Article

Adsorption Behaviors of Palladium(II) in Simulated High-Level Liquid Waste Using 2,2'-[(2-ethylhexyl)imino]bis[*N,N*-bis(2-ethylhexyl)acetamide]-impregnated Adsorbent

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Abstract

A hybrid donor compound 2,2'-[(2-ethylhexyl)imino]bis[*N,N*-bis(2-ethylhexyl)acetamide] (DAMIA-EH) impregnated silica-based adsorbent [(DAMIA-EH+1-dodecanol)/SiO₂-P] was prepared. Its adsorption performance toward Pd(II) in nitric acid solution was investigated by examining the effect of contact time, temperature etc. It was found that the adsorption rate of Pd(II) was fairly fast and can reach a constant state within only 10 min. (DAMIA-EH+1-dodecanol)/SiO₂-P exhibited an excellent recognition ability toward Pd(II) than other 14 types of co-existing metal ions and could maintain this selectivity when the concentration of HNO₃ varied from 0.5 to 5 M. On the other hand, the maximum adsorption amount of Pd(II) was calculated to be as high as 0.440 mmol/g when [HNO₃] = 2 M. Moreover, with increasing the temperature in solution, the uptake ratio of Pd(II) slightly decreased, it still exhibited a dominant selectivity toward Pd(II) in a wide temperature range from 288 to 323 K. The fitted thermodynamic parameters revealed that the adsorption process of Pd(II) was exothermic in nature and happened spontaneously.

Keywords: adsorption, adsorbent, palladium, silica-based, hybrid donor

1. Introduction

Due to the unique chemical and specific physical properties, palladium (Pd) is of great value and has been widely used in the modern industry of catalyst, electronic components, medicine etc.¹⁾ The excessive accumulation of spent Pd-containing materials in environment will cause severe human health damage such as skin irritation, degradation of DNA, enzyme activity inhibition etc.²⁾ The effective Pd recovery from both industrial waste and natural ore are very important not only from the viewpoint of resource utilization but also environmental protection³⁾. On the other hand, to circumvent the problem of growing demand for Pd, significant amount of Pd generated in spent nuclear fuel is also thought as an alternative source⁴⁾. Among all these separation methods⁵⁾, solid phase extraction (adsorption) possessing the advantages of minimum solvent requirement, no formation of third phase, high purity products etc., is considered as one of the promising

method for the recovery of Pd(II) from acidic solution⁶⁾.

To date, carbon nanotubes, polymer resins, porous silica, zeolite, or metal organic frameworks (MOFs) etc. are categorized as commonly used support materials of adsorbent⁷⁾. Organic ligands which can provide binding ability to certain metal ions are generally impregnated into the pores of support materials or grafted/immobilized onto their surfaces^{8,9)}. Based on previously studies, attributing the merits of high adsorption capacity, wide specific surface area, radiolytic stability etc. porous silica support synthesized in our group is considered as a widely accepted component for the preparation of adsorbent using in the recovery of different kinds of metal ion in acidic condition¹⁰⁾. According to the theory of hard and soft acids and bases (*HSAB*), nitrogen and sulfur containing ligands as electron acceptors exhibit superior affinity to soft acid Pd(II)¹¹⁾. Comparing with S donor, N donor is considered to be more environmentally friendly. However, in the case of

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non-heterocyclic N donor compound or heterocyclic compound containing few numbers of N atoms, such as pyridine, pyrazine etc., their property of protonation in highly acidic solution is frustrating¹². Wu et al. introduced a novel poly-azamacrocyclic receptor impregnated resin to recover Pd(II) in nitric acid solution. Their results found the resin exhibited a good selectivity toward Pd(II) without the inference of other 17 kinds of co-existing metal ions in the solution, and had a relatively high adsorbent capacity of 169.5 mg/g when $[\text{HNO}_3] = 1 \text{ M}$. With increasing the concentration of HNO_3 from 1 to 5 M, the uptake percentage decreased drastically from more than 90% to 20%, which can be explained as the protonation of cyclic N atoms¹³. Daliran et al. prepared a porous pyridyltriazol functionalized zirconium metal organic framework. Their MOFs consisted of 12-coordinate hexanuclear Zr nodes connected with each other by 12 pyridyltriazol functional group of the links to give octahedral and super tetrahedral cages. A high adsorption amount of Pd(II), calculated as 294.1 mg/g at pH = 4.5 was attributed as the high surface area of the octahedral structure. The acid resistance ability was proved to be poor because of introduction of pyridine group. When pH decreased from 4.5 to 1, the uptake percentage decreased from 100 % to around 20 %¹⁴. On the other hand, abundant N containing heterocyclic ligand, such as 2,6-bis-1,2,4-triazin-3-yl-pyridines (BTPs) derivatives and {(RS)-1-[2-(2,4-dichlorophenyl)pentyl]-1H-1,2,4-triazole} maintained a good adsorption performance of Pd(II) even in high concentration of HNO_3 , though the stability is a problem^{15,16}. Based on the results introduced above, even though soft N donor can maintain the selectivity toward metal ion, in order to use in a wide HNO_3 concentration, the introduction of hard O donor such as amide oxygen unit can lower the basicity of the soft ligand and then could be utilized in a more acidic condition¹⁷.

In this research, a novel macro-porous silica-based (DAMIA-EH+1-dodecanol)/SiO₂-P adsorbent was prepared by impregnating a non-heterocyclic N donor ligand combining two amide unit 2,2'-[(2-ethylhexyl)imino]bis[N,N-bis(2-ethylhexyl)acetamide] (DAMIA-EH) extractant and a molecule modifier (1-dodecanol) into a macroreticular styrene-divinylbenzene copolymer that is immobilized in porous silica particles with a diameter of 50 μm. Adsorption behavior (adsorption characteristics, Langmuir adsorption model, Freundlich isotherm equation and adsorption thermodynamics of adsorption process) of platinum group metals (PGMs) and some specific fission products (FPs) such as Zr, Mo, Re etc. from simulated high-level liquid waste (HLLW) solution onto adsorbent was studied by batch methods.

2. Experimental

2.1 Reagent

Chemical reagents such as alkali metal nitrate (CsNO_3), alkaline earth nitrate [$\text{Sr}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$], rare earth element (REE) [$\text{REE}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, REE = La, Ce, Nd, Sm, Eu, Gd], $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and Re_2O_7 were of analytical grade and purchased from Wako Pure Chemical Industries, Inc. Palladium (II) nitrate [$\text{Pd}(\text{NO}_3)_2$], ruthenium(III) nitrosyl nitrate [$\text{Ru}(\text{NO})(\text{NO}_3)_x(\text{OH})_y$, $x + y = 3$], rhodium (III) nitrate [$\text{Rh}(\text{NO}_3)_3$] etc. were employed as commercially received from Aladdin Industrial, Inc. The extractant DAMIA-EH (chemical structure is shown in **Fig. 1**) was directly purchased from Chemicrea Inc. and used directly without further purification. The porous silica particles ($\text{SiO}_2\text{-P}$) with a mean diameter of $50\text{ }\mu\text{m}$ and a mean pore size of $40\text{--}50\text{ nm}$ was synthesized by polymerization reaction between inorganic silica source, initiator, organic monomer. The letter “P” means styrene-divinylbenzene copolymer. Stock solution containing 15 types of 50 mM representative metal nitrates were prepared in advance. Then by diluting stock solution into deionized water with a specific resistance of $18.3\text{ M}\Omega\cdot\text{cm}$ or greater to obtain working solutions. The acidity in working solution was adjusted by diluting concentrated nitric acid.

2.2 Synthesis of (DAMIA-EH+1-dodecanol)/SiO₂-P adsorbent

In order to clean the industrial residuals in the inner pores and further increase the affinity of SiO₂-P support, prior to the synthesis of (DAMIA-EH+1-dodecanol)/SiO₂-P adsorbent, the SiO₂-P particles were washed several times using common organic solvent methanol (MeOH). And the synthesis procedures were briefly explained as follows¹⁸⁾: Firstly, equal qualities of 10 g light-brown DAMIA-EH and 1-dodecanol (as diluent) was dissolved with 300 mL of dichloromethane (CH₂Cl₂) in a 500 mL beaker. At the same time, 20 g of dried SiO₂-P particles was weighed in a round bottle flask. Then, the above solution was slowly poured into flask. The residuals in beaker was washed by 5 mL MeOH, 3 times. After the mixture was mechanically stirred using EYELA OSB-2100 rotary evaporator over 1 h at room temperature. The temperature in water bath was maintained

Fig. 1 Chemical structural of DAMIA-EH and 1-dodecanol.

at 318 K for about 480 min. The CH_2Cl_2 was gradually evaporated under the reduced pressure and high temperature to impregnate DAMIA-EH and 1-dodecanol into the pores of SiO_2 -P particles. Following drying in a vacuum oven at 338 K for more than 24 h to further remove the remaining CH_2Cl_2 in pores, a light yellow (DAMIA-EH+1-dodecanol)/ SiO_2 -P adsorbent was obtained. Surface morphology of the synthesized adsorbent was checked by scanning electron microscopy (SEM, Hitachi S-3100H) as illustrated in **Fig. 2**. The photos of smooth surface of particle proved the successful preparation of (DAMIA-EH+1-dodecanol)/ SiO_2 -P adsorbent.

2.3 Adsorption experiments procedures

Batch adsorption experiments of (DAMIA-EH+1-dodecanol)/ SiO_2 -P adsorbent toward tested metal ions were conducted in NTS-4000B thermo-stated water bath shaker. Each sample in experiment was prepared by adding 4 mL of HNO_3 solution containing Ru(III), Rh(III), Pd(II), Zr(IV), Mo(VI), Re(VII), Cs(I), Sr(II), Ba(II), La(III), Ce(III), Nd(III), Sm(III), Eu(III), Gd(III) (as aqueous phase) into 0.2 g (DAMIA-EH+1-dodecanol)/ SiO_2 -P adsorbent (as solid phase) in a 13.5 mL glass vial with a plastic stopper. The sample was vigorously shaken at 160 rpm for a desired contact time, concentration of metal ions, concentration of HNO_3 , temperature, followed by a phase separation by syringe and nylon net filter (20–40 μm pores). The concentration of tested metal ions before and after adsorption experiments were measured three times by inductively coupled plasma atomic emission spectrometer (ICP-AES, Shimadzu ICPS-7510), except the elements of Cs(I) which was detected by atomic absorption photometer (AAS, Shimadzu AA-6200) at a wavelength of 363.5 nm using acetylene flame. The adsorption

percentage (E , %), distribution coefficient (K_d , cm^3/g) and adsorbed amount (q , mmol/g) of the tested metal ions toward (DAMIA-EH+1-dodecanol)/ SiO_2 -P adsorbent were recorded according to the following equations¹⁹⁾:

$$E = 100 \times (C_0 - C_t)/C_0 \quad (1)$$

$$K_d = [(C_0 - C_e) \cdot V]/[C_e \cdot m] \quad (2)$$

$$q = (C_0 - C_t) \cdot V/m \quad (3)$$

where, C_0 represents the concentration of each tested metal ion at the initial state in the aqueous phase (mM), C_t denotes the concentration of each tested metal ion at a later time in the aqueous phase (mM), C_e denote the concentration of each metal ion at equilibrium state in the aqueous phase (mM), m indicates the weight of dry adsorbent (g), V means the volume of the aqueous phase in the experiments (L).

3. Result and discussion

3.1 Effect of contact time

The experiments regarding the effect of contact time of representative 15 kinds of metal ions Ru(III), Rh(III), Pd(II), Zr(IV), Mo(VI), Re(VII), Cs(I), Sr(II), Ba(II), La(III), Ce(III), Nd(III), Sm(III), Eu(III), Gd(III) on (DAMIA-EH+1-dodecanol)/ SiO_2 -P adsorbent in 2 M HNO_3 was carried out at 298 K and the experimental results were summarized as shown in **Fig. 3**. It was found that the adsorption rate of (DAMIA-EH+1-dodecanol)/ SiO_2 -P adsorbent toward all the tested metal ions were relatively quick comparing with previous studies. Especially, for Pd(II) and Re(VII), the adsorption rate was fairly fast and could reach a equilibrium state within in just 10 min. For other metal ions, with an increase in the contact time, the uptake ratio increased gradually, and after about

Fig. 2 A typical SEM of synthesized (DAMIA-EH+1-dodecanol)/ SiO_2 -P adsorbent.

Fig. 3 Relationship between uptake ratio of 15 ions and contact time onto (DAMIA-EH+1-dodecanol)/ SiO_2 -P adsorbent in 2 M HNO_3 solution at 298 K. [Metal] = 5 mM; $[\text{HNO}_3]$ = 2 M; V/m = 0.02 L/g.

5 h, almost all the metal ions can approach to a constant state. On the other hand, the experimental results also revealed that (DAMIA-EH+1-dodecanol)/SiO₂-P adsorbent showed a better affinity toward Pd(II) with a uptake ratio of 82.95%, which was much higher than the uptake ratio of Re(VII) (26.73%) and other metal ions (around 15%). Such a high uptake ratio toward Pd(II) was attributed to the strong complexation ability from soft N donors originated in DAMIA-EH extractant. Due to the involvement of hard O donors, (DAMIA-EH+1-dodecanol)/SiO₂-P adsorbent also exhibited some adsorption performances toward other metal ions except Pd(II). Overall, the recognition affinity toward Pd(II) was better. Through introduction of hard O donors, the adsorption performance toward Pd(II) could still be well-maintained even in 2 M HNO₃ solution²⁰. On the other hand, in order to have a deep understanding about the relationship of contact time with adsorption kinetics, above experimental data for the selected representative metal ions were further fitted using linear pseudo-second order model to calculate the rate constant and clarify the possible adsorption mechanism. The expression of pseudo-second order model was described as follows²¹:

$$t/q_t = 1/(k_2 \cdot q_e^2) + t/q_e \quad (4)$$

where, q_t (mg/g) is the amount of metal ions adsorbed onto the surface of adsorbent at any time t , q_e (mg/g) is the amount of metal ions adsorbed onto the surface of adsorbent at equilibrium state, k_2 (g/(mg·h)) means the rate constant of the second order at the equilibrium state.

The plots of t versus t/q_t gave three straight lines for the selected metal ions as shown in Fig. 4 and the calculated rate constants were summarized in Table 1. The good fitting results with regression coefficients above 0.9 indicated that

Fig. 4 Pseudo-second order kinetic fitting results for metal ions adsorption onto (DAMIA-EH+1-dodecanol)/SiO₂-P adsorbent.

the obtained experimental results were in a good consistent with linear pseudo-second order model, and the rate controlling step of this adsorption experiments was governed by a chemical adsorption process²². On the other hand, the calculated values of q_e for Pd(II), Ru(III) and Re(VII) were 9.820, 1.097, and 5.042 mg/g, respectively, which was found to be similar with the experimental ones.

3.2 Effect of HNO₃ concentration

In order to understand the effect of concentration of HNO₃, adsorption experiments of (DAMIA-EH+1-dodecanol)/SiO₂-P toward Cs(I), Ba(II), Sr(II), La(III), Ce(III), Pd(II), Ru(III), Re(VII) etc. were carried out by varying the concentration of HNO₃ from 0.1 to 5 M at 298 K and the obtained results were shown as in Fig. 5. As introduced above, DAMIA-EH was consisted of soft N donor and hard O donor, in the adsorption process, the complexation reaction of DAMIA-EH with metal ions and proton were considered as two competitive reactions. The association of DAMIA-EH with HNO₃ could decrease the complexation of DAMIA-EH with the tested metal ions.

This might finally cause a decrease in the adsorption performance of (DAMIA-EH+1-dodecanol)/SiO₂-P toward tested metal ions. Fig. 5 showed with increasing the concentration of HNO₃ from 0.1 to 0.5 M, for Pd(II), its uptake ratio increased slightly at the first beginning from 82.99% to 90.03%, which

Table 1 Summary for the fitting results of pseudo-second order kinetic model

	K_2 (g/(mg·h))	Calculated q_e (mg/g)	Experimental q_e (mg/g)	R^2
Pd(II)	15.901	9.820	9.795	1.000
Ru(III)	0.788	1.097	1.062	0.997
Re(VII)	2.077	5.042	5.024	1.000

Fig. 5 Effect of concentration of nitric acid on the adsorption of 15 ions onto (DAMIA-EH+1-dodecanol)/SiO₂-P adsorbent at 298 K. [Metal] = 5 mM; [HNO₃] = 0.1–5 M; $V/m = 0.02$ L/g.

could be explained as the nitrate ions participated in the formation of complex²³. When the concentration of HNO_3 further increased to a more acidic condition, the uptake ratio of Pd(II) decreased gradually to 45.88% when $[\text{HNO}_3] = 5 \text{ M}$. As a comparison, the uptake ratio of Re(VII) exhibited an obvious decrease from 89.05% to 4.3% when the concentration of HNO_3 varied from 0.1 to 5 M. The uptake ratio of other metal ions showed no sensitivity toward the variation of concentration of HNO_3 and still maintained in a relatively low level. As a result, it implied that using (DAMIA-EH+1-dodecanol)/ SiO_2 -P adsorbent, it was possible to separate Pd(II) selectively in a wide HNO_3 range. And it was also revealed that by introduction of hard O donor into a soft ligand, its application in a more acidic condition was considered to be feasible.

3.3 Investigation of adsorption isotherm

The adsorption capacity of (DAMIA-EH+1-dodecanol)/ SiO_2 -P adsorbent toward selected metal ions was investigated by varying the concentration of metal ions from 1 to 100 mM in the working solution and the obtained results were shown in **Fig. 6**. For Pd(II) and Re(VII), with increasing the concentration of metal ions, the adsorption amount drastically increased at the very beginning and then gradually approached to an equilibrium state which meant saturated. The maximum adsorption amount of Pd(II) and Re(VII) were

Fig. 6 Non-Linear adsorption isotherm fitting for metal ions onto (DAMIA-EH+1-dodecanol)/ SiO_2 -P adsorbent at 298 K. [Metal] = 1–100 mM; $[\text{HNO}_3] = 2 \text{ M}$; $V/m = 0.02 \text{ L/g}$.

recorded as 0.440 mmol/g and 0.309 mmol/g, respectively. While for Ru(III), it still hasn't reached a constant state. Furthermore, in order to clarify the possible relationship between adsorption amount versus equilibrium concentration, the typical Langmuir and Freundlich models were adopted to study the adsorption isotherm and their expressions were described as below²⁴:

$$Q_{eq} = \frac{Q_{max} K_L C_{eq}}{(1 + K_L C_{eq})} \quad (5)$$

$$Q_{eq} = K_F C_{eq}^{1/n} \quad (6)$$

where, C_{eq} (mmol/L) means the equilibrium concentration, Q_{eq} (mmol/g) is the amount of metal ions adsorbed at equilibrium state, Q_{max} (mmol/g) defines the theoretical maximum of metal adsorbed, K_L (L/mmol) is the Langmuir constant, K_F (mmol/g) is the Langmuir and Freundlich constant, $1/n$ is the Freundlich isotherm exponent constant.

The theoretical fitting results were illustrated in solid line for Langmuir model and dot line for Freundlich model as shown in **Fig. 6**. The calculated fitting parameters were listed in **Table 2**. According to the fitting results, it was found that, in the case of Pd(II) and Re(VII), the regression coefficients of Freundlich model were higher than Langmuir model, indicating that the adsorption of Pd(II) and Re(VII) onto (DAMIA-EH+1-dodecanol)/ SiO_2 -P adsorbent occurred on a heterogeneous surface. While in the case of Re(VII), in a good accordance with Langmuir model revealed that one on one single layer adsorption was more dominant in the adsorption process²⁵.

3.4 Effect of temperature

The adsorption performance of (DAMIA-EH+1-dodecanol)/ SiO_2 -P adsorbent toward tested metal ions under the effect of temperature was investigated by varying the temperature in solution from 288 to 323 K. From the results shown in **Fig. 7**, with increasing the temperature in solution, the uptake ratio of Pd(II) and Re(VII) decreased slightly from 85.51% to 70.44%, and from 29.25% to 22.73%, respectively, indicating the high temperature was not beneficial for the adsorption process of Pd(II) and Re(VII). While the uptake ratio toward Ru(III) slightly increased from 4.95% to 8.15%. The change

Table 2 Summary for the fitting results of non-linear Langmuir and Freundlich isotherm models

Metal ion	Langmuir model parameters			Freundlich model parameters		
	Q_{max} (mmol/g)	K_L (L/mmol)	R^2	K_F (mmol/g)	$1/n_i$	R^2
Pd(II)	0.440	0.177	0.991	0.109	0.331	0.955
Ru(III)	0.260	0.011	0.819	0.003	0.841	0.955
Re(VII)	0.309	0.038	0.999	0.013	0.714	0.975

Fig. 7 Effect of temperature on the adsorption of (DAMIA-EH+1-dodecanol)/SiO₂-P adsorbent for 15 ions at 288–323 K. [Metal] = 5 mM; [HNO₃] = 2 M; V/m = 0.02 L/g.

Fig. 8 Relationship between $\ln K_d$ versus $1/T$ for the adsorption of metal ions onto (DAMIA-EH+1-dodecanol)/SiO₂-P adsorbent.

of temperature had no effect on the adsorption of other metal ions. And the good selectivity toward Pd(II) was still dominant in the whole tested temperature area. In order to have a better understanding about the influence of temperature, van't Hoff equations shown as follows were used by plotting $\ln K_d$ against $1/T$ as shown in Fig. 8²⁶. Thermodynamic parameters such as ΔH^0 and ΔS^0 (as shown in Table 3) can be respectively calculated from the slope and intercept on the basis of van't Hoff

equations. The negative value of ΔH^0 for Pd(II) and Re(VII) (−20.12 and −5.95 kJ/mol, respectively) indicated the adsorption process was exothermic in nature. While the positive values of ΔH^0 for Ru(III) (13.72 kJ/mol) revealed its adsorption process was endothermic. The negative value of ΔG^0 verified that the metal ions adsorption was happened spontaneously²⁷.

$$\ln K_d = -\Delta H^0/(R \cdot T) + \Delta S^0/R \quad (7)$$

$$\Delta G^0 = \Delta H^0 - \Delta S^0 \cdot T \quad (8)$$

where, K_d means distribution coefficient of each metal ion, ΔG^0 , ΔH^0 , ΔS^0 represents the standard changes in Gibbs free energy (kJ/mol), enthalpy (kJ/mol), entropy (J/(K·mol)), respectively. R is the universal gas constant (8.314 J/(K·mol)).

4. Conclusion

A silica-based hybrid soft N and hard O donor (DAMIA-EH+1-dodecanol)/SiO₂-P adsorbent was synthesized by wet impregnation method. Its adsorption behaviors toward 15 tested types of metal ions were investigated in nitric acid solution as an effect of contact time, effect of temperature etc. The adsorption rate of Pd(II) and Re(VII) were fairly fast than other metal ions, which can attain equilibrium state in only 10 min. With increasing the concentration of HNO₃ in solution, the uptake ratio toward Pd(II) gradually decreased, which can be explained as the protonation of soft N donor and finally lost its complexation ability. Comparing to other co-existing metal ions, the adsorption performance of (DAMIA-EH+1-dodecanol)/SiO₂-P adsorbent toward Pd(II) still found to be dominant almost in the whole nitric acid range. Moreover, the adsorption capacity of Pd(II) fitted well with Freundlich isotherm model, indicating the adsorption of Pd(II) onto (DAMIA-EH+1-dodecanol)/SiO₂-P adsorbent occurred on a heterogeneous surface. The effect of temperature experiments revealed that high temperature was not beneficial for the separation of Pd(II) and Re(VII). Based on the experimental results introduced above, it demonstrated that (DAMIA-EH+1-dodecanol)/SiO₂-P adsorbent as a hybrid donor can maintain the good selectivity toward Pd(II) in a more acidic condition, which supports a possibility for its practical utilization in the separation of Pd(II) from high-level liquid waste.

Table 3 Summary of calculated thermodynamic parameters

Temp (K)	ΔG^0 (kJ/mol)			ΔH^0 (kJ/mol)			ΔS^0 (J/mol·K)		
	Pd(II)	Ru(III)	Re(VII)	Pd(II)	Ru(III)	Re(VII)	Pd(II)	Ru(III)	Re(VII)
288	−11.57	0.08	−5.06	−20.12	13.72	−5.95	−0.03	0.05	−0.003
298	−11.28	−0.39	−5.03						
308	−10.98	−0.86	−5.00						
323	−10.53	−1.57	−4.95						

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