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Analysis of Adsorption Effects on Characteristics of Complexes with Mixed Ligands

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Abstract

Creating and characterizing a new mixed ligand complex from the reaction of ligand [4-(5,5-dimethyl-3-oxocyclohex-1-enylamino)-N-(5-methylisoxazol-3-yl) benzene sulfonamide] is the goal of the work. The primary ligand was [H2L], and the secondary ligand was 3-amino phenol [HA] with cobalt ion (Π) at reflux utilizing ethanol as a solvent and KOH as a base. The component $[Co(H_2L)(HA)]$ was complexed with a molar ratio of 1:1:1. FT-IR, UV-Vis spectroscopy, elemental analysis (A.A.), and molar conductance were used to describe the complex. Tetrahedral geometry was seen around the Co ion in these studies. This paper uses a UV-spectrophotometric approach to investigate the adsorption isotherm on the surface of bentonite at various temperatures (10, 25, 37.5, and 50°C). The quantity of adsorption and the application of Langmuir equations were demonstrated experimentally.

Keywords: Adsorption; Metal complexes; Mixed ligands; Spectroscopic analysis

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1. Introduction

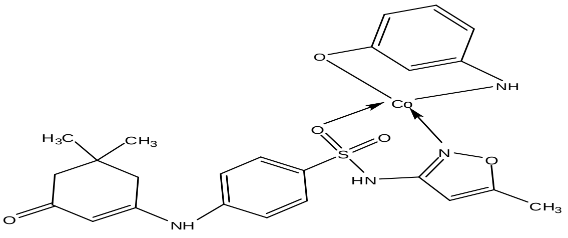
Cobalt is a metallic chemical element in the periodic table with the symbol Co, atomic number 27 and gray color. It is a hard, shiny metal in various materials, and is used in the preparation of alloys resistant to magnetic corrosion and very hard alloys. Its compounds are used in the production of inks and dyes and give a blue color to glass and ceramics [1]. Cobalt is used in the preparation of many complexes, including mixed ligand complexes, which are considered of great importance in the field of chemistry and various other fields, especially in the field of medicine, industry, and agriculture. In addition, it plays an important role in many chemical and biological systems such as water desalination, ion exchange, electroplating, dyes, antioxidants, photosynthesis in plants, and the removal of unwanted and harmful metals from living organisms. Mixed complexes are also suitable for stimulating the role of ionic elements in nature [2]. In this research, a new mixed ligand complex was prepared. Among the chemical and physical techniques used to study the complex is the adsorption technique because it is low cost due to the availability of many natural resources that can be used as adsorbent surfaces such as: (clays, activated carbon, zeolites, organic blocks, agricultural wastes, etc.) [3]. Adsorption is defined as a phenomenon of the accumulation of a gaseous or liquid substance in the form of molecules, atoms, or ions of a specific substance called the adsorbate on the surface of another solid porous substance called the adsorbent [4]. The adsorption process is a spontaneous process that occurs under suitable conditions of pressure and temperature, i.e., it is accompanied by a decrease in free energy accompanied by a decrease in entropy and enthalpy because the adsorbed molecule or atom is restricted to the surface when it is adsorbed. Adsorption on solids has wide uses in many fields including (medicine and pharmacy, pollution, industry, poisoning treatment, chromatographic analysis and catalysis) [5].

2. Materials and Methods

In this study, clear materials and solvents prepared by international companies were used, which were characterized by their micrometer purity between 98-99%.

The preparation was diagnosed using several qualitative techniques, including the infrared spectrum using a Shimadzu (8300) (FT-IR) Spectrophotometer)) within the range of (4000-400) cm-1 using the Bromide Pirates program (KBr), the electronic spectrum will be able to operate the Shimadzu UV- 160- Spectrophotometer)) within the range of 200-1100 nm and the atomic emission spectrum caused the Shimadzu (A-A680) (F.A.A) spectrophotometer and the molar conductivity measurements of the computer (Philips pw-Digital). It was changed from using some other devices such as the melting meter of the type (Stuart Automatic Melt point|SMP40|) and the pH-Meter.

In a round-bottomed flask with a capacity of 100 ml, 0.061 g, 0.26 mmole of the metal chloride salt ($CoCl_2.6H_2O$) was dissolved in 10 ml) of ethanol with stirring for 10 minutes, then 0.03 g, 0.027 mmole of the ligand 3-amino phenol (HA) was added, dissolved in 10 ml of ethanol after adding a few drops of KOH solution to adjust the acidity to (pH=8), and finally 0.1 g, 0.026 mmole of the prepared ligand (H_2L) [6] was added, dissolved in 10 ml of ethanol, then the mixture was left for the reflux process for 3 hours, the solution was filtered while it was hot, and a blue-green precipitate was obtained, which was washed with ethanol, then It was dried and weighed (wt.=0.13g) and the percentage of the resulting complex was 93.5%). Figure (1) shows the chemical structure of the prepared complex and table (1) shows its physical properties.



[Co(H_2L)(HA)]

Fig. (1) Chemical structure of cobalt (II) complex

Bentonite clay used in the complex adsorption study was obtained from the General Company for Geological Survey and Mining. Its powder was washed with sufficient amount of distilled water for a number of times to remove foreign materials and water-soluble materials, then dried in an oven at a temperature of 140 °C for three hours. Then the dried clay was ground to obtain fine particles, after which the ground powder was sieved using suitable sieves to obtain the required particles size. The size of 75 µm was chosen in all experiments related to this study, while the sizes of 250,150 µm were used for the purpose of studying the effect of surface area.

A standard solution (stock solution) with a concentration of (100) mg/L of the cobalt complex was prepared, the adsorption of which was to be studied on the surface of bentonite, by dissolving (0.01) g of the complex in a small amount of ethanol. At the above concentration, a series of solutions were prepared with different concentrations ranging from (2.5-100) mg/L. Then, the absorbance for each concentration was recorded to obtain the calibration curve at a wavelength of (477) nm, which is shown in Fig. (2). It was found that the best concentration of the complex is (50) mg/L.

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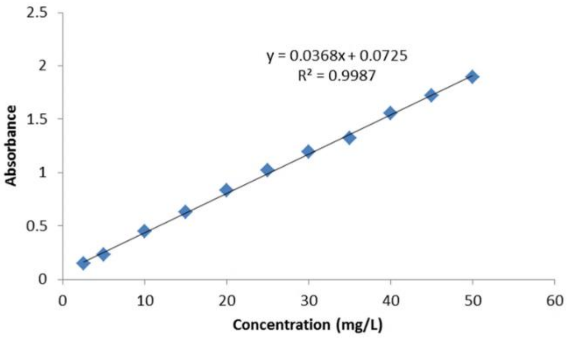

Fig. (2) Calibration curve of cobalt (II) complex

The equilibrium time was determined between the adsorbent surface and the adsorbent by fixing all the conditions, which are (concentration of the adsorbent, weight of the adsorbent surface, volume of the solution, temperature), while the time factor remained the variable in the experiment. (10) ml of cobalt complex solutions was taken at a concentration of 50) mg/L and added to a specific weight of the adsorbent (0.1) g at laboratory temperature. After that, the solutions were placed in a shaking water bath and samples were taken at different time periods (15, 30, 45, 60, 75, 90, 120) min. Their absorbance was measured after the separation and filtration processes were carried out. By following the change in absorbance with time, the equilibrium time for the complex was determined, which was (75) min.

Different concentration solutions of the complex were prepared within the range (5-50) mg/L, then 10 ml of each concentration were taken and placed in volumetric vials, then placed in a water bath equipped with a shaker at 298 K, then 0.3 gm of the surface (bentonite clay) was placed and the solution was left in contact with the adsorbent for 75 min. Then the absorbance of the solutions was measured using a UV/VIS spectrometer at a wavelength of 477 nm. Then the equilibrium concentration of the solution (mg/L) Ce was determined, and the amount of adsorbed material (mg/g) Qe was calculated according to the relationship: ($Qe = (C° – Ce). Vsol / m$) where: Qe represents the amount of adsorbed material (mg/g), Ce represents the equilibrium concentration of the adsorbed material (mg/L), Vsol represents the total volume of the adsorbed material solution (L), m represents the weight of the adsorbent (g), C° represents the initial concentration of the adsorbed material (mg/L).

The adsorption isotherm was studied according to the above paragraph for the complex at different temperatures (10, 25, 37.5, 50) °C.

The effect of solution acidity on the adsorption isotherm was studied within a range of pH values (pH = 1.6-10). The pH values were controlled using dilute solutions of hydrochloric acid (0.1N) and sodium hydroxide (0.1N). Using a pH-meter, the pH values were adjusted.

In order to study the effect of the size of the adsorbent particles (surface area) on the adsorption capacity, three different particle sizes of the adsorbent were used, namely 75, 150, and 250 µm. These experiments were conducted using a fixed concentration (50) mg/L of the prepared complex solution and the same weight of the adsorbent (0.3) g with different particle sizes at laboratory temperature.

3. Results and discussion

The infrared spectrum of the complex showed an absorption band at 1629 cm^{-1} (1629) attributed to the υ(C=N) bond shifted towards a higher frequency than it was in the free state of the ligand [H2L] [6] by 1 cm^{-1} (17). The shift in the band is evidence of the coordination of the cobalt ion and its association with the nitrogen atom of the υ(C=N) group in the ligand [H_2L] and the nitrogen atom of the υ (NH2) group in the 3-aminophenol [HA] ligand [7]. This association is reinforced by the appearance of weak absorption bands at 1543,514 cm-1 (1543,514) attributed to the υ (Co-N) bond in the cobalt complex [8], while the υ (C-NH) and υ (S-NH) bands did not suffer any clear change, which indicates that coordination did not occur through them. The infrared spectrum of the complex showed a shift in the absorption band of the υ (S=O) group, appearing at the position cm^{-1}(1328,1163) compared to the positions of the same bands in the free state of the ligand [H_2L] at cm^{-1}(1363,1137). This indicates the coordination of the metal ions with the oxygen of the υ (S=O) group in the ligand [H_2L] and the oxygen of the υ (O-H) group in the ligand [[HA [9]]. What strengthens this connection is the appearance of weak absorption bands at positions (cm^{-1} 474,437) attributed to the υ (Co-O) bond in the cobalt complex [10], in addition to the appearance of an absorption band around cm-1(1570) for the complex attributed to the υ (C=O) bond in the ligand [H_2L], its position did not change from [7] The locations of the characteristic bands of the mixed ligands and the prepared complex were recorded in table (2), and figure (3) shows the infrared spectrum of the prepared complex.

The UV-Vis spectrum of the cobalt complex and mixed ligands was measured and the results were recorded in tables (3) and (4), where five peaks appeared, the first peak at (268) nm and the second peak at (353) nm. The origin of these two peaks is attributed to the ligand field [6] with a slight displacement and change in the shape of each of the two peaks, which supports the coordination between the ligand and the metal ion. As for the third peak, it appeared at (477) nm. This peak is attributed to the charge transfer spectrum (C.T). As for the fourth peak, it appeared at (613) nm and the fifth peak appeared at (679) nm. The origin of these two peaks is attributed to the electronic transitions (d-d) type (F) $^4A_2 \rightarrow {}^4T_2$ and (F) $^4A_2 \rightarrow {}^4T_1$, respectively. In light of these results, the proposed geometric shape of the prepared complex is tetrahedral [11] as shown in Fig. (4).

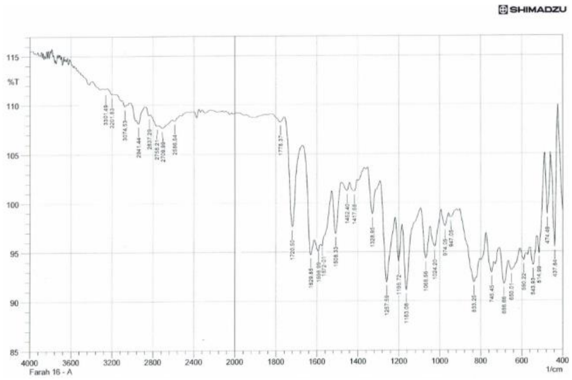

Fig. (3) FTIR spectrum of cobalt (II) complex

Table (3) UV spectrum data for mixed ligands

Ligand	λ (nm)	υ^{-} cm^{-1}	ε_{max} molar^{-1}cm^{-1}	Assignments
[H_2L]	268 330	37313 30303	973 1920	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
[HA]	230 269	43478 37174	2283 2196	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$

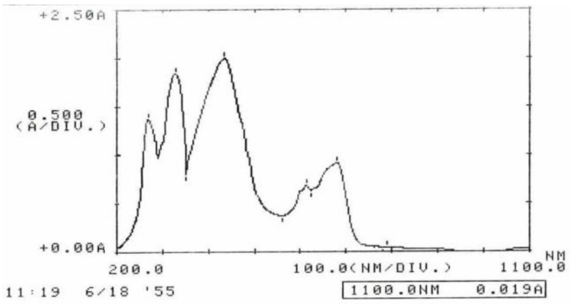

Fig. (4) UV-visible spectrum of cobalt (II) complex

The ionic character of the complex can be known by measuring its molar conductivity. The molar conductivity of the prepared complex solution was measured by preparing it at a concentration of (1×10^{-3} M) in dimethyl sulfur dioxide (DMSO) solvent and laboratory temperature. It was found that the molar conductivity value of the complex [Co(H_2L)(HA)] is

$ohm^{-1}.cm^{2}.mol^{-1}$ (17.02), which proves that the prepared cobalt complex is non-electrolyte (neutral).

A study was conducted on the adsorption of the cobalt complex and the amount of its adsorption on the bentonite surface, then the amount of the substance was calculated in the equilibrium time as shown in table (5) and according to the following relationship: $Qe = (C° – Ce). Vsol / m$ [12]. The amount of the adsorbed substance (Qe) was also plotted against the equilibrium concentration (Ce) to give the general form of the adsorption method as shown in Fig. (5). From the plot, it is clear that the general form of the adsorption isotherm of the cobalt complex on the bentonite surface is of the (L_1) type according to the Giles classification, which indicates that the adsorption isotherm of the complex on the surface follows the linear equation of the Inkmuir: $Ce/Qe = 1/ba + Ce/b$ as in Fig. (6). A study was conducted on the same complex prepared on the surface of bentonite at different temperatures (10, 25, 37.5, 50 °C), using 0.3 g of bentonite and pH ≈ 8-8.5 and the size of the adsorbent particles μm (75) as shown in table (5). It was found that the amount of adsorbed material Qe increases with increasing temperature, i.e., the adsorption is endothermic as shown in Fig. (5).

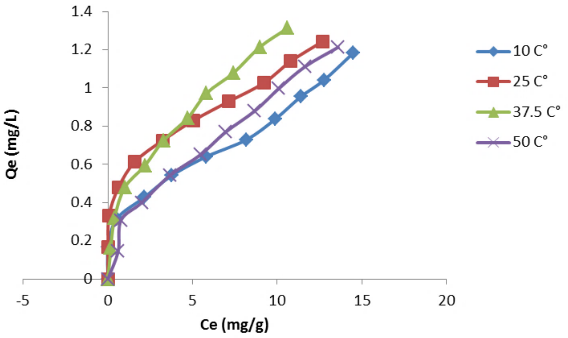

Fig. (5) Adsorption isotherms of cobalt (II) complex adsorbed on the surface of bentonite

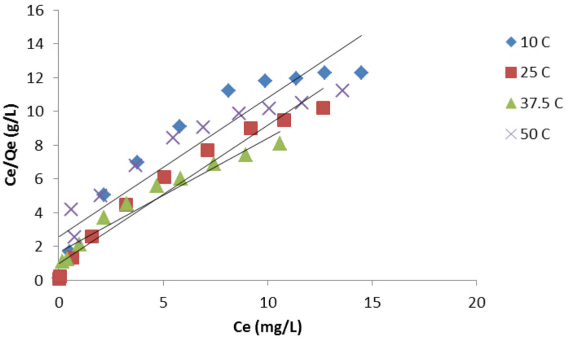

Fig. (6) Linear image of the Langmuir isotherm of the cobalt (II) complex

Also, the effect of changing the acidity function for the complex adsorption on the surface of bentonite was studied at different acidity functions and at fixed concentrations (50) mg/L of the complex and temperature (25) °C and the size of the adsorbent particles is (75) μm. The results are shown in table (6). It was found that the amount of adsorbed material has a greater value in the basic environment as in Fig. (7). When studying the effect of the size of the particles of the adsorbent (surface area) using 0.3 g of bentonite, the results showed a decrease in the amount of adsorption with increasing the size of the particles of the complex. This is attributed to the fact that the surface area of the adsorbent increases with decreasing the granular size of its particles [13] as shown in Fig. (8).

Table (6) Values of the adsorption amount of the cobalt (II) complex when the acidity function on the surface of bentonite changes

pH	C_e(mg/L)	Qe(mg/g)
1.6	48.5724	0.0475
2	47.2364	0.0921
3	45.9591	0.1346
4	45.7245	0.1425
5	45.5758	0.1474
6.3	45.3899	0.1536
7	45.2412	0.1586
8	45.1669	0.1611
9	44.9935	0.1668
10	44.9192	0.16936

Thermodynamic functions were calculated, including the change in enthalpy (ΔH) by plotting the values of the logarithm of the equilibrium constant versus the values of the reciprocal of temperature (1/T) based on the following Van't Hoff equation [14].

$\ln k=(-\Delta H)/RT + Constant$

We get a linear relationship with a slope of (-ΔH)/RT and a constant intercept. In addition, the free energy of Gibbs (ΔG) was calculated from the following equation: $\Delta G = -RT\ 1n\ K$

As for the change in entropy (ΔS), it is calculated by applying the Gibbs equation for equilibrium. $\Delta G = \Delta H – T\ \Delta S$.

The results of this study for the complex were recorded in tables (7) and (8), while figure (9) shows the linear relationship of the values of ln Q_{max} with the absolute values of 1/T.

Table (8) Thermodynamic functions for adsorption of the prepared complex on the bentonite surface

ΔG ($kJ.mol^{-1}$)	ΔH ($kJ.mol^{-1}$)	ΔS ($J.mol^{-1}.K^{-1}$)
-8.7227	+ 2.3559	39.1471
-10.2541		42.3154
-10.3499		40.9204
-10.3335		39.2860

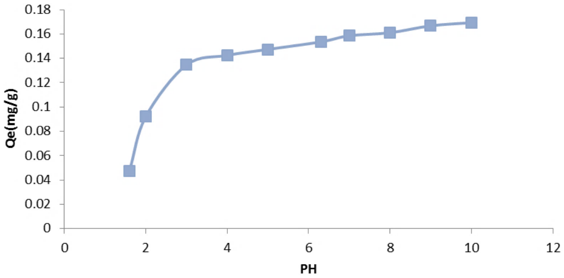

Fig. (7) Effect of acid function on adsorption of cobalt (II) complex

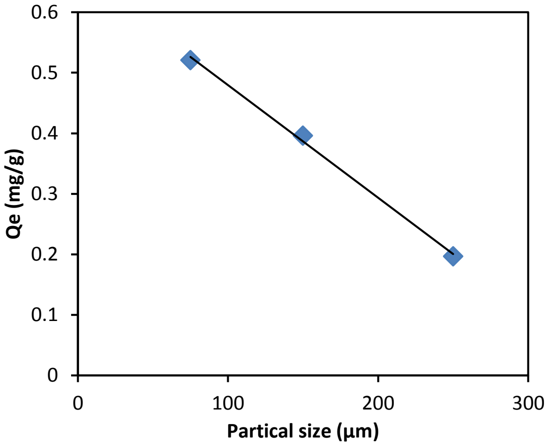

Fig. (8) Effect of the size of the adsorbent particles on the adsorption of the cobalt (II) complex

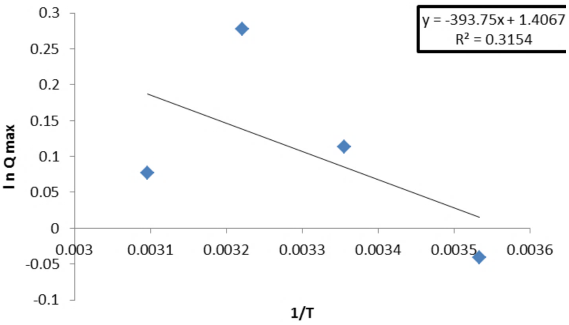

Fig. (9) Values of complex adsorption on the bentonite surface 1/T versus ln Q_{max}

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Table (1) Some physical properties and molar conductivity of the cobalt complex

Empirical Formula	M.Wt	Color	M.P °C	M Found, (Calc)%	Yield %	Λ_m S.cm^2 molar^{-1}
[Co(H_2L)(HA)]	556.52	Bluish green	112	9.98 , (10.59)	93.5	17.02

M.P= melting point Calc=calculated

Table (2) Infrared spectrum values of cobalt (II) complex and mixed ligands in cm^{-1}

Compound	υ(OH) Phenol	υ(NH_2)	υ(S-NH)	υ(C-NH)	υ(C=N)	υ(C=O)	υ_{as}(S=O) υ_s(S=O)	υ(Co–N)	υ(Co–O)
[H_2L]	_	_	3302	3205	1612	1571	1363 1137	_	_
Ligand [HA]	3548	3362 3298	_	_	_	_	_	_	_
[Co(H_2L)(HA)]	_	_	3301	3201	1629	1572	1328 1163	543 514	474 437

Table (4) UV-Vis spectral data for cobalt (II) complex

Compound	Wave number		ε_{max} molar^{-1} cm^{-1}	Assignment	Suggested structure
	nm	cm^{-1}			
[Co(H_2L)(HA)]	268	37313	1425	L.F	Td
	353	28328	1897	L.F	
	477	22371	1985	C.T	
	613	16313	685	$^4A_2 \rightarrow {}^4T_2$ (F)	
	679	14727	913	$^4A_2 \rightarrow {}^4T_1$ (F)	

Table (5) Values for adsorption of cobalt (II) complex on the surface of bentonite at different temperatures

C_o (mg/L)	10°C			25°C			37.5°C			50°C		
	C_e (mg/L)	Q_e (mg/g)	C_e/Q_e (g/L)	C_e (mg/L)	Q_e (mg/g)	C_e/Q_e (g/L)	C_e (mg/L)	Q_e (mg/g)	C_e/Q_e (g/L)	C_e (mg/L)	Q_e (mg/g)	C_e/Q_e (g/L)
5	0.0211	0.1659	0.127185	0.0135	0.1662	0.081227	0.1766	0.1607	1.098942	0.6114	0.1462	4.181943
10	0.5298	0.3156	1.678707	0.0679	0.3311	0.205074	0.3941	0.3201	1.231178	0.7744	0.3075	2.518374
15	2.1603	0.4279	5.048609	0.6282	0.479	1.311482	0.9987	0.4796	2.08236	2.0027	0.3999	5.008002
20	3.7635	0.5412	6.953991	1.5941	0.6135	2.59837	2.1875	0.5937	3.684521	3.6821	0.5439	6.769811
25	5.8016	0.6399	9.066417	3.2364	0.7254	4.461538	3.2744	0.7241	4.522027	5.4755	0.6508	8.413491
30	8.1611	0.7279	11.21184	5.0701	0.8309	6.101938	4.7146	0.8428	5.593972	6.9429	0.7685	9.034353
35	9.8854	0.8371	11.8091	7.1321	0.9289	7.678006	5.8288	0.9723	5.994858	8.6548	0.8781	9.856281
40	11.3862	0.9537	11.93897	9.2114	1.0262	8.976223	7.4222	1.0792	6.877502	10.0951	0.9968	10.12751
45	12.7635	1.0412	12.25845	10.8016	1.1399	9.475919	8.9733	1.2142	7.390298	11.6441	1.1118	10.4732
50	14.4972	1.1834	12.25046	12.6821	1.2439	10.19543	10.6114	1.3129	8.082413	13.6005	1.2133	11.20951

Table (7) Effect of temperature on the thermodynamic equilibrium constant for adsorption of cobalt (II) complex on the bentonite surface

C_e (mg/L)	T(°C)	T(K)	1/T (K^{-1})	Q_e (mg/g)	Equilibrium constant (K)	l n Q_{max}	lnK
10.6	10.0	283.0	0.003534	0.96	72.4528	-0.0408	4.2829
	25.0	298.0	0.003356	1.12	84.5283	0.1133	4.4370
	37.5	310.5	0.003221	1.32	99.6226	0.2776	4.6013
	50.0	323.0	0.003096	1.08	81.5094	0.0769	4.4007