Q2

In SXR205 Activity B, the kinetics of the reaction between the square-planar platinum complex
dichloro-(2,2'-bipyridine) platinum (II),Pt(bipy)Cl2,

and 1,2-diaminoethane,en,

were investigated. In a different study of this reaction, the data in Table 1 were obtained manually using a spectrometer set at a fixed wavelength of 274nm, the wavelength at which the reactant platinum complex,Pi(bipy)Cl2,absorbs.

The equation for the reaction is,

Pt(bipy)Cl2 + en = {Pt(bipy)(en)Cl}2+ + 2Cl- (3)

The concentration of Pt(bipy)Cl2 and 1,2-diaminoethane in the reaction mixture in methanol at the beginning of the experiment (after mixing) were

4.0 x 10-5 and 4.0 x 10-2 mol dm-3,respectively.

Table 1 Absorbance values versus time.

Time/s	Absorbance
25	0.671
50	0.640
75	0.610
100	0.581
150	0.483
200	0.442
250	0.405
300	0.343
400	0.255
600	0.200
800	0.165
1000	0.143
1200	0.129
1400	0.129
1600	0.120
2000	0.111
2400	0.109
2800	0.106
3200	0.105
3600	0.105

(a) (i) Suggest a reason why the absorbance of the solution does not fall to zero, but becomes constant.
You can assume that the reaction has gone to completion and that all of the Pt(bipy)Cl2 has been used up once the absorbance value has become constant.

(ii)Explain why short time intervals between absorbance readings were used for the early part of the kinetic run.

(iii)Beer's law states that, for dilute solutions, the absorbance of a fixed path length (i.e. 'thickness') of a solution of the absorbing species is directly proportional to the concentration of the absorbing species in the solution.

Use the data in Table 1 to calculate the absorbance at each time caused by Pt(bipy)Cl2

(iv)
Plot your new absorbance data against time.
Make sure you give your graph a title and label the axes.

(v)From your graph, obtain three successive 'half-lives', and from these confirm whether or not the reaction is first-order with respect to Pt(bipy)Cl2.

(vi)Explain how you would determine the pseudo rate constant, Kr' ,for the reaction from a suitable graph using the data in Table 1 and part (a) and (iii).

(b) In three separate experiments similar to above experiment, the following results (Table 2) were obtained.

Note that the concentrations in Table 2 are those in the reaction mixture at the beginning of the reaction.

Explain how these results show that the reaction is first order with respect to 1,2-diaminoethane.

Table 2 pseudo rate constant, Kr', for reaction 3.

[Pt(bipy)Cl2]0/ mol dm-3 [en]0/mol dm-3

4.0 x 10-5 0.080
4.0 x 10-5 0.100
4.0 x 10-5 0.140

Kr' /s
4.76 x 10-3
5.95 x 10-3
8.33 x 10-3