 | -0.15 | -0.20 | -0.25 | -0.30 |
|---|---|---|---|---|---|---|
| 0.40 mF | 0.535 | 0.282 | -0.108 | - | - | -0.372 |

$[Cl^-]$ = 1.00 F

| $[Cd^{+2}]$ \ $E_i$ (volts) | -0.15 | -0.20 | -0.25 | -0.30 |
|---|---|---|---|---|
| 0.40 mF | 0.184 | - | - | -0.75 |

C)

$[SCN^-]$ = 0.10 F

| $[Cd^{+2}]$ \ $E_i$ (volts) | -0.025 | -0.05 | -0.075 | -0.10 | -0.15 | -0.20 | -0.25 | -0.30 | -0.35 | -0.40 |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.20 mF | 14.82 | 13.90 | 14.08 | 13.71 | 13.25 | 11.66 | 10.07 | 7.86 | 6.26 | 4.45 |

Table IV

Data Summary for Cadmium (II) plus $KNO_3$ only

Ionic strength is unity. $E_f$ =-1.00 volts

$I_f$ = forward intercept
$I_b^f$ = back intercept
$S_b$ = forward slope
$S_b^f$ = back slope
$Q_{bl}$ is averaged from a separate experiment

$[Cd^{+2}]$ = 0.20 mF

| $E_i$ (volts) | $I_f$ | $I_b$ | $Q_{bl}$ | $S_f$ | $S_b$ |
|---|---|---|---|---|---|
| -0.15 | 20.51 | 21.01 | 20.83 | 117.4 | 121.0 |
| -0.15 | 20.76 | 21.26 | 20.83 | 119.0 | 122.9 |
| -0.15 | 20.99 | 21.50 | 20.83 | 119.5 | 123.6 |
| -0.20 | 19.51 | 19.97 | 19.82 | 118.0 | 122.0 |
| -0.20 | 18.93 | 19.47 | 19.82 | 117.8 | 120.7 |
| -0.20 | 19.58 | 20.05 | 19.82 | 121.1 | 124.4 |
| -0.25 | 18.45 | 18.58 | 18.85 | 118.9 | 124.1 |
| -0.25 | 17.97 | 18.28 | 18.85 | 117.8 | 121.6 |
| -0.25 | 17.91 | 18.20 | 18.85 | 117.6 | 121.4 |
| -0.30 | 16.84 | 17.26 | 17.04 | 118.4 | 122.9 |
| -0.30 | 16.99 | 17.44 | 17.04 | 118.8 | 123.3 |
| -0.35 | 15.91 | 16.29 | 15.83 | 120.4 | 125.2 |
| -0.35 | 15.87 | 16.15 | 15.83 | 119.4 | 124.1 |
| -0.40 | 14.64 | 14.95 | 14.57 | 120.8 | 126.0 |
| -0.40 | 14.45 | 14.88 | 14.57 | 119.2 | 123.7 |
| -0.45 | 13.08 | 13.29 | 13.23 | 118.6 | 123.6 |
| -0.45 | 13.04 | 13.38 | 13.23 | 119.1 | 124.5 |
| -0.50 | 10.63 | 10.89 | 11.38 | 117.4 | 120.8 |
| -0.50 | 11.24 | 11.73 | 11.38 | 119.5 | 123.8 |
| -0.50 | 11.48 | 11.83 | 11.38 | 120.2 | 125.2 |

Table IV (cont.)

$[Cd^{+2}]$ = 0.40 mF

| $E_i$ (volts) | $I_f$ | $I_b$ | $Q_{bl}$ | $S_f$ | $S_b$ |
|---|---|---|---|---|---|
| -0.15 | 20.27 | 20.95 | 20.83 | 223.8 | 230.1 |
| -0.15 | 20.83 | 21.64 | 20.83 | 227.8 | 233.4 |
| -0.15 | 20.62 | 21.34 | 20.83 | 224.2 | 229.7 |
| -0.20 | 19.54 | 20.06 | 19.82 | 225.9 | 231.9 |
| -0.20 | 19.73 | 20.26 | 19.82 | 226.8 | 232.7 |
| -0.25 | 18.26 | 18.64 | 18.85 | 222.4 | 228.5 |
| -0.25 | 18.42 | 19.00 | 18.85 | 226.7 | 232.9 |
| -0.30 | 16.94 | 17.44 | 17.04 | 222.7 | 229.2 |
| -0.30 | 16.99 | 17.56 | 17.04 | 223.9 | 230.8 |
| -0.35 | 15.80 | 16.23 | 15.83 | 225.3 | 232.1 |
| -0.35 | 15.61 | 16.01 | 15.83 | 224.5 | 231.2 |
| -0.40 | 14.25 | 14.59 | 14.57 | 223.5 | 231.5 |
| -0.40 | 14.53 | 14.85 | 14.57 | 225.6 | 233.3 |
| -0.45 | 12.81 | 13.11 | 13.23 | 221.6 | 229.2 |
| -0.45 | 12.99 | 13.33 | 13.23 | 225.6 | 233.7 |
| -0.45 | 12.77 | 13.08 | 13.23 | 223.3 | 232.3 |
| -0.50 | 11.17 | 11.48 | 11.38 | 220.7 | 228.8 |
| -0.50 | 11.45 | 11.74 | 11.38 | 224.9 | 233.1 |
| -0.50 | 11.27 | 11.63 | 11.38 | 223.4 | 231.1 |

Table IV (cont.)

$[Cd^{+2}]$ = 0.40 mF

| $E_i$ (volts) | $I_f$ | $I_b$ | $Q_{bl}$ | $S_f$ | $S_b$ |
|---|---|---|---|---|---|
| -0.15 | 20.47 | 20.90 | 21.53 | 206.1 | 211.7 |
| -0.15 | 21.08 | 21.61 | 21.53 | 212.9 | 218.3 |
| -0.15 | 20.61 | 21.08 | 21.53 | 207.9 | 214.0 |
| -0.20 | 18.88 | 19.44 | 20.30 | 203.6 | 208.4 |
| -0.20 | 20.09 | 20.63 | 20.30 | 215.4 | 221.0 |
| -0.20 | 19.67 | 20.11 | 20.30 | 210.7 | 215.8 |
| -0.25 | 18.22 | 18.66 | 19.00 | 213.1 | 217.3 |
| -0.25 | 18.46 | 19.00 | 19.00 | 211.8 | 217.6 |
| -0.30 | 17.14 | 17.53 | 17.88 | 210.6 | 217.2 |
| -0.30 | 16.94 | 17.31 | 17.88 | 207.5 | 213.5 |
| -0.35 | 15.72 | 16.01 | 16.52 | 208.2 | 214.9 |
| -0.35 | 15.73 | 16.20 | 16.52 | 210.0 | 216.5 |
| -0.40 | 14.27 | 14.63 | 14.60 | 207.6 | 215.0 |
| -0.40 | 13.97 | 14.62 | 14.60 | 207.4 | 214.7 |
| -0.45 | 12.95 | 13.28 | 13.54 | 210.8 | 218.2 |
| -0.45 | 12.44 | 12.81 | 13.54 | 203.7 | 211.1 |
| -0.45 | 13.17 | 13.51 | 13.54 | 213.4 | 220.4 |
| -0.45 | 12.94 | 13.34 | 13.54 | 210.5 | 217.5 |
| -0.50 | 11.13 | 11.42 | 11.86 | 205.7 | 213.7 |
| -0.50 | 11.62 | 11.90 | 11.86 | 214.8 | 223.1 |

Table IV (cont.)

$[Cd^{+2}] = 0.80$ F

| $E_i$ (volts) | $I_f$ | $I_b$ | $Q_{b1}$ | $S_f$ | $S_b$ |
|---|---|---|---|---|---|
| -0.15 | 20.61 | 21.30 | 21.53 | 430.0 | 438.3 |
| -0.15 | 19.94 | 20.82 | 21.53 | 416.6 | 422.9 |
| -0.15 | 19.41 | 20.42 | 21.53 | 413.5 | 417.7 |
| -0.15 | 20.38 | 21.26 | 21.53 | 429.1 | 434.5 |
| -0.15 | 20.53 | 21.19 | 21.53 | 425.8 | 432.1 |
| -0.20 | 19.15 | 20.02 | 20.30 | 426.7 | 433.8 |
| -0.20 | 20.03 | 20.87 | 20.30 | 447.5 | 454.4 |
| -0.20 | 19.65 | 20.14 | 20.30 | 428.2 | 436.1 |
| -0.25 | 18.32 | 19.04 | 19.00 | 433.4 | 441.1 |
| -0.25 | 18.76 | 19.45 | 19.00 | 439.7 | 447.5 |
| -0.25 | 18.18 | 18.79 | 19.00 | 422.7 | 430.1 |
| -0.30 | 17.00 | 17.34 | 17.88 | 425.1 | 433.9 |
| -0.30 | 17.17 | 17.84 | 17.88 | 433.0 | 441.5 |
| -0.30 | 16.57 | 17.08 | 17.88 | 415.9 | 424.2 |
| -0.30 | 17.13 | 17.68 | 17.88 | 429.6 | 438.7 |
| -0.35 | 15.13 | 15.46 | 16.52 | 411.1 | 422.6 |
| -0.35 | 15.75 | 16.13 | 16.52 | 428.0 | 438.0 |
| -0.35 | 15.65 | 16.12 | 16.52 | 429.6 | 440.0 |
| -0.40 | 14.28 | 14.57 | 14.60 | 425.6 | 438.6 |
| -0.40 | 13.83 | 14.36 | 14.60 | 416.2 | 426.5 |
| -0.40 | 14.45 | 14.77 | 14.60 | 429.6 | 441.6 |
| -0.45 | 12.83 | 13.01 | 13.54 | 425.8 | 439.6 |
| -0.45 | 12.36 | 12.50 | 13.54 | 410.1 | 423.0 |
| -0.45 | 13.02 | 13.22 | 13.54 | 431.2 | 444.5 |
| -0.50 | 10.86 | 11.04 | 11.86 | 426.3 | 442.1 |
| -0.50 | 11.23 | 11.72 | 11.86 | 427.1 | 443.6 |

Table V

Data Summary for Adsorption of Cadmium (II)
from Bromide Solutions versus Initial Charge

Ionic Strength is balanced by $KNO_3$ to unity.
$[Cd^{+2}]$ = 0.40 mF

| $[Br^-]$ = 0.10 F | | $[Br^-]$ = 0.30 F | | $[Br^-]$ = 0.40 F | | $[Br^-]$ = 0.50 F | |
|---|---|---|---|---|---|---|---|
| $Q_i$ | nF | $Q_i$ | nF | $Q_i$ | nF | $Q_i$ | nF |
| 40.37 | 4.488 | 20.25 | 7.995 | 20.94 | 7.651 | 23.92 | 7.357 |
| 40.02 | 4.439 | 20.36 | 7.965 | 21.18 | 7.954 | 23.72 | 6.873 |
| 24.77 | 5.451 | 15.77 | 8.833 | 21.30 | 7.961 | 24.57 | 7.432 |
| 25.03 | 5.267 | 15.59 | 8.651 | 16.47 | 9.181 | 17.55 | 8.942 |
| 15.85 | 6.099 | 15.73 | 8.692 | 16.10 | 9.080 | 18.40 | 9.133 |
| 16.84 | 5.824 | 12.39 | 8.720 | 16.32 | 9.148 | 18.39 | 9.019 |
| 17.92 | 5.702 | 12.72 | 8.876 | 16.35 | 9.377 | 12.86 | 9.374 |
| 18.39 | 5.672 | 9.93 | 8.468 | 16.45 | 9.158 | 15.15 | 9.660 |
| 12.60 | 5.497 | 9.57 | 8.200 | 12.04 | 9.371 | 14.73 | 9.514 |
| 12.26 | 5.676 | 9.47 | 8.211 | 12.92 | 9.400 | 11.33 | 9.230 |
| 13.34 | 5.404 | 7.93 | 7.722 | 13.00 | 9.434 | 11.59 | 9.478 |
| 10.33 | 4.623 | 7.95 | 7.644 | 10.06 | 9.250 | 12.27 | 9.655 |
| 10.29 | 4.471 | 7.66 | 7.476 | 10.06 | 9.318 | 12.04 | 9.639 |
| 7.78 | 4.175 | 5.11 | 6.551 | 10.26 | 9.267 | 8.59 | 8.724 |
| 7.64 | 3.706 | 4.77 | 6.261 | 7.50 | 8.599 | 8.39 | 8.711 |
| 5.95 | 3.194 | 4.88 | 6.412 | 7.56 | 8.603 | 6.47 | 7.886 |
| 5.51 | 3.301 | 3.09 | 4.672 | 6.99 | 8.532 | 6.17 | 7.810 |
| 5.55 | 3.001 | 2.69 | 4.750 | 7.76 | 8.577 | 3.73 | 6.398 |
| 3.76 | 2.572 | 2.89 | 4.732 | 5.20 | 7.454 | 4.02 | 6.262 |
| 3.57 | 2.169 | | | 5.28 | 7.552 | 4.25 | 6.522 |
| 3.73 | 2.762 | | | 5.28 | 7.496 | | |
| 1.25 | 1.907 | | | 3.26 | 6.368 | | |
| 1.55 | 1.901 | | | 3.02 | 6.290 | | |

Table V (cont.)

| $[Br^-]$ = 0.60 F | | $[Br^-]$ = 0.70 F | | $[Br^-]$ = 1.00 F | |
|---|---|---|---|---|---|
| $Q_i$ | nF | $Q_i$ | nF | $Q_i$ | nF |
| 19.01 | 8.196 | 27.84 | 5.608 | 20.94 | 5.680 |
| 18.18 | 7.896 | 24.71 | 5.821 | 21.48 | 5.651 |
| 18.06 | 7.763 | 26.53 | 5.411 | 21.39 | 5.654 |
| 14.25 | 8.699 | 19.35 | 7.670 | 16.05 | 5.910 |
| 14.91 | 8.901 | 19.01 | 7.183 | 16.81 | 6.138 |
| 14.52 | 8.748 | 15.54 | 8.462 | 16.88 | 6.394 |
| 12.20 | 9.391 | 14.78 | 8.130 | 16.67 | 6.020 |
| 11.36 | 8.933 | 12.09 | 8.604 | 13.98 | 6.890 |
| 11.98 | 9.385 | 11.59 | 8.532 | 13.63 | 6.660 |
| 8.84 | 8.820 | 9.81 | 8.503 | 10.57 | 7.005 |
| 9.03 | 8.766 | 8.99 | 8.286 | 10.10 | 7.017 |
| 6.46 | 8.237 | 6.80 | 8.054 | 8.07 | 6.639 |
| 6.43 | 8.098 | 6.33 | 7.649 | 8.39 | 6.933 |
| | | 5.84 | 8.093 | 8.20 | 6.659 |
| | | 4.73 | 7.269 | 5.53 | 6.218 |
| | | 5.07 | 7.362 | 5.60 | 6.251 |

Table VI

Data Summary for Adsorption of Cadmium (II)
from Bromide Solutions versus Initial Charge
for Various Cadmium Concentrations

Soln. is 0.10 F KBr and 0.90 F $KNO_3$

| $[Cd^{+2}]$ = 0.2 mF | | $[Cd^{+2}]$ = 0.4 mF | | $[Cd^{+2}]$ = 0.8 mF | | $[Cd^{+2}]$ = 1.2 mF | |
|---|---|---|---|---|---|---|---|
| $Q_i$ | nF | $Q_i$ | nF | $Q_i$ | nF | $Q_i$ | nF |
| 42.23 | 3.015 | 40.37 | 4.488 | 38.17 | 6.838 | 40.39 | 5.475 |
| 41.11 | 3.161 | 40.02 | 4.439 | 37.93 | 6.032 | 42.49 | 5.040 |
| 41.33 | 3.199 | 24.77 | 5.451 | 37.51 | 7.270 | 41.35 | 5.959 |
| 26.36 | 2.802 | 25.03 | 5.267 | 37.52 | 6.516 | 42.40 | 5.595 |
| 25.54 | 2.771 | 15.85 | 6.099 | 22.96 | 8.018 | 40.36 | 5.439 |
| 17.42 | 3.522 | 16.84 | 5.824 | 22.85 | 8.804 | 25.07 | 8.730 |
| 17.92 | 2.865 | 17.92 | 5.702 | 22.93 | 7.603 | 26.03 | 7.977 |
| 18.28 | 2.599 | 18.39 | 5.672 | 23.85 | 8.164 | 25.33 | 8.215 |
| 18.96 | 2.933 | 12.60 | 5.497 | 23.11 | 7.787 | 25.99 | 8.565 |
| 19.29 | 2.850 | 12.26 | 5.676 | 17.05 | 8.616 | 20.05 | 9.555 |
| 18.42 | 2.562 | 13.34 | 5.404 | 16.89 | 8.600 | 17.92 | 9.697 |
| 14.57 | 2.479 | 10.33 | 4.623 | 16.83 | 7.650 | 18.48 | 9.615 |
| 14.69 | 2.588 | 10.29 | 4.471 | 13.23 | 7.771 | 18.67 | 9.424 |
| 14.24 | 2.526 | 7.78 | 4.175 | 12.84 | 7.675 | 15.45 | 9.380 |
| 10.73 | 2.036 | 7.64 | 3.706 | 9.56 | 6.971 | 14.78 | 9.457 |
| 10.53 | 2.063 | 5.95 | 3.194 | 9.57 | 6.696 | 15.48 | 9.663 |
| 6.77 | 1.583 | 5.51 | 3.301 | 6.74 | 5.787 | 11.45 | 8.947 |
| 7.76 | 1.670 | 5.55 | 3.001 | 7.15 | 5.774 | 11.13 | 8.506 |
| 7.78 | 1.466 | 3.76 | 2.572 | 6.11 | 4.827 | 11.68 | 8.071 |
| 6.34 | 1.256 | 3.57 | 2.169 | 5.38 | 4.615 | 8.86 | 7.301 |
| 6.84 | 1.527 | 3.73 | 2.762 | 4.86 | 4.737 | 8.60 | 7.203 |
| 5.93 | 1.190 | 1.25 | 1.907 | 5.53 | 5.043 | 8.33 | 7.639 |
| 4.24 | 1.155 | 1.55 | 1.901 | 3.47 | 4.053 | 8.57 | 7.196 |
| 4.04 | 0.708 | | | 4.85 | 3.990 | 8.60 | 7.348 |
| 3.76 | 0.699 | | | 4.51 | 4.132 | 6.84 | 6.146 |
| 1.97 | 0.621 | | | 4.15 | 4.370 | 7.25 | 5.944 |
| 1.89 | 0.452 | | | 3.11 | 4.108 | 6.74 | 6.266 |
| | | | | 0.79 | 3.321 | 3.57 | 5.432 |
| | | | | 0.79 | 3.176 | 2.86 | 4.372 |
| | | | | | | 3.38 | 4.133 |

Table VII

Data Summary for Adsorption of Cadmium(II)
from Bromide Solutions versus Initial Charge
for Various Cadmium Concentrations

Soln. is o.5 F KBr + 0.5 F $KNO_3$

| $[Cd^{+2}]$ = 0.2 mF | | $[Cd^{+2}]$ = 0.4 mF | | $[Cd^{+2}]$ = 0.8 mF | | $[Cd^{+2}]$ = 1.2 mF | |
|---|---|---|---|---|---|---|---|
| $Q_i$ | nF | $Q_i$ | nF | $Q_i$ | nF | $Q_i$ | nF |
| 24.29 | 4.655 | 23.92 | 7.357 | 23.08 | 10.72 | 24.21 | 11.96 |
| 25.04 | 4.749 | 23.72 | 6.873 | 24.19 | 11.00 | 24.24 | 12.81 |
| 24.53 | 4.527 | 24.57 | 7.432 | 23.49 | 11.17 | 23.99 | 12.10 |
| 18.63 | 5.824 | 17.55 | 8.942 | 18.08 | 13.15 | 17.95 | 13.34 |
| 18.91 | 5.766 | 18.40 | 9.133 | 18.62 | 13.06 | 18.87 | 14.85 |
| 18.65 | 6.116 | 18.39 | 9.019 | 14.14 | 13.79 | 19.00 | 13.99 |
| 14.49 | 6.141 | 13.86 | 9.374 | 14.69 | 13.81 | 15.02 | 15.64 |
| 15.11 | 6.424 | 15.15 | 9.660 | 14.77 | 14.06 | 15.12 | 14.54 |
| 14.49 | 6.409 | 14.73 | 9.514 | 8.87 | 13.59 | 8.66 | 15.16 |
| 11.47 | 6.297 | 11.33 | 9.230 | 11.84 | 13.76 | 11.44 | 14.96 |
| 11.98 | 6.494 | 11.59 | 9.478 | 11.62 | 14.27 | 11.39 | 15.03 |
| 11.20 | 6.180 | 12.27 | 9.655 | 8.81 | 13.18 | 8.97 | 13.94 |
| 9.08 | 6.202 | 12.04 | 9.639 | 9.14 | 13.22 | 8.62 | 13.86 |
| 8.99 | 6.114 | 8.59 | 8.724 | 6.30 | 12.18 | 6.90 | 13.19 |
| 6.51 | 5.236 | 8.39 | 8.711 | 6.20 | 11.91 | 6.50 | 14.09 |
| 5.88 | 5.253 | 6.47 | 7.886 | 4.04 | 10.58 | 6.63 | 13.25 |
| 6.56 | 5.296 | 6.17 | 7.810 | 4.09 | 10.37 | 4.63 | 11.27 |
| 4.50 | 4.448 | 3.73 | 6.398 | | | 3.97 | 10.35 |
| 4.25 | 4.472 | 3.02 | 6.262 | | | 4.31 | 10.64 |
| | | 3.25 | 6.522 | | | | |

Figure 1

Dependence of Cd(II) adsorption on the concn. of cadmium for four potential steps. Soln. is 0.1 F KBr + 0.9 F $KNO_3$.

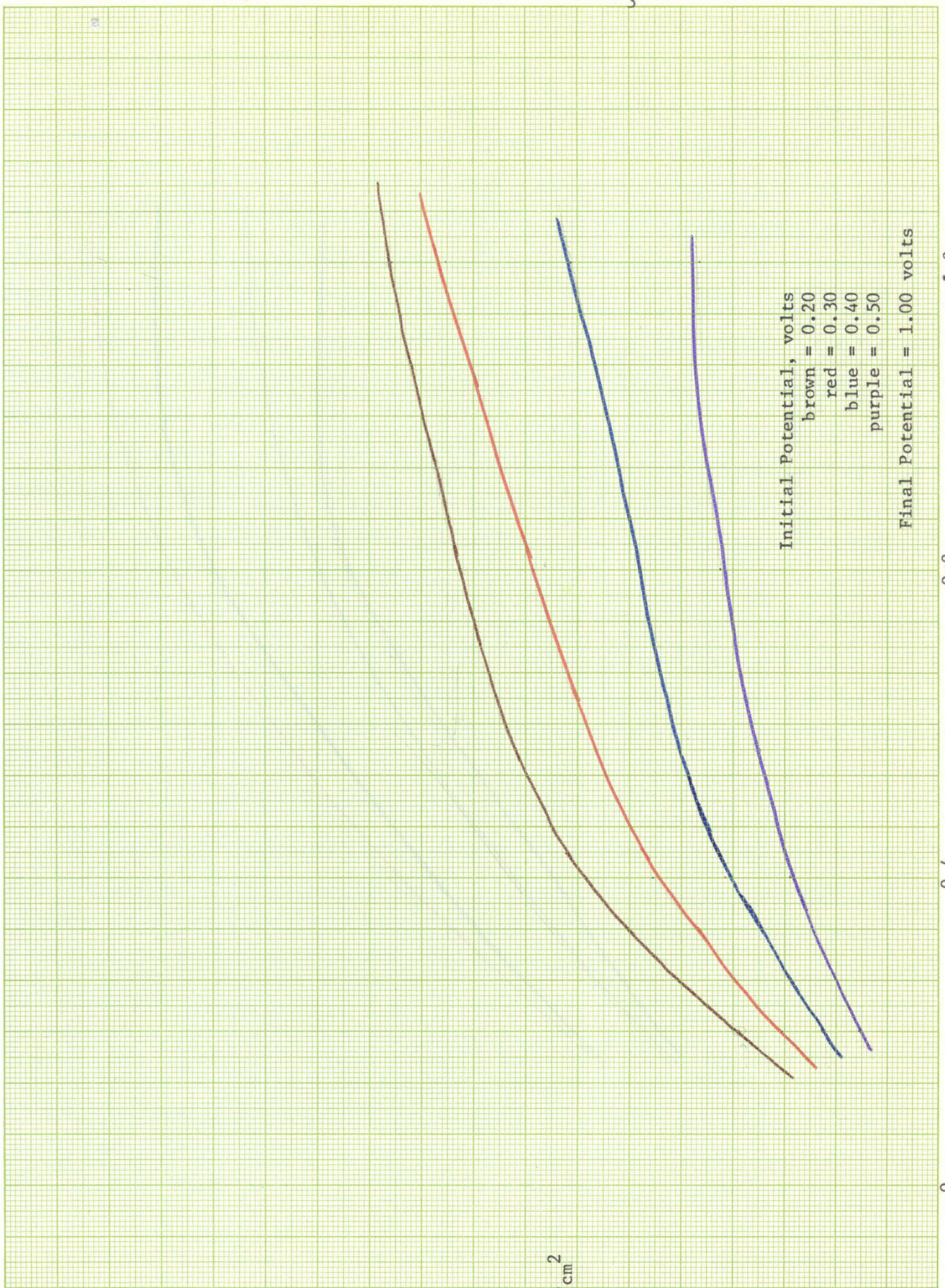


Figure 2

Dependence of Cd(II) adsorption on the concn. of cadmium for four potential steps. Soln. is 0.5 F KBr + 0.5 F $KNO_3$.

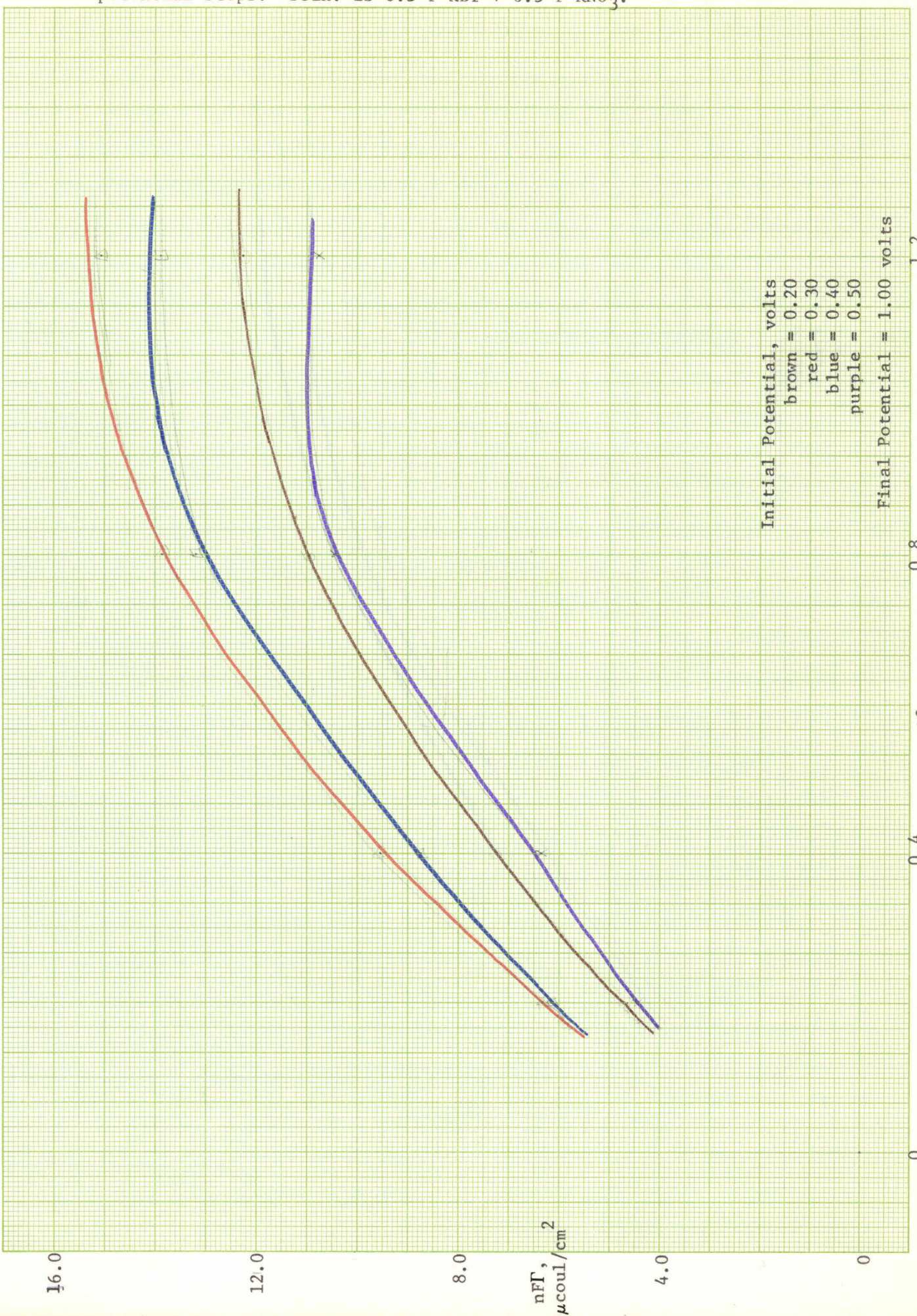


Figure 3

Dependence of Cd(II) adsorption on the concn. of cadmium for three potential steps. Soln. is 1.0 F KBr.

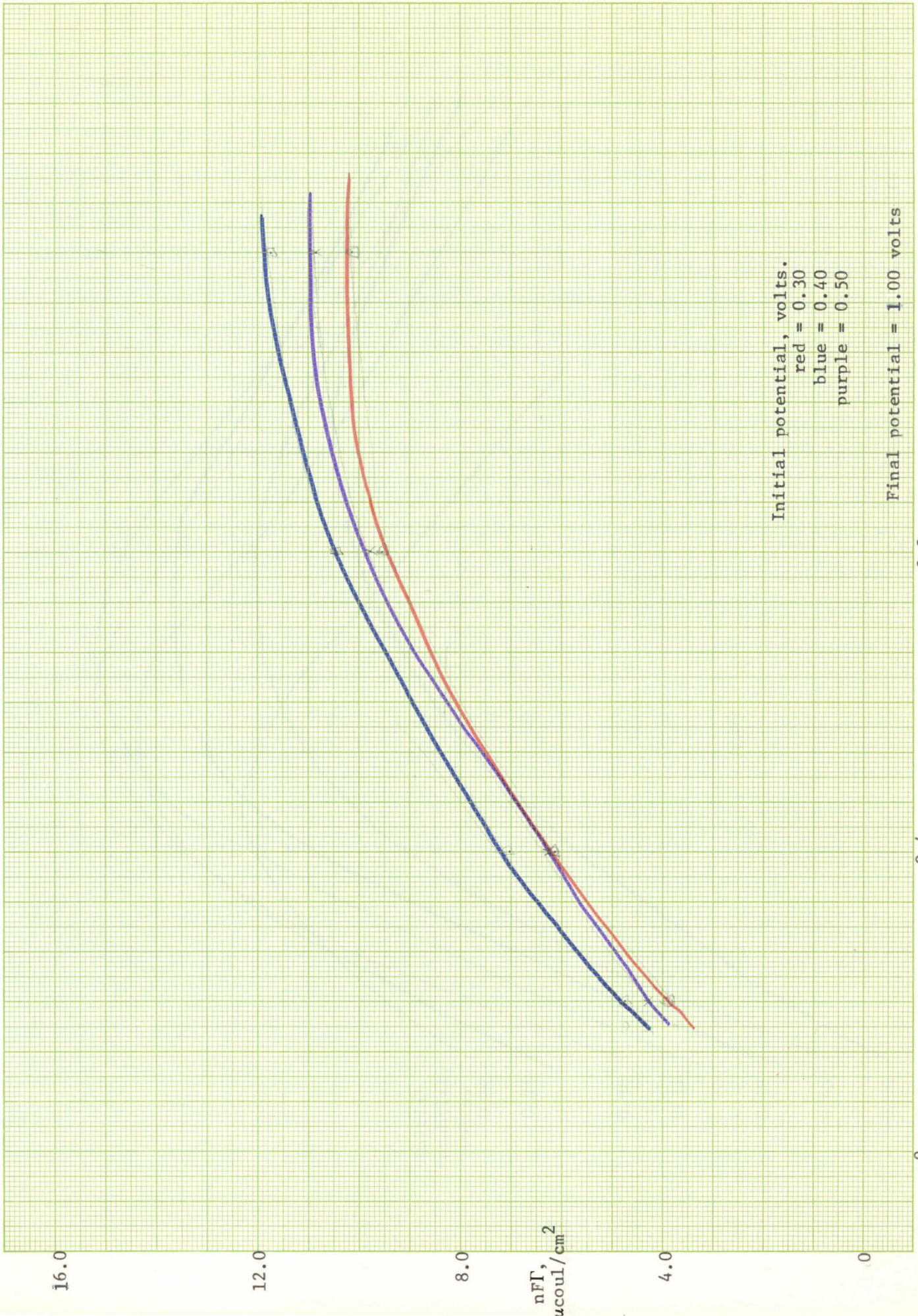


Figure 4

Dependence of Cd(II) adsorption on the concn. of bromide for seven potential steps. 0.4 mF Cd(II), ionic strength maintained at 1 with $KNO_3$.

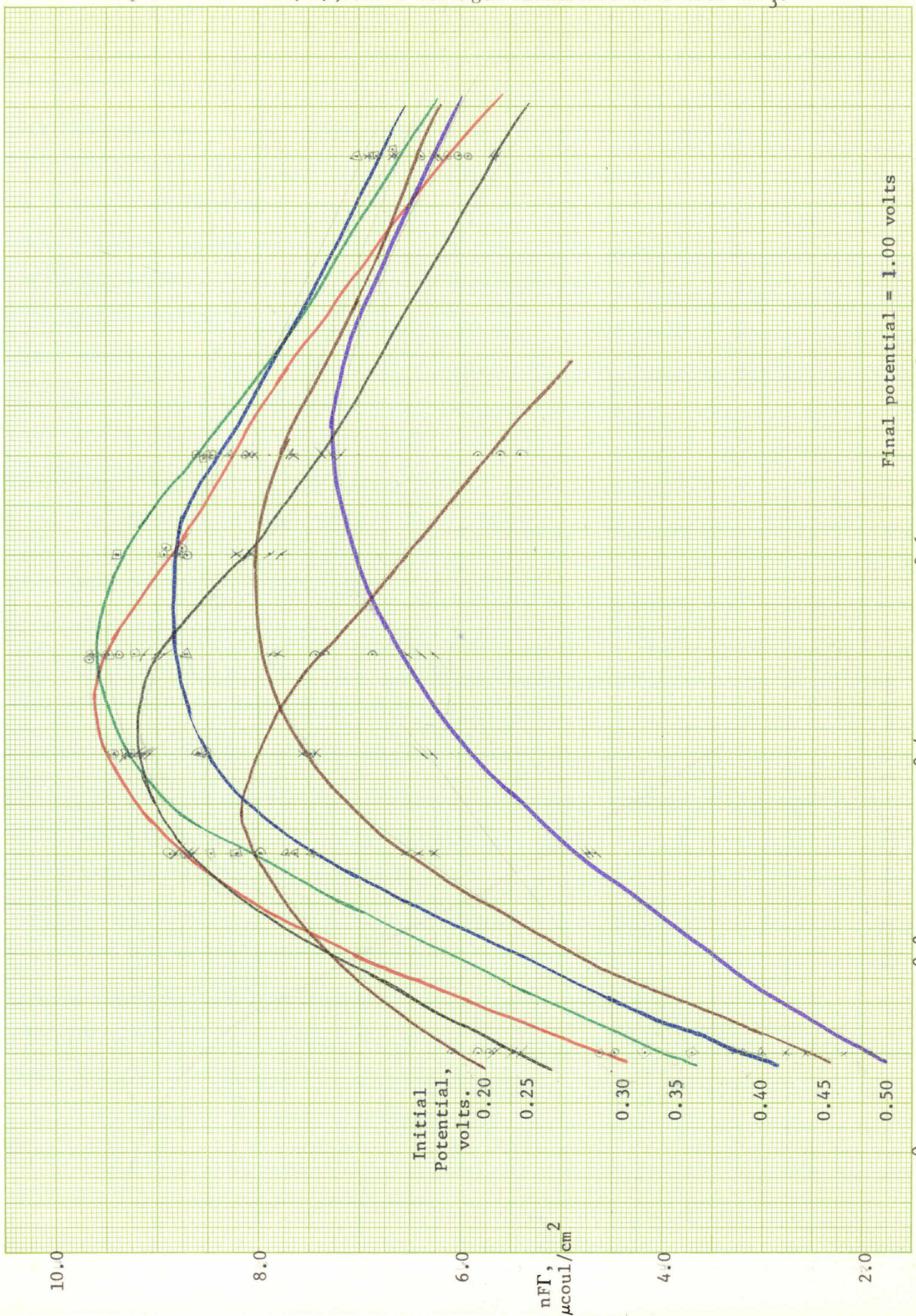
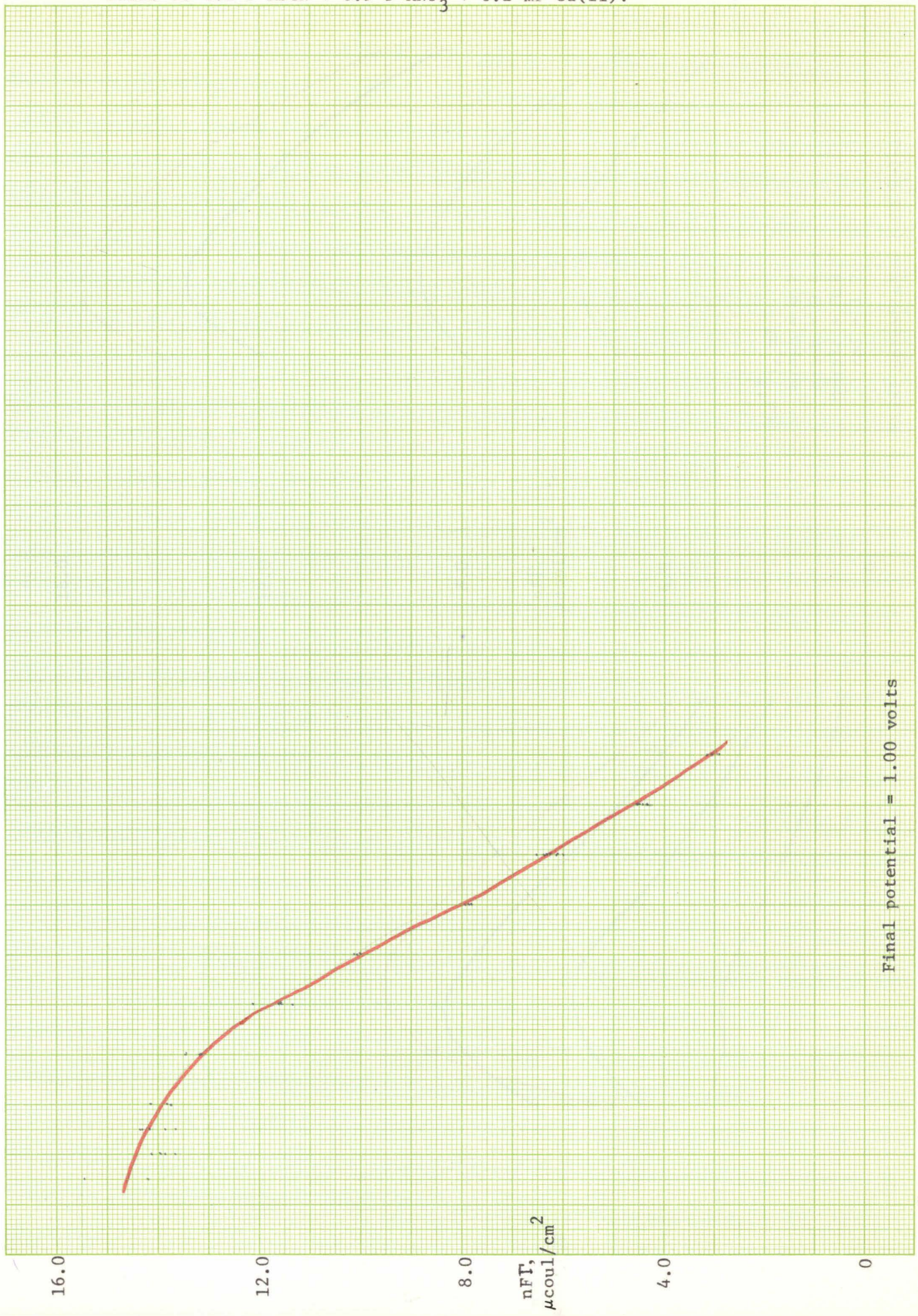


Figure 5

Dependence of cadmium(II) thiocyanate adsorption on the initial potential. Soln. is 0.1 F KSCN + 0.9 F $KNO_3$ + 0.2 mF Cd(II).



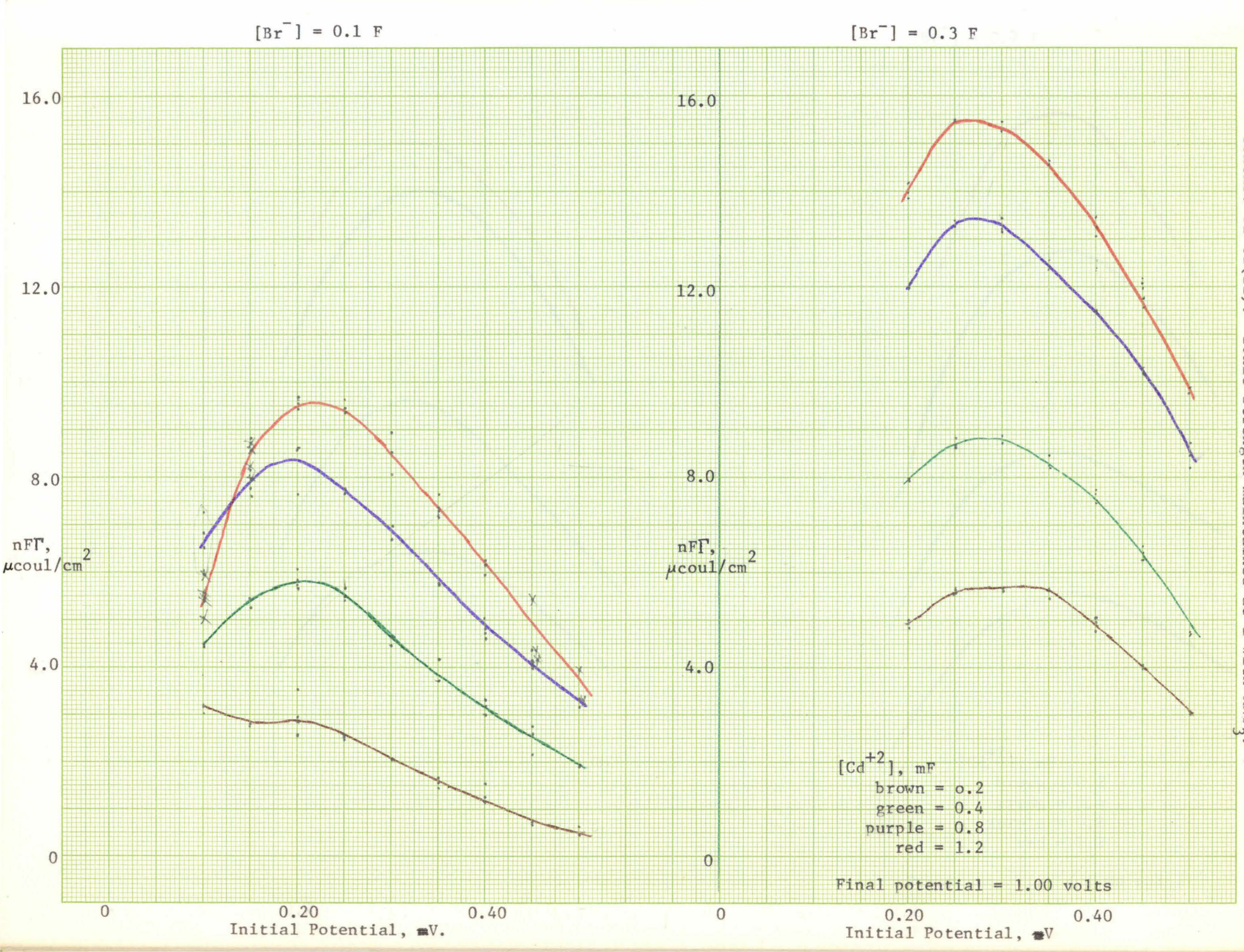



Figure 6 Dependence of Cd(II) adsorption on the initial potential for four concns. of Cd(II). Ionic strength maintained at 1 with $KNO_3$.

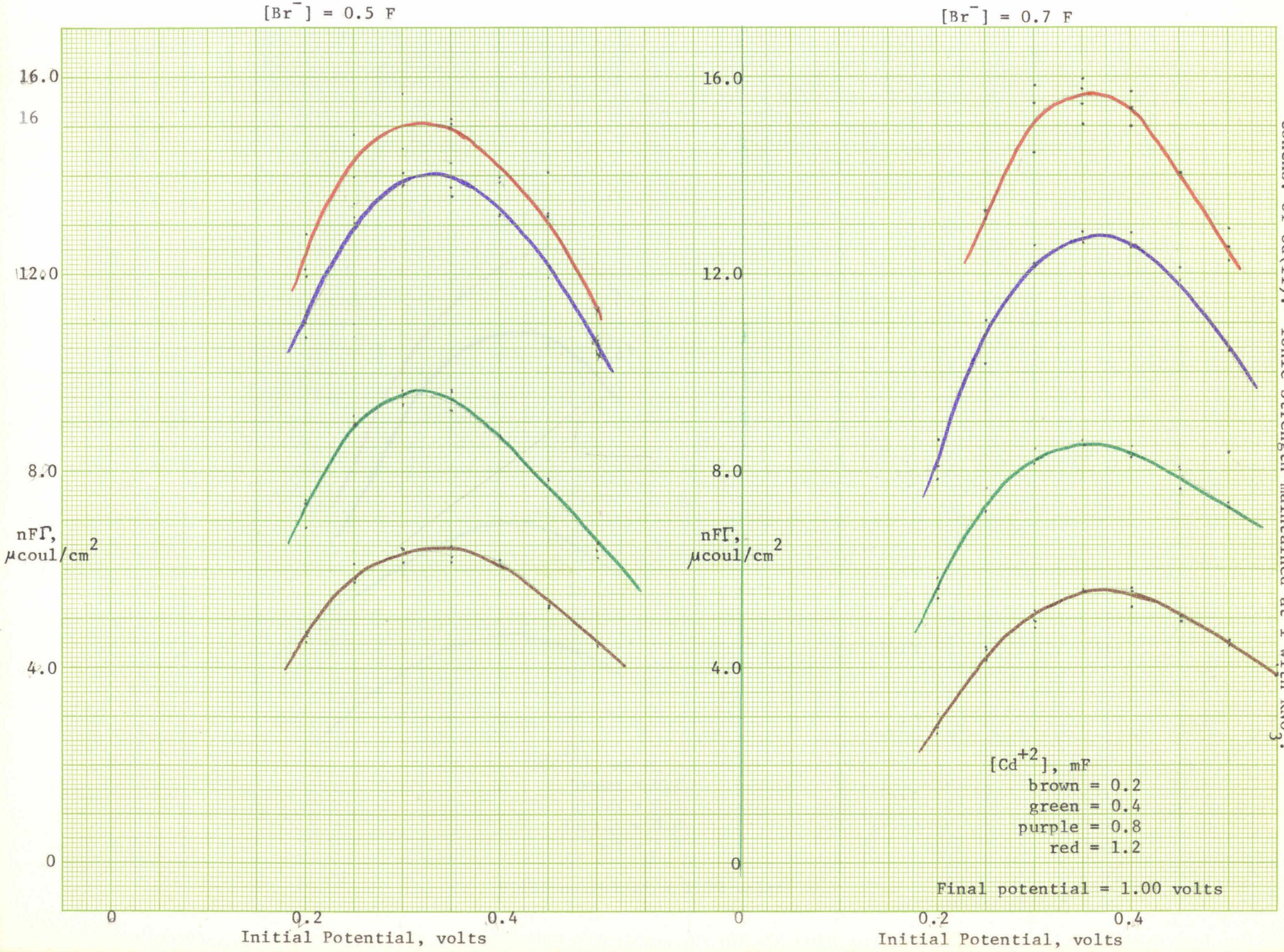



Figure 7 Dependence of Cd(II) adsorption on the initial potential for four concns. of Cd(II). Ionic strength maintained at 1 with $KNO_3$.

Figure 8

Dependence of Cd(II) adsorption on the initial potential for four concns. of Cd(II). Ionic strength is unity.

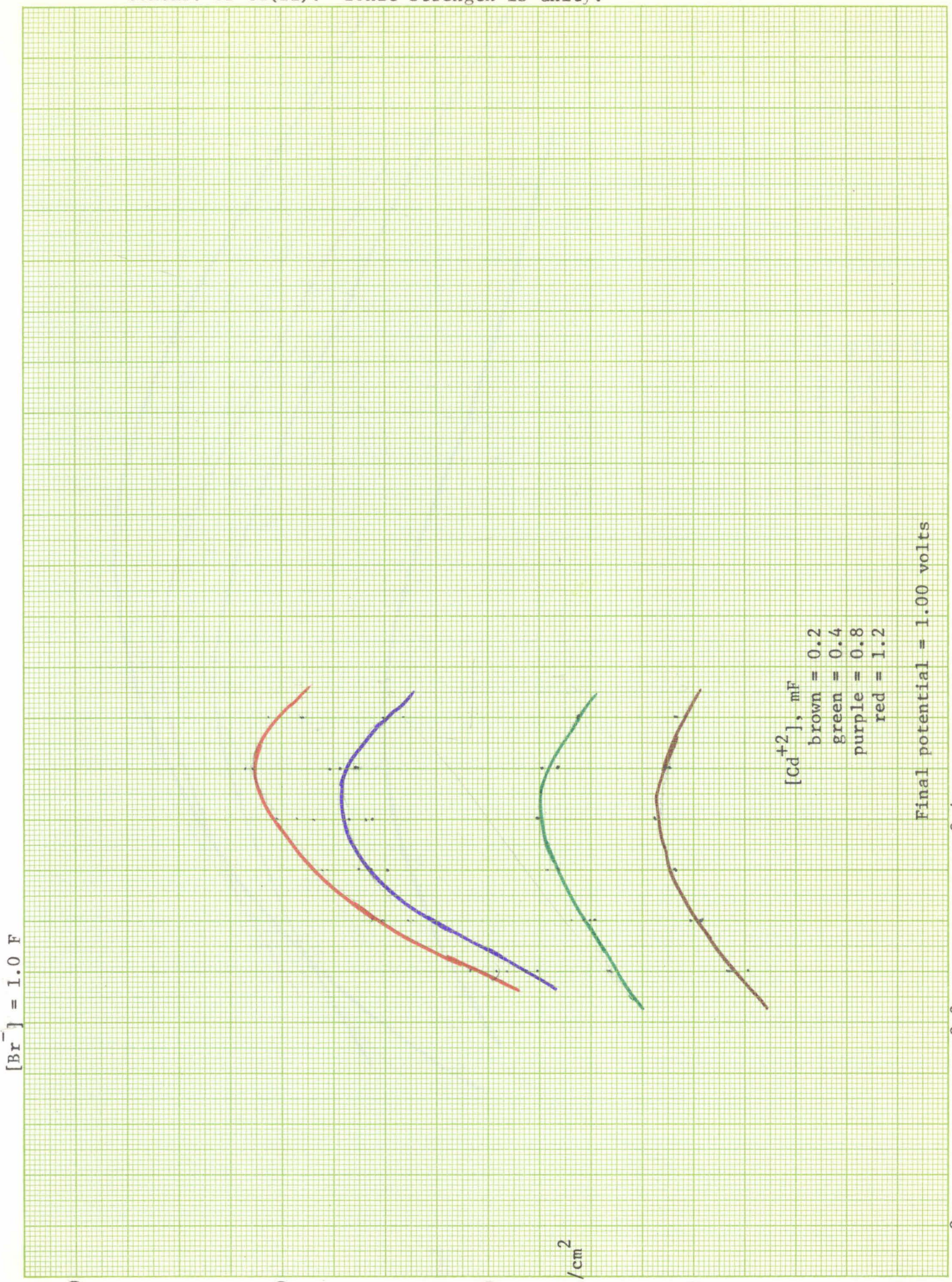


Figure 9

Dependence of Cd(II) adsorption on the initial double layer charge for four concentrations of bromide. 0.4 mF Cd(II), ionic strength is unity.

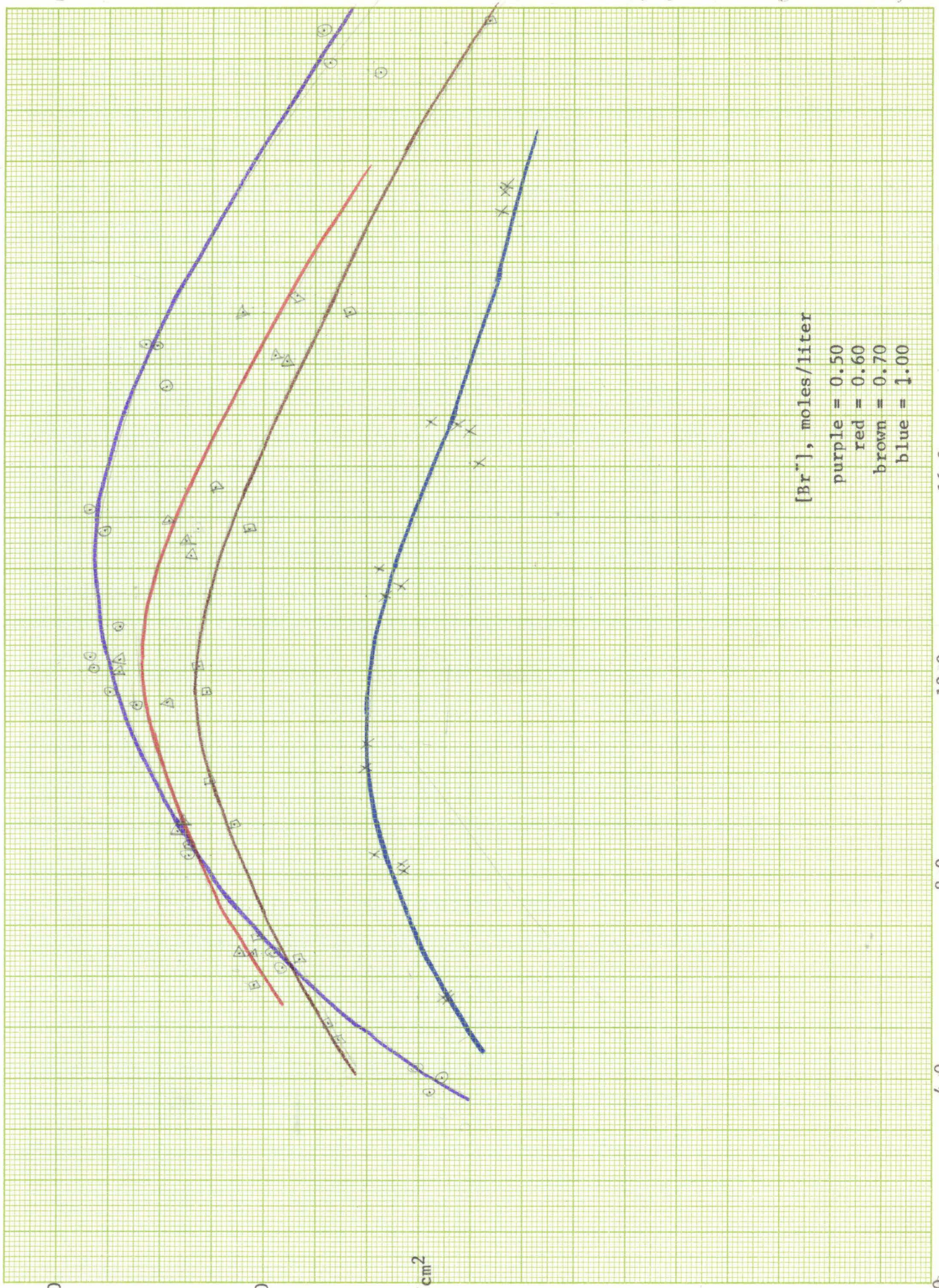


Figure 9(cont.)
Dependence of Cd(II) adsorption on the initial double layer charge continued for three concentrations of bromide. 0.4 mF Cd(II), ionic strength is unity.

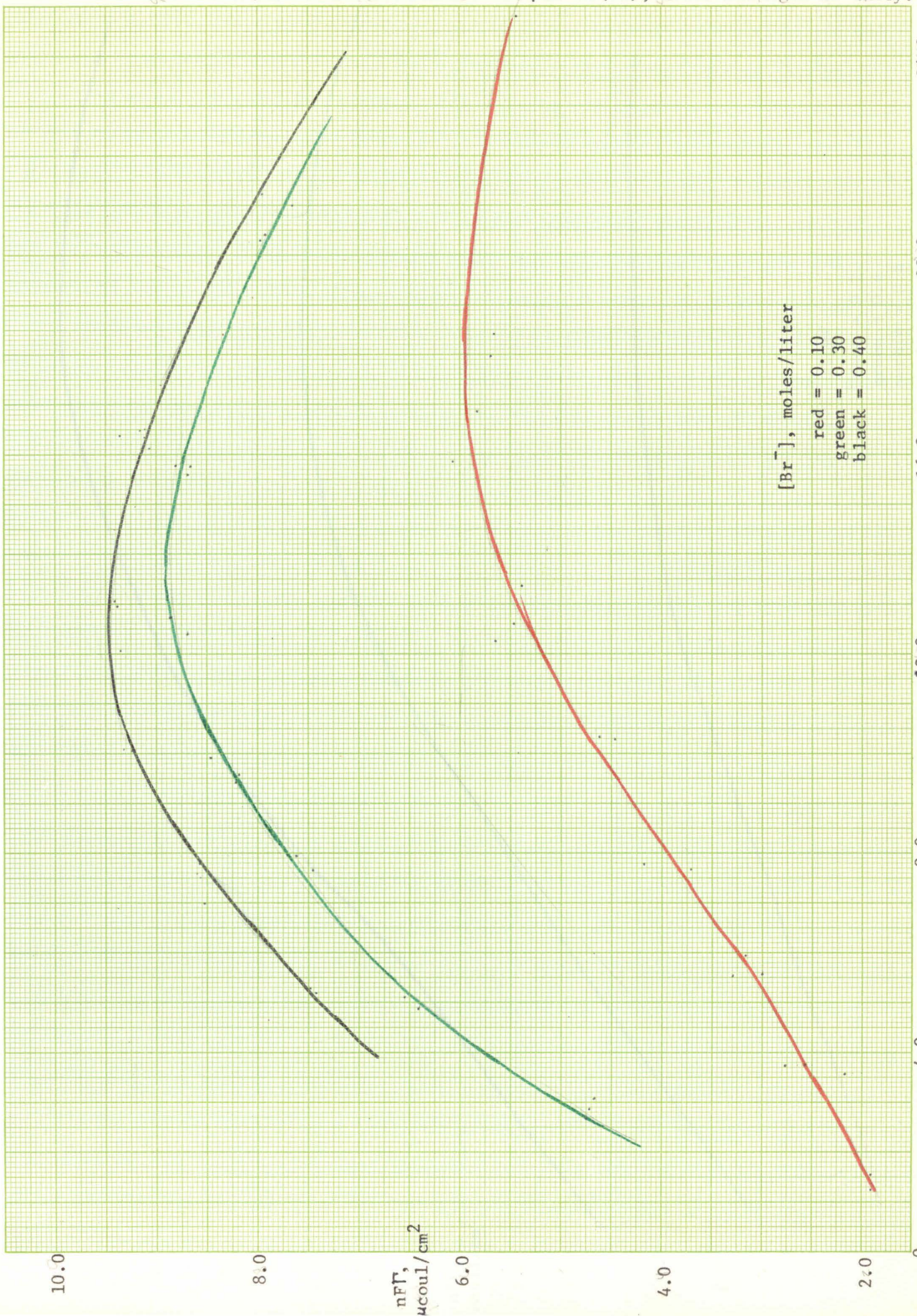


Figure 10

Dependence of Cd(II) adsorption on the initial double layer charge for three concentrations of Cd(II). Soln. is 0.1 F KBr + 0.9 F $KNO_3$.

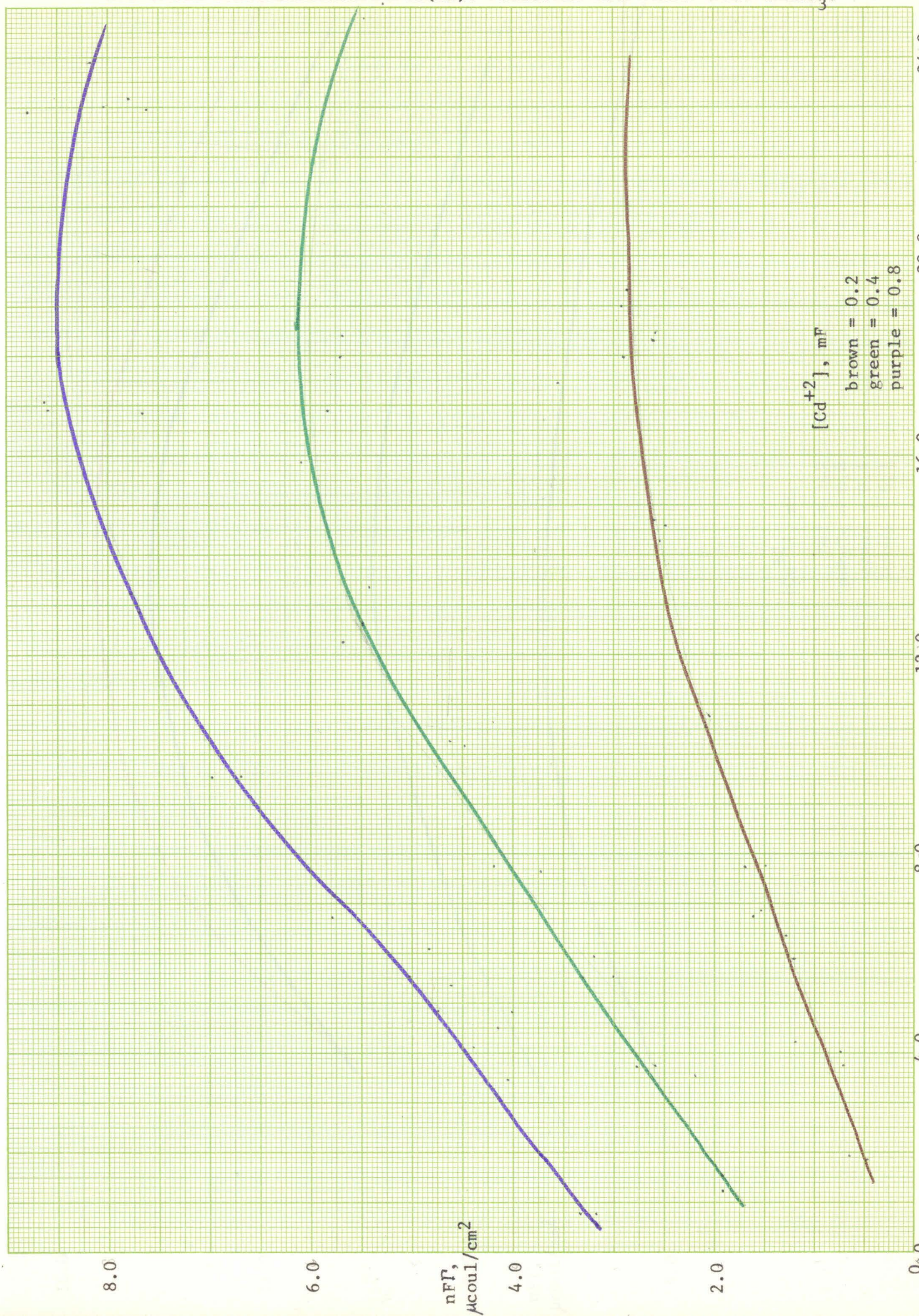


Figure 11

Dependence of Cd(II) adsorption on the initial double layer charge for four concentrations of Cd(II). Soln. is 0.5 F KBr + 0.5 F $KNO_3$.