

Fig. 5:- Repetitive spectral scan of the  $[\text{Pt}(\text{dien})\text{I}]^+$  and L-cystine mixture at pH = 2.30 and temperature =  $46^\circ\text{C}$ . Scan (1) = 0 min.(2) = 2 min, (3) = 7 min, (4) = 24 mins.

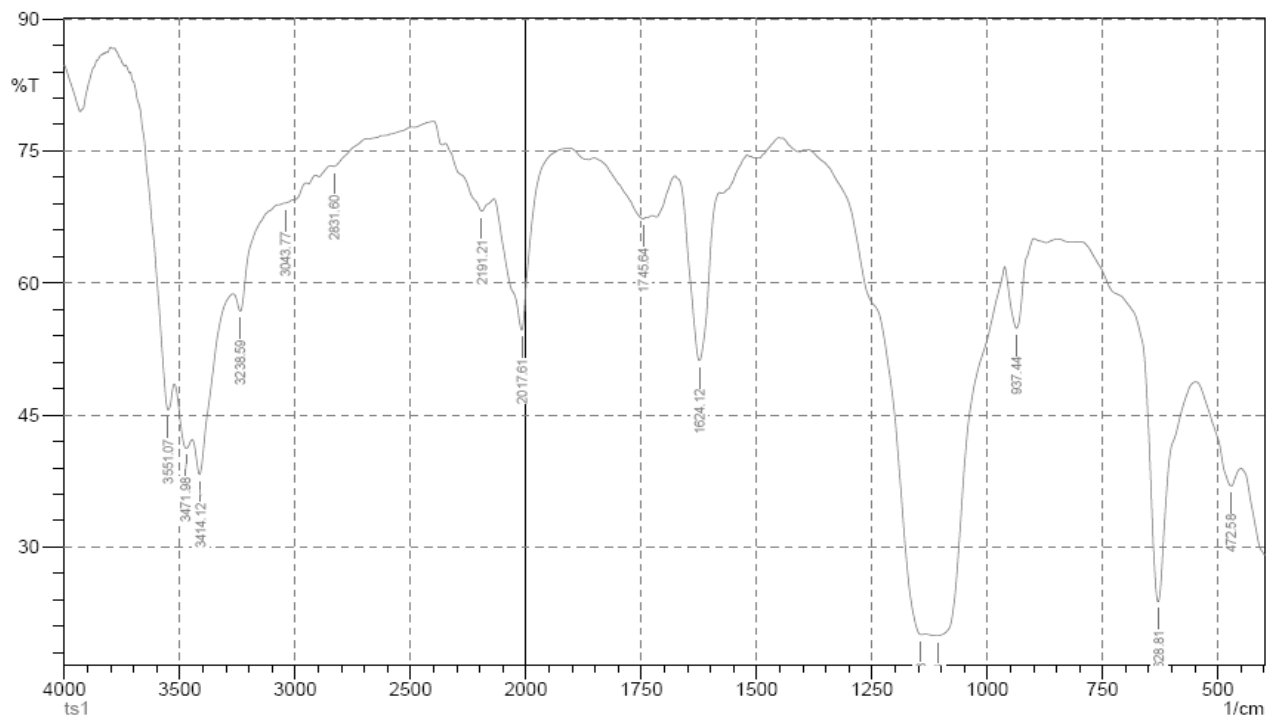


Fig. 6: Ir spectra of the product of  $[\text{Pt}(\text{dien})\text{I}]$  with cystine at room temperature of pH 1.85

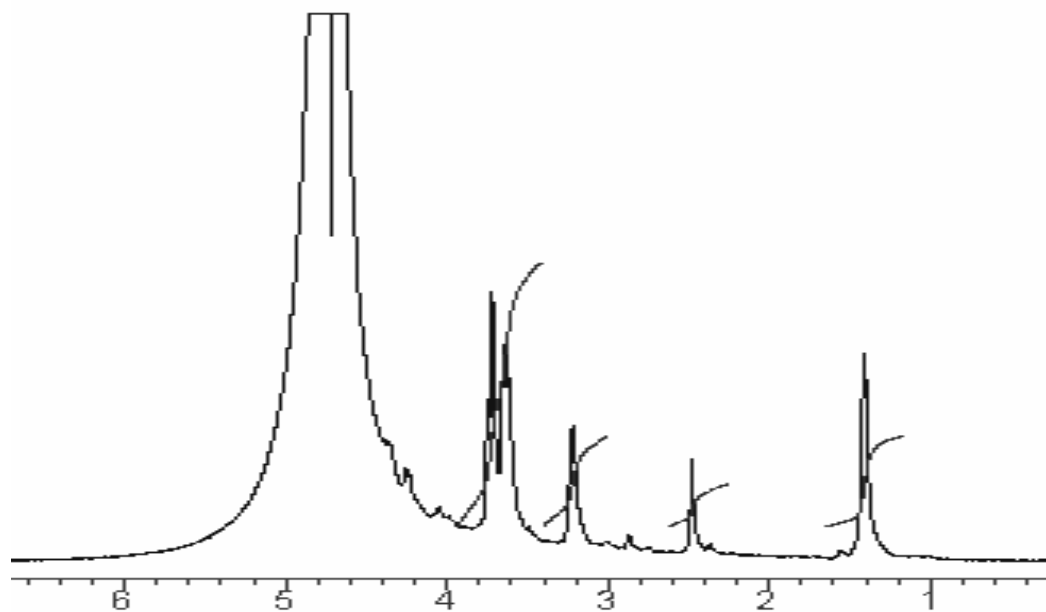


Fig. 7:  $^1\text{H}$  NMR spectra of the product of  $[\text{Pt}(\text{dien})\text{I}]^+$  with L-cystine at  $\text{pH} = 1.85$  and temperature  $35^\circ\text{C}$ . Here dien ring is opened through  $\text{NH}_2$  and the product is  $[\{\text{Pt}(\text{dien})\}(\text{cys})_2]^{4+}$

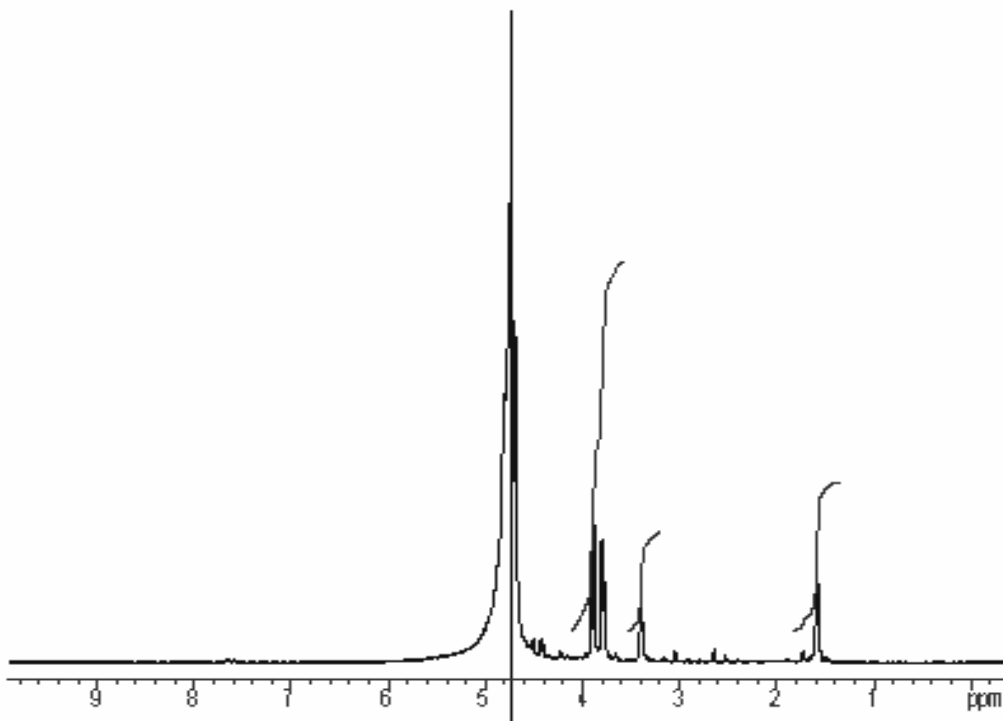


Fig. 8:  $^1\text{H}$  NMR spectra of the product of  $[\text{Pt}(\text{dien})\text{I}]^+$  with L-cystine at  $\text{pH} = 1.85$  and temperature  $50^\circ\text{C}$ .

Table-3: Table-3: Rate constants of product formation for the substitution reactions of Pt(II) complex with L-cystine in I = 0.10 M NaClO<sub>4</sub>, [Pt<sup>II</sup>] = 1.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>, [cystine] = 1.0 × 10<sup>-3</sup> – 3.0 × 10<sup>-3</sup> mol dm<sup>-3</sup> and 30 ≤ t<sup>o</sup>C ≤ 50.

Sl.No.	pH	Temp. (K)	k <sub>3</sub> × 10 <sup>5</sup> (M <sup>-1</sup> s <sup>-1</sup> )	k <sub>-3</sub> × 10 <sup>2</sup> (s <sup>-1</sup> )
1	1.00	303	1.42 ± 0.01	0.13 ± 0.01
		308	0.68 ± 0.02	0.19 ± 0.02
		313	0.46 ± 0.02	0.18 ± 0.01
		318	0.45 ± 0.01	0.23 ± 0.01
		323	1.05 ± 0.01	0.68 ± 0.03
2	1.40	303	1.47 ± 0.02	0.39 ± 0.01
		308	0.68 ± 0.02	0.23 ± 0.01
		313	0.65 ± 0.01	0.26 ± 0.04
		318	0.67 ± 0.03	0.32 ± 0.01
		323	1.55 ± 0.01	0.88 ± 0.02
3	1.85	303	2.42 ± 0.02	0.79 ± 0.02
		308	0.68 ± 0.01	0.27 ± 0.01
		313	1.03 ± 0.01	0.44 ± 0.01
		318	1.26 ± 0.02	0.58 ± 0.02
		323	2.95 ± 0.01	1.45 ± 0.01
4	2.30	303	2.69 ± 0.11	1.03 ± 0.02
		308	0.75 ± 0.01	0.36 ± 0.01
		313	0.50 ± 0.14	0.10 ± 0.02
		318	2.92 ± 0.10	1.21 ± 0.01
		323	12.71 ± 0.02	5.39 ± 0.06

Table-4: Rate constants of product formation ( $k_4, s^{-1}$ ) for substitution reactions of Pt (II)

complex with L-cystine in I = 0.10 M NaClO<sub>4</sub>, [Pt<sup>II</sup>] =  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>,  $1.0 \times 10^{-3}$   
 $\leq$  [cystine]  $\leq 3.0 \times 10^{-3}$ ,  $30 \leq t^\circ C \leq 50$ .

L-Cys	25°C	30°C	35°C	40°C	45°C	50°C
pH = 1.00						
$1.0 \times 10^{-3}$	$1.727 \times 10^{-2}$	$2.161 \times 10^{-2}$	$2.985 \times 10^{-2}$	$3.809 \times 10^{-2}$	$4.633 \times 10^{-2}$	$5.458 \times 10^{-2}$
$1.5 \times 10^{-3}$	$1.221 \times 10^{-2}$	$1.573 \times 10^{-2}$	$2.382 \times 10^{-2}$	$3.191 \times 10^{-2}$	$3.993 \times 10^{-2}$	$4.795 \times 10^{-2}$
$2.0 \times 10^{-3}$	$1.087 \times 10^{-2}$	$1.399 \times 10^{-2}$	$2.185 \times 10^{-2}$	$2.971 \times 10^{-2}$	$3.757 \times 10^{-2}$	$4.544 \times 10^{-2}$
$3.0 \times 10^{-3}$	$9.597 \times 10^{-3}$	$1.244 \times 10^{-2}$	$2.003 \times 10^{-2}$	$2.761 \times 10^{-2}$	$3.524 \times 10^{-2}$	$4.288 \times 10^{-2}$
L-Cys	25°C	30°C	35°C	40°C	45°C	50°C
pH = 1.40						
$1.0 \times 10^{-3}$	$1.584 \times 10^{-2}$	$1.982 \times 10^{-2}$	$2.738 \times 10^{-2}$	$3.494 \times 10^{-2}$	$4.250 \times 10^{-2}$	$5.006 \times 10^{-2}$
$1.5 \times 10^{-3}$	$1.164 \times 10^{-2}$	$1.500 \times 10^{-2}$	$2.271 \times 10^{-2}$	$3.042 \times 10^{-2}$	$3.813 \times 10^{-2}$	$4.585 \times 10^{-2}$
$2.0 \times 10^{-3}$	$1.050 \times 10^{-2}$	$1.351 \times 10^{-2}$	$2.110 \times 10^{-2}$	$2.869 \times 10^{-2}$	$3.628 \times 10^{-2}$	$4.388 \times 10^{-2}$
$3.0 \times 10^{-3}$	$9.303 \times 10^{-3}$	$1.209 \times 10^{-2}$	$1.956 \times 10^{-2}$	$2.704 \times 10^{-2}$	$3.451 \times 10^{-2}$	$4.199 \times 10^{-2}$
L-Cys	25°C	30°C	35°C	40°C	45°C	50°C
pH = 1.85						
$1.0 \times 10^{-3}$	$1.364 \times 10^{-2}$	$1.823 \times 10^{-2}$	$2.435 \times 10^{-2}$	$3.252 \times 10^{-2}$	$4.008 \times 10^{-2}$	$4.765 \times 10^{-2}$
$1.5 \times 10^{-3}$	$4.444 \times 10^{-3}$	$8.248 \times 10^{-3}$	$1.465 \times 10^{-2}$	$2.602 \times 10^{-2}$	$3.498 \times 10^{-2}$	$4.395 \times 10^{-2}$
$2.0 \times 10^{-3}$	$3.387 \times 10^{-3}$	$6.473 \times 10^{-3}$	$1.237 \times 10^{-2}$	$2.364 \times 10^{-2}$	$3.298 \times 10^{-2}$	$4.232 \times 10^{-2}$
$3.0 \times 10^{-3}$	$2.631 \times 10^{-3}$	$5.268 \times 10^{-3}$	$1.055 \times 10^{-2}$	$2.158 \times 10^{-2}$	$3.115 \times 10^{-2}$	$4.073 \times 10^{-2}$
L-Cys	25°C	30°C	35°C	40°C	45°C	50°C
pH = 2.30						
$1.0 \times 10^{-3}$	$1.207 \times 10^{-2}$	$1.614 \times 10^{-2}$	$2.116 \times 10^{-2}$	$2.879 \times 10^{-2}$	$3.549 \times 10^{-2}$	$4.219 \times 10^{-2}$
$1.5 \times 10^{-3}$	$4.269 \times 10^{-3}$	$7.738 \times 10^{-3}$	$1.374 \times 10^{-2}$	$2.441 \times 10^{-2}$	$3.292 \times 10^{-2}$	$4.123 \times 10^{-2}$
$2.0 \times 10^{-3}$	$3.266 \times 10^{-3}$	$6.242 \times 10^{-3}$	$1.192 \times 10^{-2}$	$2.279 \times 10^{-2}$	$3.180 \times 10^{-2}$	$4.081 \times 10^{-2}$
$3.0 \times 10^{-3}$	$2.607 \times 10^{-3}$	$5.220 \times 10^{-3}$	$1.034 \times 10^{-2}$	$2.138 \times 10^{-2}$	$3.067 \times 10^{-2}$	$4.036 \times 10^{-2}$

Table 5: Rate constants of product formation ( $k_5, s^{-1}$ ) for the substitution reactions of Pt (II) complex with L-cystine in I = 0.10 M NaClO<sub>4</sub>, [Pt<sup>II</sup>] = 1.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>, 1.0 × 10<sup>-3</sup> ≤ [cystine] ≤ 3.0 × 10<sup>-3</sup>, 30 ≤ t°C ≤ 50.

[L-cys]	30 °C	35 °C	40 °C	45 °C	50 °C
<b>pH = 1.00</b>					
1.0 × 10 <sup>-3</sup>	4.799 × 10 <sup>-3</sup>	3.907 × 10 <sup>-3</sup>	3.335 × 10 <sup>-3</sup>	2.827 × 10 <sup>-3</sup>	2.404 × 10 <sup>-3</sup>
1.5 × 10 <sup>-3</sup>	4.008 × 10 <sup>-3</sup>	3.414 × 10 <sup>-3</sup>	2.921 × 10 <sup>-3</sup>	2.461 × 10 <sup>-3</sup>	2.098 × 10 <sup>-3</sup>
2.0 × 10 <sup>-3</sup>	3.651 × 10 <sup>-3</sup>	3.161 × 10 <sup>-3</sup>	2.736 × 10 <sup>-3</sup>	2.319 × 10 <sup>-3</sup>	1.972 × 10 <sup>-3</sup>
3.0 × 10 <sup>-3</sup>	3.385 × 10 <sup>-3</sup>	2.992 × 10 <sup>-3</sup>	2.568 × 10 <sup>-3</sup>	2.197 × 10 <sup>-3</sup>	1.875 × 10 <sup>-3</sup>
<b>pH = 1.40</b>					
1.0 × 10 <sup>-3</sup>	4.393 × 10 <sup>-3</sup>	3.363 × 10 <sup>-3</sup>	2.574 × 10 <sup>-3</sup>	1.971 × 10 <sup>-3</sup>	1.509 × 10 <sup>-3</sup>
1.5 × 10 <sup>-3</sup>	3.251 × 10 <sup>-3</sup>	2.580 × 10 <sup>-3</sup>	2.047 × 10 <sup>-3</sup>	1.600 × 10 <sup>-3</sup>	1.270 × 10 <sup>-3</sup>
2.0 × 10 <sup>-3</sup>	2.905 × 10 <sup>-3</sup>	2.303 × 10 <sup>-3</sup>	1.826 × 10 <sup>-3</sup>	1.447 × 10 <sup>-3</sup>	1.177 × 10 <sup>-3</sup>
3.0 × 10 <sup>-3</sup>	2.578 × 10 <sup>-3</sup>	2.088 × 10 <sup>-3</sup>	1.671 × 10 <sup>-3</sup>	1.353 × 10 <sup>-3</sup>	1.096 × 10 <sup>-3</sup>
<b>pH = 1.85</b>					
1.0 × 10 <sup>-3</sup>	4.208 × 10 <sup>-3</sup>	3.249 × 10 <sup>-3</sup>	2.508 × 10 <sup>-3</sup>	1.936 × 10 <sup>-3</sup>	1.495 × 10 <sup>-3</sup>
1.5 × 10 <sup>-3</sup>	2.614 × 10 <sup>-3</sup>	2.018 × 10 <sup>-3</sup>	1.558 × 10 <sup>-3</sup>	1.203 × 10 <sup>-3</sup>	9.280 × 10 <sup>-4</sup>
2.0 × 10 <sup>-3</sup>	2.158 × 10 <sup>-3</sup>	1.666 × 10 <sup>-3</sup>	1.286 × 10 <sup>-3</sup>	9.930 × 10 <sup>-4</sup>	7.670 × 10 <sup>-4</sup>
3.0 × 10 <sup>-3</sup>	1.845 × 10 <sup>-3</sup>	1.424 × 10 <sup>-3</sup>	1.100 × 10 <sup>-3</sup>	8.490 × 10 <sup>-4</sup>	6.550 × 10 <sup>-4</sup>
<b>pH = 2.30</b>					
1.0 × 10 <sup>-3</sup>	4.031 × 10 <sup>-3</sup>	2.940 × 10 <sup>-3</sup>	2.145 × 10 <sup>-3</sup>	1.564 × 10 <sup>-3</sup>	1.141 × 10 <sup>-3</sup>
1.5 × 10 <sup>-3</sup>	2.018 × 10 <sup>-3</sup>	1.472 × 10 <sup>-3</sup>	1.074 × 10 <sup>-3</sup>	7.830 × 10 <sup>-4</sup>	5.710 × 10 <sup>-4</sup>
2.0 × 10 <sup>-3</sup>	1.603 × 10 <sup>-3</sup>	1.169 × 10 <sup>-3</sup>	8.530 × 10 <sup>-4</sup>	6.220 × 10 <sup>-4</sup>	4.540 × 10 <sup>-4</sup>
3.0 × 10 <sup>-3</sup>	1.315 × 10 <sup>-3</sup>	9.590 × 10 <sup>-4</sup>	7.000 × 10 <sup>-4</sup>	5.100 × 10 <sup>-4</sup>	3.720 × 10 <sup>-4</sup>

Table-6: Rate constants of Reversible reaction ( $k_{-4}$ ) for the substitution reactions of Pt (II)

complex with L-cystine in I = 0.10 M NaClO<sub>4</sub>, [Pt<sup>II</sup>] = 1.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>, 1.0 × 10<sup>-3</sup> ≤ [cystine] ≤ 3.0 × 10<sup>-3</sup>, 30 ≤ t°C ≤ 50.

[L-cys]	30 °C	35 °C	40 °C	45 °C	50 °C
<b>pH = 1.00</b>					
1.0 × 10 <sup>-3</sup>	9.408 × 10 <sup>-3</sup>	1.303 × 10 <sup>-2</sup>	1.854 × 10 <sup>-2</sup>	2.718 × 10 <sup>-2</sup>	2.631 × 10 <sup>-2</sup>
1.5 × 10 <sup>-3</sup>	9.552 × 10 <sup>-3</sup>	1.322 × 10 <sup>-2</sup>	1.882 × 10 <sup>-2</sup>	2.749 × 10 <sup>-2</sup>	2.649 × 10 <sup>-2</sup>
2.0 × 10 <sup>-3</sup>	9.627 × 10 <sup>-3</sup>	1.331 × 10 <sup>-2</sup>	1.895 × 10 <sup>-2</sup>	2.763 × 10 <sup>-2</sup>	2.659 × 10 <sup>-2</sup>
3.0 × 10 <sup>-3</sup>	9.701 × 10 <sup>-3</sup>	1.34 × 10 <sup>-2</sup>	1.911 × 10 <sup>-2</sup>	2.780 × 10 <sup>-2</sup>	2.668 × 10 <sup>-2</sup>
<b>pH = 1.40</b>					
1.0 × 10 <sup>-3</sup>	1.364 × 10 <sup>-2</sup>	1.664 × 10 <sup>-2</sup>	2.126 × 10 <sup>-2</sup>	2.757 × 10 <sup>-2</sup>	2.966 × 10 <sup>-2</sup>
1.5 × 10 <sup>-3</sup>	1.375 × 10 <sup>-2</sup>	1.686 × 10 <sup>-2</sup>	2.147 × 10 <sup>-2</sup>	2.790 × 10 <sup>-2</sup>	2.990 × 10 <sup>-2</sup>
2.0 × 10 <sup>-3</sup>	1.386 × 10 <sup>-2</sup>	1.697 × 10 <sup>-2</sup>	2.159 × 10 <sup>-2</sup>	2.805 × 10 <sup>-2</sup>	3.002 × 10 <sup>-2</sup>
3.0 × 10 <sup>-3</sup>	1.396 × 10 <sup>-2</sup>	1.709 × 10 <sup>-2</sup>	2.17 × 10 <sup>-2</sup>	2.822 × 10 <sup>-2</sup>	3.015 × 10 <sup>-2</sup>
<b>pH = 1.85</b>					
1.0 × 10 <sup>-3</sup>	1.766 × 10 <sup>-2</sup>	2.025 × 10 <sup>-2</sup>	2.380 × 10 <sup>-2</sup>	2.809 × 10 <sup>-2</sup>	3.308 × 10 <sup>-2</sup>
1.5 × 10 <sup>-3</sup>	1.796 × 10 <sup>-2</sup>	2.050 × 10 <sup>-2</sup>	2.410 × 10 <sup>-2</sup>	2.834 × 10 <sup>-2</sup>	3.333 × 10 <sup>-2</sup>
2.0 × 10 <sup>-3</sup>	1.810 × 10 <sup>-2</sup>	2.064 × 10 <sup>-2</sup>	2.424 × 10 <sup>-2</sup>	2.848 × 10 <sup>-2</sup>	3.346 × 10 <sup>-2</sup>
3.0 × 10 <sup>-3</sup>	1.826 × 10 <sup>-2</sup>	2.077 × 10 <sup>-2</sup>	2.438 × 10 <sup>-2</sup>	2.860 × 10 <sup>-2</sup>	3.358 × 10 <sup>-2</sup>
<b>pH = 2.30</b>					
1.0 × 10 <sup>-3</sup>	2.311 × 10 <sup>-2</sup>	2.47 × 10 <sup>-2</sup>	2.668 × 10 <sup>-2</sup>	2.848 × 10 <sup>-2</sup>	3.680 × 10 <sup>-2</sup>
1.5 × 10 <sup>-3</sup>	2.344 × 10 <sup>-2</sup>	2.49 × 10 <sup>-2</sup>	2.704 × 10 <sup>-2</sup>	2.876 × 10 <sup>-2</sup>	3.712 × 10 <sup>-2</sup>
2.0 × 10 <sup>-3</sup>	2.363 × 10 <sup>-2</sup>	2.50 × 10 <sup>-2</sup>	2.720 × 10 <sup>-2</sup>	2.891 × 10 <sup>-2</sup>	3.728 × 10 <sup>-2</sup>
3.0 × 10 <sup>-3</sup>	2.381 × 10 <sup>-2</sup>	2.51 × 10 <sup>-2</sup>	2.738 × 10 <sup>-2</sup>	2.905 × 10 <sup>-2</sup>	3.745 × 10 <sup>-2</sup>