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ПОВЕРХНОСТНЫЕ И СОЛЬВАТАЦИОННЫЕ ИЗБЫТКИ ИОНОВ ТЯЖЕЛЫХ МЕТАЛЛОВ ИЗ ВОДНЫХ РАСТВОРОВ НА ДИСПЕРГИРОВАННОЙ ГУМИНОВОЙ КИСЛОТЕ, ВЫДЕЛЕННОЙ ИЗ БУРОГО УГЛЯ

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SURFACE AND SOLVATION EXCESSES OF HEAVY METAL IONS FROM AQUEOUS SOLUTIONS ON DISPERSED HUMIC ACID EXTRACTED FROM BROWN COAL

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Исследована изотермическая адсорбция ионов тяжелых металлов из водных растворов на дисперсном образце гуминовой кислоты в твердой фазе. Рассмотрено влияние селективной сольватации ионов тяжелых металлов на реакционные центры структурной единицы супрамолекулы дисперсной гуминовой кислоты в водно-электролитных растворах заданного состава. По данным о предельных значениях поверхностных и сольватационных избытков дана размерная оценка комплекса структурной единицы супрамолекулы дисперсной гуминовой кислоты с ионами тяжелых металлов в растворе.

Ключевые слова: адсорбция; диспергированная гуминовая кислота; ионы тяжелых металлов; нулевые коэффициенты активности; поверхностные и сольватационные избытки; размерный эффект; растворимость.

The isothermal adsorption of heavy metal ions from aqueous solutions on a dispersed sample of humic acid in the solid phase has been studied. The effects of selective solvation of heavy metal ions on the reaction centers of the structural unit of the supramolecule of dispersed humic acid in water-electrolyte solutions of a given composition are considered. According to the data on the limiting values of surface and solvation excesses a dimensional estimate of the complex of the structural unit of the supramolecule of dispersed humic acid with heavy metal ions in solution is given.

Key words: adsorption; dispersed humic acid; heavy metal ions; size effect; solubility; surface and solvation excesses; zero activity coefficients.

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The establishment of a heterogeneous equilibrium at the humic acid – aqueous solution of an asymmetric electrolyte interface is accompanied by two coupled processes. Adsorption of heavy metal ions from aqueous solutions on a macromolecule in the solid phase and selective solvation of charged particles on the reaction centers of the structural unit of a supermolecule of dispersed humic acid dissolved in the liquid phase. The quantitative characteristics of these processes, under equilibrium conditions, are surface and solvation excesses. The theory and practice of ion-exchange adsorption from solutions on solid adsorbents is described in ¹. It is shown that to calculate the relative surface excess (adsorption) of ions, the following relation can be used (1):

$$a = \frac{(C_0 - C_e) \cdot V}{m} \cdot 1000, \quad (1)$$

where a – adsorption value, mmol/g;
 C_0 and C_e – initial and final (equilibrium) concentrations of adsorbate, mol/l;
 V – solution volume, l;
 m – mass of adsorbent, g;
 1000 – the conversion factor used to get the data to be expressed in mmol/g.

For non-electrolyte solutions, in which the admissible chemical reactions are homo- and hetero-association reactions, the value of the solvation excess is determined by the reference relation (2) ²:

$$\left(\frac{d \lg y_k}{d \lg a_i} \right)_{T,P,a_l} = -G_{i(j)}^k, \quad (2)$$

where $G_{i(j)}^k$ – solvation excess of a particle of type i over a particle of type j in the solvation environment of particles of type k ;

y_k – rational coefficient of activity of a particle of sort k ;
 a_i – activity of a particle of type i ;
 T – temperature; P – pressure;
 $l = i, l = j$.

The physical meaning of the solvation excess of an i -particle over j in the environment of a mole of particles of type k is determined by the relation (3):

$$G_{i(j)}^k = \frac{N_i}{V} \cdot \int_0^{r_C} (\rho_{ki} - \rho_{kj}) \cdot 4\pi r^2 dr, \quad (3)$$

where r_C – molecular correlation radius;
 N_i – number of particles of type i in volume V ;
 $\rho_{ki}(\rho_{kj})$ – radial distribution function.

If the central particle k is a macromolecule, then equation (2) is also applicable due to the thermodynamic definition of the concepts of chemical potential and activity coefficient of supramolecules ³. For example, for aqueous solutions of urea, saturated with the structural unit of a supermolecule of dispersed humic acid ², the reference relation (2) was written in the form of equation (4):

$$\left(\frac{d \lg y_{GKd}^0}{d \lg a_m} \right)_{T,P,a_{GKd}} = -G_{m(w)}^{GKd}, \quad (4)$$

where $G_{m(w)}^{GKd}$ – solvation excess of urea over water on a structural unit of a supermolecule of dispersed humic acid in solution;

y_{GKd}^0 – zero activity coefficient of a structural unit over a molecule of dispersed humic acid;
 a_m – activity of urea in aqueous solution.

Relation (2), taking into account identity (3), establishes a connection between thermodynamic quantities (left side) and radial distribution functions (right side) used in statistical thermodynamics. Moreover, from the standpoint of statistical thermodynamics, the correctness of the problem of calculating the quantity is not associated with whether the particles i, j, k have a charge or not ⁴. In this regard, for water-electrolyte solutions of a given stoichiometric composition, saturated with the structural unit of the supermolecule of dispersed humic acid ⁵, it is easy to obtain the expression:

$$\frac{1}{\nu} \cdot \left(\frac{d \lg y_{GKd}^0}{d \lg a_{\pm}} \right)_{T,P,a_{GKd}} = -\frac{1}{\nu_{z+}} \cdot G_{M^{z+}(w)}^{GKd} = -\frac{1}{\nu_{z-}} \cdot G_{A^{z-}(w)}^{GKd}, \quad (5)$$

where $G_{M^{z+}(w)}^{GKd}$ ($G_{A^{z-}(w)}^{GKd}$) – solvation excess of ion over water on the reaction centers of the structural unit over the dispersed humic acid molecule;

y_{GKd}^0 – zero activity coefficient of the structural unit of the supermolecule of dispersed humic acid;
 $a_{\pm}$ – average electrolyte activity $M_{z+}A_{z-}$;
 $\nu = (\nu_{z+} \nu_{z-})$ – stoichiometric coefficients.

For aqueous solutions of heavy metal ions ($M^{2+} = Cu^{2+}, Ni^{2+}, Cd^{2+}$), saturated with a structural unit of a supermolecule of dispersed humic acid (GKd), equation (5) takes the form:

$$G_{M^{2+}}^{GKd} = -\frac{1}{3} \left(\frac{d \lg y_{GKd}^0}{d \lg a_{\pm}} \right)_{T,P,a_{GKd}} \quad (6)$$

In equation (6), the value of the solvation excess of ion over water on the structural unit of

the supramolecule of dispersed humic acid is an analogue of the binding parameter of small ions on the macromolecule in the liquid phase, which is widely used in biothermodynamics to describe complex equilibria ⁶.

This work is devoted to the characterization of the adsorption and solvation properties of a dispersed sample of humic acid in aqueous solutions of heavy metal ions and estimation of the size effect of the complex of the structural unit of the supramolecule of dispersed humic acid with heavy metal ions in an aqueous solution.

Experiment

In the work, we used humic acid (GK), extracted from brown coal from the Kara-Keche deposit (Kyrgyzstan) according to the Orlov method ⁷. The ash content of the preparation was 10.70% and the moisture content was 3.63%. According to the data on elemental composition, atomic ratios, using Van Krevelen diagrams, it was concluded that the initial GK sample corresponds to the averaged complex of characteristic features for humic acids extracted from brown coals ⁸. Dispersed humic acid (GKd), which is the main object of this study, was obtained by mechanochemical treatment of the initial GK sample in a ball mill. Note that in order to avoid contamination of the final object with metals, grinding balls and an agate beaker were chosen. Milling was carried out at 300 rpm for 3 minutes. The local macroelement composition (C, O, N) at different points on the surface of dispersed humic acid, in contrast to the initial sample, is practically the same, which indicates the homogeneity of the studied sorbent powder. The surface of the particles of dispersed humic acid is flat, not permeated with pores and capillaries, and there are no roughnesses of any kind. The sample is characterized by the presence of condensed aromatic systems, aliphatic and alicyclic hydrocarbon groups, and oxygen-containing functional groups. As a result of the mechanochemical destruction of the aromatic

framework of the carbon matrix of humic acid, the relative amount of all functional groups in relation to the relative amount of aromatic polyconjugated systems increased markedly for the dispersed sample ⁹.

Heterogeneous equilibrium in an aqueous solution of an asymmetric electrolyte system (CuCl_2 , NiCl_2 , CdCl_2) – the dispersed humic acid in the solid phase was set in a dry – air thermostat at 298 °K for 24 hours. The mass of the adsorbent in all cases was 0.1 g, and the volume of the solution was 50 ml. In this case, the first 2 hours of the phase were mixed every 10 minutes. After the establishment of heterogeneous equilibrium, the water-electrolyte solution, saturated with the structural unit of the supermolecule of dispersed humic acid, was separated from the sorbent in the solid phase using a syringe filter with pore sizes of 1–5 μm . The resulting liquid phase (filtrate) was analyzed for changes in the concentration of heavy metal ions, pH after adsorption on a solid adsorbent. The concentration of heavy metal ions in solutions was determined by trilonometric titration. The acidity of water-electrolyte solutions saturated with the structural unit of the supermolecule of dispersed humic acid was measured by the EMF method using a galvanic pair, a glass electrode with a hydrogen function and a saturated silver chloride electrode. At this pH-metric electrodes previously calibrated by standard buffer solutions ¹⁰. Experimental data on equilibrium concentrations of heavy metal ions, pH of water-electrolyte solutions before and after adsorption on dispersed humic acid in the solid phase are given in Tab. 1.

From Tab. 1, you can see a significant decrease in the pH of water-electrolyte solutions after the adsorption of charged particles on a solid adsorbent. The obtained result indicates the ion-exchange adsorption of heavy metal ions from aqueous solutions on the acidic functional groups of dispersed humic acid in the solid phase. Obviously, these are, first of all, the carboxyl groups of the polyelectrolyte ⁹.

Table 1
Concentrations of heavy metal ions, pH of water-electrolyte solutions before and after adsorption on a dispersed sample of humic acid in a solid phase at 298 °K

$C_0^{M^{2+}}$ (mol/l)	$\text{H}_2\text{O}-\text{CuCl}_2$			$\text{H}_2\text{O}-\text{NiCl}_2$			$\text{H}_2\text{O}-\text{CdCl}_2$		
	pH ⁰	pH ^e	$C_e^{\text{Cu}^{2+}} \cdot 10^2$, mol/l	pH ⁰	pH ^e	$C_e^{\text{Ni}^{2+}} \cdot 10^2$, mol/l	pH ⁰	pH ^e	$C_e^{\text{Cd}^{2+}} \cdot 10^2$, mol/l
0.0010	5.5	3.1	0.06±0.01	6.4	3.5	0.08±0.01	6.4	3.4	0.08±0.01
0.0050	5.0	2.9	0.44±0.04	6.0	3.2	0.48±0.05	6.4	3.2	0.44±0.04
0.0100	4.8	2.8	0.93±0.09	6.1	3.1	0.96±0.10	6.4	3.1	0.92±0.09
0.0200	4.6	2.7	1.92±0.19	6.0	3.1	1.94±0.19	6.3	3.1	1.92±0.19
0.0300	4.4	2.7	2.91±0.29	6.0	3.0	2.92±0.29	6.1	3.0	2.92±0.29
0.0400	4.3	2.7	3.90±0.39	6.1	3.0	3.91±0.39	6.2	3.0	3.92±0.39

The solubility of the structural unit of the supramolecule of dispersed humic acid in an aqueous electrolyte solution of a given composition was determined spectrophotometrically at a wavelength of 340 nm. The data obtained were used to calculate the zero activity coefficients of the structural unit of the supramolecule of dispersed humic acid in the investigated water-electrolyte solutions according to the equation ¹¹:

$$\lg y_{GKd}^0 = \lg \frac{C_{GKd}^{sat.}(w)}{C_{GKd}^{sat.}(w-el)}, \quad (7)$$

where $C_{GKd}^{sat.}(w)$ – solubility of a structural unit of a supramolecule of dispersed humic acid in water, g/l;

$C_{GKd}^{sat.}(w-el)$ – solubility of a structural unit of a supramolecule of dispersed humic acid in a water-electrolyte solution of a given composition, g/l;

by the normalization condition = 1 at $a_w = 1$ (in pure water).

The calculation results are shown in Tab. 2. There are also presented the values of both the average activities and the average activity coefficients of the studied asymmetric electrolytes, obtained by the second approximation of the Debye-Huckel theory in the form of the Guntelberg equation ¹².

Tab. 2 shows that with an increase in the concentration of heavy metal chlorides in aqueous solutions, the structural unit of the supramolecule of dispersed humic acid in the liquid phase stabilizes, since the logarithms of the zero activity coefficients of the polyelectrolyte decrease. However, the dependence of (MCl_2) on the composition of the water-electrolyte solution indicates the manifestation of the effects of selective solvation in the systems under study ¹¹.

The data in Tab. 1 and 2 were the basis for further calculations of the surface and solvation excess of heavy metal ions at the reaction centers of dispersed humic acid in the solid phase, a structural unit of a supermolecule in solution.

Results and discussion

Using the data in Tab. 1, according to equation (1), the surface excesses (adsorption) of heavy metal ions from aqueous solutions on dispersed humic acid in the solid phase were calculated. The calculation results are shown in Fig. 1.

Table 2

Zero activity coefficients of the structural unit of the supramolecule of dispersed humic acid in water-electrolyte solutions at 298 °K

C_{MCl_2} , mol/l	$\lg y_{\pm}$	$\lg a_{\pm}$	$\lg y_{GKd}^0 (CuCl_2)$	$\lg y_{GKd}^0 (NiCl_2)$	$\lg y_{GKd}^0 (CdCl_2)$
0.0010	-0.053	-2.852	0.071±0.007	0.097±0.010	0.084±0.008
0.0050	-0.132	-2.211	0.071±0.007	0.097±0.010	0.115±0.012
0.0100	-0.177	-1.949	-0.051±0.005	-0.028±0.003	0.097±0.010
0.0200	-0.199	-1.698	-0.146±0.015	-0.061±0.006	0.084±0.008
0.0300	-0.234	-1.556	-0.237±0.024	-0.176±0.018	0.050±0.005
0.0400	-0.261	-1.458	-0.296±0.030	-0.235±0.024	0.066±0.007

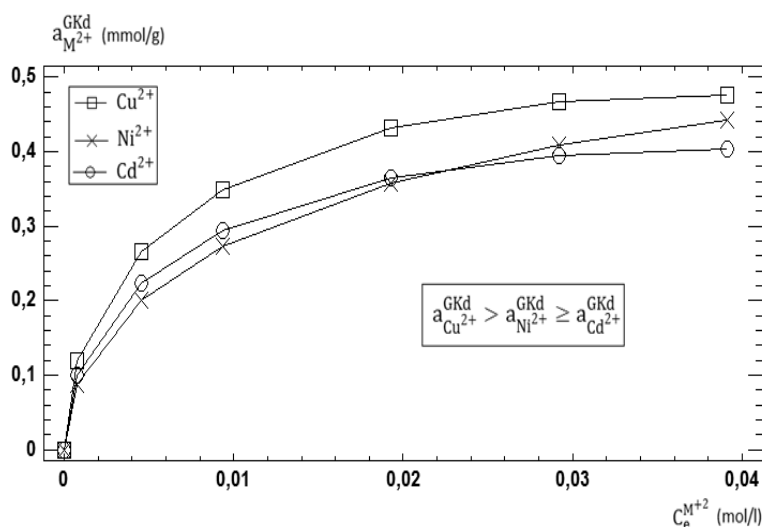


Fig. 1. Isotherms of adsorption of heavy metal ions from water solutions on dispersed humic acid in solid phase at 298 °K

It is easy to see that Langmuir-type adsorption isotherms are observed. In this case, the values of adsorption of heavy ions from aqueous solutions on a dispersed sample of humic acid in all considered cases are arranged in a row, similar to the row for the stability constants of acetate complexes of copper (II), nickel (II), cadmium (II) ions ¹³. Thus, the adsorption of heavy metal ions from aqueous solutions on dispersed humic acid in the solid phase is provided mainly by the surface carboxyl groups of the sorbent.

To calculate the solvation excesses, the logarithms of the zero activity coefficients of the structural unit of the supramolecule of dispersed humic acid (Tab. 2) were described by the method of nonlinear regression by quadratic functions of the average activity of the electrolyte in solution. By analytical differentiation of the obtained polynomials, according to equation (6), we calculated the solvation excess of heavy metal ions over water on the structural unit of the supramolecule of dispersed humic acid in solution. The results of calculations of solvation excesses are shown in Fig. 2 depending on the equilibrium concentrations of heavy metal ions in solution.

Fig. 2 shows that the isotherms of solvation excess of heavy metal ions over water on the structural unit of the supramolecule of dispersed humic acid are positive and increase with increasing equilibrium concentrations of charged particles in solution. The obtained result suggests that the formation of solvation excess is provided by the predominant filling of the reaction centers of the structural unit of the supramolecule of dispersed humic acid with heavy metal ions in a water-electrolyte solution of a given composition. In this case, the values of

solvation excesses are arranged in a row similar to the row for the stability constants of acetate complexes of copper (II), nickel (II), cadmium (II) ions ¹³.

According to the theory ^{2,5}, the radius of the structural unit of the supramolecule of dispersed humic acid, the reaction centers of which are maximally filled with heavy metal ions in the solution, can be written as the ratio:

$$r_{M^{2+}}^{GKd} = \sqrt{\frac{S_{GKd}^{\infty} \cdot G_{M^{2+}}^{GKd}(\infty)}{4\pi N_A \cdot a_{M^{2+}}^{GKd}(\infty)}}, \quad (8)$$

where $r_{M^{2+}}^{GKd}$ – the radius of the structural unit of the supramolecule of dispersed humic acid in solution with the maximum filling of its reaction centers with heavy metal ions;

$G_{M^{2+}}^{GKd}(\infty)$ – limiting solvation excess of a

heavy metal ion over water on the structural unit of the supramolecule of dispersed humic acid in solution;

$a_{M^{2+}}^{GKd}(\infty)$ – limiting adsorption of a heavy metal ion from a solution on dispersed humic acid in the solid phase;

S_{GKd}^{∞} – the limiting value of the specific surface area of the dispersed humic acid in the solid phase;

N_A – Avogadro's number.

In equation (8), the limiting value of the solvation excess $G_{M^{2+}}^{GKd}(\infty)$ is provided by the maximum saturation of the reaction centers of the structural unit above the dispersed humic acid molecule with heavy metal ions in solution. For this value ($G_{M^{2+}}^{GKd}(\infty)$), by analogy with the Scatchard equation ⁶, we can write the expression:

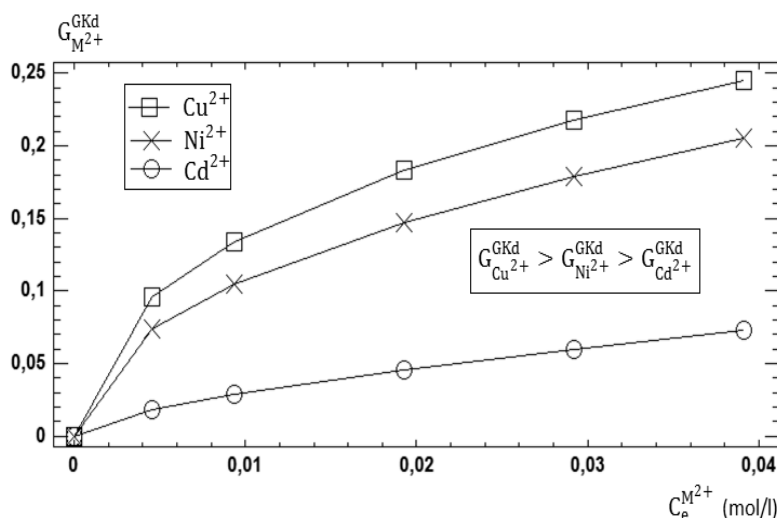


Fig. 2. Isotherms of the solvation excess of heavy metal ions over water on the structural unit of the supramolecule of dispersed humic acid in solution at 298 °K

$$\frac{G_{M^{2+}}^{GKd}}{C_e^{M^{2+}}} = G_{M^{2+}}^{GKd}(\infty) \cdot K - K \cdot G_{M^{2+}}^{GKd}, \quad (9)$$

where K – the constant of binding of a doubly charged ion at the reaction center by a structural unit of a supramolecule of dispersed humic acid in a solution;

$C_e^{M^{2+}}$ – equilibrium concentration of a heavy metal ion in solution;

$G_{M^{2+}}^{GKd}$ – solvation excess of an ion on a structural unit per molecule of dispersed humic acid in a water-electrolyte solution of a given composition.

Limit value of adsorption $a_{M^{2+}}^{GKd}(\infty)$, obviously, it is also due to the maximum filling of the sorbent surface in the solid phase with metal ions from the solution. To calculate this value ($a_{M^{2+}}^{GKd}(\infty)$) the Langmuir equation ¹⁴ was used in the form of the ratio:

$$\frac{a_{M^{2+}}^{GKd}}{C_e^{M^{2+}}} = a_{M^{2+}}^{GKd}(\infty) \cdot K' - K' \cdot a_{M^{2+}}^{GKd}, \quad (10)$$

where K' – constant of adsorption equilibrium;

$C_e^{M^{2+}}$ – equilibrium concentration of a heavy metal ion in solution;

$a_{M^{2+}}^{GKd}$ – adsorption of a heavy metal ion from a water-electrolyte solution of a given composition on dispersed humic acid in a solid phase.

Note that surface and solvation excesses by their nature are excess thermodynamic quantities ¹⁵, the use of which to describe equilibria in homogeneous and heterogeneous systems ^{6,16,17}

is associated with the use of the law of mass action. This explains the uniformity of equations (9), (10).

Tab. 4 shows the values of all limiting values that are on the right side of equation (9). The size of the limiting area (S_{GKd}^{∞}), occupied by the supramolecule of dispersed humic acid, was obtained by the adsorption method, using a ferric cation as a probe particle ¹⁸. To calculate the limiting values of surface and solvation excesses, the experimental data in Fig. 1 and 2 are considered in the coordinates of equations (9) and (10). The corresponding linear regression equations (k_{corr} is 0.98) are shown in Tab. 4. There are also given the radii ($r_{M^{2+}}^{GKd}$) complex particles of the structural unit of the supramolecule of dispersed humic acid with heavy metal ions in aqueous solutions, calculated according to equation (8).

Tab. 4 shows that in all cases the sizes of the complexes of the structural unit of the supramolecule of dispersed humic acid with heavy metal ions in solution ($r_{M^{2+}}^{GKd}$) are less than one nanometer. Thus, when a heterogeneous equilibrium is established between the investigated sample of dispersed humic acid in the solid phase and an aqueous solution of an asymmetric electrolyte, as a result of the effects of solvation selectivity, true weakly acid solutions of complex compounds of small-sized structural units of the polyelectrolyte supramolecule with heavy metal ions are formed.

Table 4

Radii of complexes of the structural unit of the supramolecule of dispersed humic acid with heavy metal ions in aqueous solutions at 298 °K

Ion	Linear regression equations	S_{GKd}^{∞} , m ² /g	$a_{M^{2+}}^{GKd}(\infty)$, mmol/g	$G_{M^{2+}}^{GKd}(\infty)$	$r_{M^{2+}}^{GKd}$, nm
Cu ²⁺	$\frac{G_{Cu^{2+}}^{GKd}}{C_e^{Cu^{2+}}} = 208 - 728 \cdot G_{Cu^{2+}}^{GKd}$	315.9	0.54±0.05	0.32±0.03	0.16±0.02
	$\frac{a_{Cu^{2+}}^{GKd}}{C_e^{Cu^{2+}}} = 137.3 - 254.3 \cdot a_{Cu^{2+}}^{GKd}$				
Ni ²⁺	$\frac{G_{Ni^{2+}}^{GKd}}{C_e^{Ni^{2+}}} = 328 - 1491 \cdot G_{Ni^{2+}}^{GKd}$	315.9	0.49±0.05	0.30±0.03	0.16±0.02
	$\frac{a_{Ni^{2+}}^{GKd}}{C_e^{Ni^{2+}}} = 145.7 - 297.3 \cdot a_{Ni^{2+}}^{GKd}$				
Cd ²⁺	$\frac{G_{Cd^{2+}}^{GKd}}{C_e^{Cd^{2+}}} = 13.7 - 151.8 \cdot G_{Cd^{2+}}^{GKd}$	315.9	0.44±0.04	0.11±0.01	0.10±0.01
	$\frac{a_{Cd^{2+}}^{GKd}}{C_e^{Cd^{2+}}} = 151.7 - 344.7 \cdot a_{Cd^{2+}}^{GKd}$				

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