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Thermodynamic Model of Ion-Exchange Process as Exemplified by Cerium Sorption from Multisalt Solutions

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A complex heterogeneous process of ion exchange can be defined with an isotherm-isobar equation of the chemical reaction, which describes differential affinity between the process and its effect – the law of mass action. Ion exchange includes processes accompanied by changes in the charge of ions and functional groups caused by the passing of ionic bond into covalent one. Hence isotherm equations of ion exchange for such processes must differ from conventional stoichiometric equations, but they can be obtained by classical study approaches to ion exchange equilibrium. The paper describes a new thermodynamic model, based on linearization of mass action law, modified for the ion exchange equation. The application of this model allows to define stoichiometry of ion exchange and the shape of ions adsorbed by the solid phase of ion-exchange resins, as well as to estimate equilibrium constant and Gibbs free energy of the process. Comparative analysis has been carried out for the thermodynamic model of cerium sorption in the form of anionic complex with Trilon B from a multisalt solution with ionic strength of 1 mol/kg (NaNO₃) under pH = 3 and temperature 298 K on a test sample of weak-base anion-exchange resin Cybber EV009. Experimental isotherm of the sorption has been obtained. Calculations of thermodynamic parameters have been performed using Langmuir, Freundlich, Dubinin – Radushkevich, Temkin and Flory – Huggins models, as well as thermodynamic model of linearized mass action law, proposed by the authors. Calculated values of the equilibrium constant and Gibbs energy – $K = 9.0 \pm 0.5$ and $\Delta_r G^0_{298} = -5.54 \pm 0.27$ kJ/mol – characterize the sorption of EDTA cerate ions by ion-exchange resin. The shape of adsorbed ions has been defined in Stern-Helmholtz layer of CeTr, and total capacity of anion resin EV009 for EDTA cerate ions has been estimated as $q_{\infty} = 2.0 \pm 0.1$ mol/kg.

Key words: thermodynamics of sorption and ion exchange; equilibrium constant and Gibbs energy; Langmuir, Freundlich, Dubinin – Radushkevich, Temkin and Flory – Huggins thermodynamic models; cerium; EDTA cerate ions

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Introduction. Modern sorption processes play a leading role in the extraction of precious components from various raw materials and are widely used in metallurgy, chemical industry, medicine and environmental protection.

In hydrometallurgy sorption is used in almost any technology of metal extraction from complex materials and their separation from accessory agents, the concentration of which greatly exceeds the concentration of the precious component.

In order to introduce a sorption device into the technological process, an initial estimation is carried out, the results of which influence parameters of the installed sorption system. Firstly, laboratory investigation is carried out in order to obtain thermodynamic data necessary for the calculation of installation parameters. An important role belongs to the selection of sorbents, selective for substance concentration, that is justified by experimentally supported values of threshold sorption and total capacity of the sorbent, as well as equilibrium constant and Gibbs energy.

Most often thermodynamic characteristics are assessed via processing of experimental data [2], mainly using equations to plot sorption isotherms – Henry's equation for low concentrations, Freundlich equation for medium ones and Langmuir equation for a wide range of concentrations [5]. To calculate parameters of ion exchange processes, numerically equal to the respective coefficients in the equations mentioned, graphical analysis is performed and sorption isotherms are plotted in the following sets of coordinates:

- for Henry's equation $q = f(c)$;
- for Freundlich equation $\lg q = f(\lg c)$;
- for Langmuir equation $c/q = f(c)$,

where q – sorption value, mol/kg (eq/kg); c – value of equilibrium concentration, mol/l (eq/l).

Different calculation models can be used to describe sorption equilibrium depending on technical characteristics of the sorbent, e.g., its porosity. For smooth macroporous sorbents it is feasible to use universal thermodynamic model by O.G.Larionov and the method based on Aranovich – Tolmachev equation. For microporous sorbents – mainly for vapor sorption on coals researchers apply the theory of micropore volume filling (MVF) and its equations: Dubinin – Radushkevich, Dubinin – Astakhov, Tolmachev – Aranovich [6].

The study [19] examines terbium adsorption by compound materials based on poly (hydroxyethylmethacrylate) hydroxyapatite composite, modified with phytic acid. The main compound sorbents are (poly(hydroxyethylmethacrylate) hydroxyapatite P(HEMA-Hap) and poly (hydroxyethylmethacrylate) hydroxyapatite, modified with phytic acid (P(HEMA-Hap)-phy).

The paper estimates a dependency between sorption capacity of applied compounds, pH and temperature. Authors draw a conclusion that in the interval of pH = 1-5 the capacity equals 0.41-0.44 mol/kg for P(HEMA-Hap) and 0.34-0.52 mol/kg for P(HEMA-Hap)-phy. Positive changes of enthalpy and entropy ($\Delta H > 0$ and $\Delta S > 0$) for P(HEMA-Hap) and P(HEMA-Hap)-phy point to the endothermic sorption process on the surface of a solid phase. Negative change of Gibbs energy ($\Delta G < 0$), obtained by the authors, proves spontaneity of the process (note that Gibbs energy for P(HEMA-Hap) is lower than for P(HEMA-Hap)-phy).

Thermodynamic calculations have been performed using Langmuir, Freundlich and Dubinin – Radushkevich isotherm models:

$$Q = \frac{K_L X_L C_e}{1 + K_L C_e};$$

$$Q = X_F C_e^\beta;$$

$$Q = X_{D-R} e^{-K_{D-R} \varepsilon^2},$$

where Q – sorption capacity, mol/kg; K_L – Langmuir equilibrium constant, l/mol; X_L – sorption value for Langmuir model, mol/kg; C_e – equilibrium concentration Tb^{3+} , mol/l; X_F – Freundlich equilibrium constant; β – empirical Freundlich constant; K_{D-R} – Dubinin – Radushkevich equilibrium constant; ε – Dubinin – Radushkevich constant, mol^2/kJ ; X_{D-R} – sorption value for Dubinin – Radushkevich model, mol/kg.

According to thermodynamic data, obtained by the authors, an endothermic sorption process is accompanied by an increase in the entropy factor, which is responsible for spontaneous character of the process ($\Delta G < 0$). In addition to that, the possibility of sorbent reutilization (up to 5 times) has been proven, as well as the absence of ionic strength influence on terbium sorption.

Similar models based on Langmuir, Freundlich and Dubinin – Radushkevich equations have been used to describe and calculate thermodynamic characteristics of sorption separation of radioactive uranium and thorium in the form of ions UO_2^{2+} and Th^{4+} in water solutions on a compound material – poly(hydroxyethylmethacrylate)hydroxyapatite P(HEMA-Hap) in the study [18].

Thermodynamic isotherm description of Europium sorption, based on linear equation of Langmuir isotherm

$$\frac{C}{E} = \frac{1}{K_{ex} E_0} + \frac{C_0}{E_0}$$

allowed the authors of paper [20] to estimate threshold distribution coefficient $K_d^{\max} = 2,55 \cdot 10^3 \text{ cm}^3/\text{g}$; maximum exchange capacity $E^{\max} = 249.0 \text{ mg/g}$, or 73 mg/cm^3 , and ion-exchange constant $K_{\text{ex}} = 8.7$ for Europium on cation resin S-957.

Authors have examined the impact of solution's pH in the presence of a single-charged ion on the distribution coefficient of Europium on cation resin S-957 and concluded that K_d^{Eu} decreases with rising pH of acid solution. Distribution coefficient K_d^{Eu} equals $7 \cdot 10^{-4}$ – $3 \cdot 10^{-4} \text{ cm}^3/\text{g}$ in the interval of HNO_3 concentration $0.001 \div 0.2 \text{ M}$. To estimate the impact of a single-charged ion, the sorption has been performed in NaNO_3 solution of various concentrations $0.4 \div 2.5 \text{ M}$ for the feed with pH 2.5 and 0.9. In both cases K_d^{Eu} decreased with the rising concentration of sodium nitrate. K_d^{Eu} measured $4.2 \cdot 10^{-4} \text{ cm}^3/\text{g}$ under $\text{pH} = 2.5$ and NaNO_3 concentration of 0.4 M and $K_d^{\text{Eu}} = 3 \cdot 10^{-4} \text{ cm}^3/\text{g}$ under $\text{pH} = 0.9$ and the same concentration of sodium nitrate.

Under dynamic conditions of the experiment in NaNO_3 and HNO_3 solutions, a negative impact of sodium and hydrogen ions on Europium sorption has been identified. Under HNO_3 concentration of 0.006 M ($\text{pH} = 2.2$) in the presence of NaNO_3 0.5 M total exchange capacity (TEC) decreased from 65 to 55 mg/cm^3 , whereas during sorption from HNO_3 solution of 0.2 M in the presence of NaNO_3 0.3 M TEC dropped from 40 to 33 mg/cm^3 .

Hence, the authors have identified a competing sorption effect of single-charged ions of sodium and hydroxonium, which reduces the rate of Europium extraction into the solid phase of ion-exchange resin.

The paper [7] describes ion-exchange equilibrium using linear forms of Langmuir and Freundlich equations, as well as Redlich-Peterson empirical equation, which generalizes standard sorption isotherms. These equations can be used to estimate ion exchange constant $K = 159 \pm 25$, Gibbs energy $\Delta_r G_{298} = -12.6 \pm 0.5 \text{ kJ/mol}$ and the capacity of anion resin D-403 (1.05 eq/kg), adequately comparable to the total capacity of anion-exchange resin certified as 1.22 eq/kg .

By means of Langmuir, Freundlich and Temkin models, the authors of study [3] examine the sorption of iron (III) hydroxide and copper (II) ions on cation resin KU-2x8. However, the most accurate thermodynamic description has been obtained using Langmuir equation: obtained values of threshold adsorption and equilibrium constant being 1.85 mmol/g and 19.73 l/mmol respectively.

Various thermodynamic models: Langmuir, Freundlich, Dubinin – Radushkevich, Temkin, Brunauer, Emmett, Teller (BET), Flory – Huggins, Harkins – Jura, Frenkel – Halsey – Hill have been used by the authors of study [8] to describe the sorption of iron (III) ions, modified with sugar-beet pulp, which is an example of microcrystalline cellulose. According to authors, the most suitable model to describe the system under examination is Dubinin – Radushkevich equation, using which the values of maximum sorption and Gibbs energy have been estimated as 1.21 mg/dm^3 and 8.22 kJ/mol respectively.

Critical analysis of various two- and three-parameter models has been performed by the authors of publication [15]. Two-parameter isotherms included Langmuir, Freundlich, Dubinin – Radushkevich, Temkin, Flory – Huggins and Hill models; three-parameter isotherms included Redlich – Peterson, Sips, Toth, Koble – Corrigan, Khan, Radke – Prauznitz models. Authors believe that linear models provide the most accurate thermodynamic description of the sorption process.

According to study [1], to identify a sorption mechanism it is recommended to apply Dubinin – Radushkevich model, which utilizes energy sorption parameter that defines physical or chemical character of the process. The authors studied fluorine sorption from water solution on activated alumina and performed thermodynamic description of the process, among others using Langmuir,



Freundlich, BET and Redlich – Peterson models. In authors' opinion, the most accurate description of ion-exchange sorption of fluoride ions on the alumina surface can be obtained in the context of Freundlich model. Thus authors propose to use two sorption equations for thermodynamic description of ion exchange.

Despite using various thermodynamic models to describe sorption equilibrium, it is critical to take into account specific characteristics of studied processes in each individual case (e.g., Langmuir model describes the theory of monolayer adsorption). It means that sorption occurs not from the entire surface of the sorbent, but only from its active centers that can only interact with one molecule or one ion of adsorbed substance – it is an equilibrium process that can be reversed. The model suggests uniform adsorption energy and no transfer of the adsorbed matter across the surface [11, 12].

Literature review demonstrates that Langmuir model provides quantitative characteristic of the adsorption process in cases of either low or high concentrations of the adsorbed substance.

As opposed to Freundlich isotherm equation, all parameters of Langmuir equation have distinct physical significance and are theoretically justified.

A certain approximation of Langmuir model, Freundlich isotherm also describes monolayer sorption and takes into account surface heterogeneity, which means the presence of different adsorption centers with different affinity to the adsorbed substances [10, 14]. Empirical equation of Freundlich isotherm is usually applied to mid-range concentrations.

Dubinin – Radushkevich model is utilized to express the adsorption mechanism with Gauss energy distribution across heterogeneous surface, which allows to identify physical or chemical character of the process. As compared to Langmuir model, this one is more generalized as it does not imply homogeneity of the surface or consistency of adsorption potential [9, 16].

Temkin model takes into account interaction between sorbent and adsorbed substance and assumes that adsorption heat (a function of temperature) of all the molecules in the layer decreases in a linear fashion as the layer gets filled [16]. However, this model cannot be applied in case of extremely low or high concentrations.

Flory – Huggins model has been conceived on the basis of excessive Gibbs energy. The theory suggests that the solution is regular and that chain links are evenly distributed in the entire volume, so it is only applicable to moderately concentrated or diluted solutions. The model estimates the coverage of sorbent surface by the adsorbed matter, which can occur spontaneously in the sorption process [13, 17].

Problem statement. Analysis of literary sources has demonstrated that up to date there are several mathematical models describing thermodynamics of the sorption process. In each particular case, a range of parameters has to be taken into account: sorbent porosity, solution concentration, dynamic mode etc. Hence, development of a new thermodynamic model to describe sorption processes that would fit any concentration system is a relevant task.

The study offers comparative analysis of two-parameter mathematical models that provide thermodynamic description of cerium sorption from multisalt solutions on anion resin EV009 in the form of trilon B complexes, and proposes a new thermodynamic model of sorption equilibrium that allows to define stoichiometry of ion exchange and the shape of ions adsorbed in the Stern-Helmholtz layer of the solid phase of ion-exchange resin.

Methodology. The test sample used in the study is anion resin Cybber EV009 produced by NVK «Syntez» (Saint-Petersburg). Cybber EV009 is a weak-base macroporous anion resin with a styrene-divinylbenzene matrix (styrene-DVB), resistant to oxidation and high pressure. Its macroporous structure adsorbs large organic molecules, which can easily be removed in the process of regeneration. An active functional group is tertiary amine.



Ion-exchange resin has been designed to clean high-valent metals and ions of transition elements. Main physical and chemical properties of anion resin Cybber EV009 are listed below:

Polymer structure	Macroporous polystyrene
Colour	From milky-white to yellow
Ionic form	Free base
Total exchange capacity, eq/ml	≥ 2.0
Humidity, %	55-65
Loose density, g/ml	0.68-0.78
Real density, g/ml	1.04-1.10
Particle size, mm	(0.315-1.25 mm) ≥ 95
Homogeneity factor	≤ 1.6
Sphericity	≥ 95
Transition from OH ⁻ → Cl ⁻ , %	≤ 25
Maximum operating temperature, °C	60
Operating pH range	1-9

Before application anion resin has been transformed to nitrate.

The sorption process has been studied in statistic conditions using alternate concentrations method under 1:5 liquid-to-solid ratio (4 cm³ of anion resin:20 ml of solution), temperature 298 K and constant ionic strength of 1 mol/kg (NaNO₃). Cerium-trilon B anionic complexes (EDTA cerate ions) have been obtained by mixing the solution of cerium nitrate and trilon B in the exact proportion of 1:1 following the stoichiometry of reaction $H_2Tr^{2-} + Ce^{3+} \leftrightarrow [CeTr]^{-} + 2H^{+}$.

Anion solution has been kept in equilibrium by constant mixing over the course of 5-6 hours. Cerium concentration in the samples before and after the sorption has been estimated with spectrophotometric method with arsenazo III and X-ray fluorescent method on Epsilon 3 device produced by «PANalytical».

Experiment results. Experimental data on EDTA cerate-ion sorption (initial and equilibrium concentrations, values of sorption, ionic strength and activity coefficient) are presented in Table 1. Sorption value has been estimated using formula below:

$$q = \frac{(C_0 - C_{\infty})V}{m},$$

where C_0 and C_{∞} – initial and equilibrium concentrations of complex ions in the solution, mol/kg; V – volume (20 cm³); m – mass of dry anion resin, g.

Table 1

Experimental data on EDTA cerate ion sorption on anion resin EV009 in nitrate form, pH = 3

C_0 , mmol/kg	C_{∞} , mmol/kg	q , mol/kg	[NO ₃ ⁻], mol/kg	I, mol/kg	γ_{NaNO_3}	$\gamma_{CH_3COONa}^*$
79.7	53.4	0.1822	1.2675	1.2675	0.5384	0.8239
66.0	41.6	0.1686	1.2235	1.2235	0.5388	0.8128
53.5	32.5	0.1453	1.1797	1.1797	0.5396	0.8040
35.5	21.9	0.0943	1.1188	1.1188	0.5404	0.7935
24.0	14.7	0.0645	1.0817	1.0817	0.5408	0.7882
8.80	5.50	0.0230	1.0300	1.0300	0.5415	0.7829
7.30	4.60	0.0187	1.0247	1.0247	0.5416	0.7825

* Average ion activity coefficients for NaCeTr compound have been considered equal to CH₃COONa under given ionic strength [3].

The sorption isotherm is presented in Fig.1.

Average ion activity coefficients have been estimated using the most accurate mathematical description from reference data, taking into account a strong dependency of activity coefficients

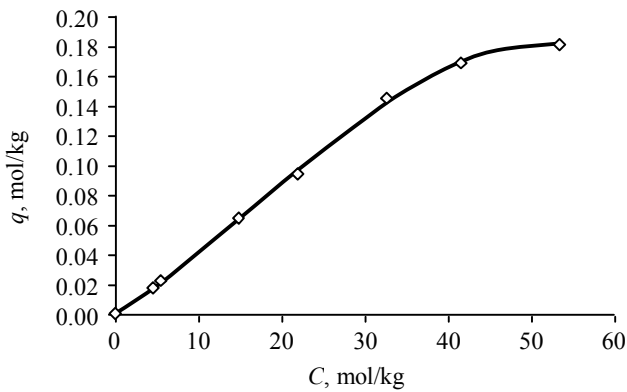
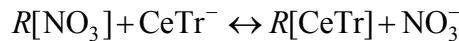


Fig. 1. Sorption isotherm of anion cerium complexes with trilon B on anion resin EV009 under pH = 3

on ion charge and ionic strength of the solution, as well as a weaker dependency on individual anion characteristics, including complex ions. When compared to simple electrolytes, complex ions do not demonstrate any remarkable behavior regarding activity coefficients [4].

Authors of current research have developed a thermodynamic model describing sorption equilibrium, which is based on linearization of mass action law equation (LMAL). Modified linear form of equation allows to use it for the description of ion-exchange equilibria.

For ion-exchange reaction:



expression of mass action law is derived as follows:

$$K = \frac{q_{CeTr^-} \cdot a_{NO_3^-}}{q_{NO_3^-} \cdot a_{CeTr^-}} = \frac{q_{CeTr^-} [NO_3^-] \gamma_{NO_3^-}}{q_{NO_3^-} [CeTr^-] \gamma_{CeTr^-}}$$

where K – constant of ion-exchange equilibrium; q_{CeTr^-} , $q_{NO_3^-}$ – ion concentration in the solid phase of anion resin, mol/kg; $a_{NO_3^-}$, a_{CeTr^-} – activities of nitrate and EDTA cerate ions, mol/kg; $[NO_3^-]$, $[CeTr^-]$ – concentrations of nitrate and EDTA cerate ions, mol/kg; $\gamma_{NO_3^-}$, γ_{CeTr^-} – activity coefficients of nitrate and EDTA cerate ions.

Mathematical transformations of sorption values of EDTA cerate ions using threshold sorption H_∞ , as well as expression of activity coefficients of individual ions through average ion coefficients of respective electrolytes γ_{\pm} :

$$q_\infty = q_{NO_3^-} + q_{CeTr^-} \Rightarrow q_{NO_3^-} = q_\infty - q_{CeTr^-};$$

$$\gamma_{\pm NaNO_3} = \sqrt{\gamma_{Na^+} \gamma_{NO_3^-}} \Rightarrow \gamma_{NO_3^-} = \frac{\gamma_{\pm NaNO_3}^2}{\gamma_{Na^+}};$$

$$\gamma_{\pm NaCeTr} = \sqrt{\gamma_{Na^+} \gamma_{CeTr^-}} \Rightarrow \gamma_{CeTr^-} = \frac{\gamma_{\pm NaCeTr}^2}{\gamma_{Na^+}}$$

allow to obtain an equation

$$q_{CeTr^-} = \frac{K q_\infty [CeTr^-] \gamma_{\pm NaCeTr}^2}{[NO_3^-] \gamma_{\pm NaNO_3}^2 + K [CeTr^-] \gamma_{\pm NaCeTr}^2},$$

the linear form of which can be expressed as:

$$\frac{1}{q_{CeTr^-}} = \frac{1}{q_\infty} + \frac{[NO_3^-] \gamma_{\pm NaNO_3}^2}{K q_\infty [CeTr^-] \gamma_{\pm NaCeTr}^2}.$$

The coordinates for plotting linear form of sorption isotherm are concentration

$$f(c) = \frac{C_{NO_3^-} \cdot \gamma_{\pm NaNO_3}^2}{C_\infty \cdot \gamma_{\pm NaCeTr}^2} \text{ (x-axis) and inverse sorption } 1/q \text{ (y-axis).}$$

Non-linear and linear forms of sorption equations in Langmuir, Freundlich, Dubinin – Radushkevich, Temkin, Flory – Huggins models, as well as coordinates of characteristic curves compared to modified mass action law describing ion-exchange equilibria as exemplified by EDTA cerate ion sorption on anion resin EV009 under pH = 3, $T = 298$ K, are presented in Table 2.

Table 2

Thermodynamic models of sorption equilibrium [15]

Model	Non-linear form	Linear form	Coordinates	Equation parameters
Langmuir	$q = q_{\infty} \frac{K_L C_{\infty}}{1 + K_L C_{\infty}}$	$\frac{C_{\infty}}{q} = \frac{C_{\infty}}{q_{\infty}} + \frac{1}{q_{\infty} K_L}$	$\frac{C_{\infty}}{q} = f(C_{\infty})$	K_L, q_{∞}
Freundlich	$q = K_F C_{\infty}^{1/q_{\infty}}$	$\log q = \log K_F + \frac{1}{q_{\infty}} \log C_{\infty}$	$\log q = f(\log C_{\infty})$	K_F, q_{∞}
Dubinin – Radushkevich	$q = q_{\infty} e^{-K_{D-R} \varepsilon^2}$	$\ln q = \ln q_{\infty} - K_{D-R} \varepsilon^2$	$\ln q = f(\varepsilon^2)$	K_{D-R}, q_{∞}
Temkin	$q = \frac{RT}{K_T} \ln q_{\infty} C_{\infty}$	$q = \frac{RT}{K_T} \ln q_{\infty} + \frac{RT}{K_T} \ln C_{\infty}$	$q = f(\ln C_{\infty})$	K_T, q_{∞}
Flory – Huggins	$\frac{\theta}{C_{\infty}} = K_{F-H} (1 - \theta)^{q_{\infty}}$	$\log\left(\frac{\theta}{C_{\infty}}\right) = \log K_{F-H} + q_{\infty} \log(1 - \theta)$	$\log\left(\frac{\theta}{C_{\infty}}\right) = f(\log(1 - \theta))$	K_{F-H}, q_{∞}
Modified equation of ion exchange (LMAL)	$q = \frac{K_{LMAL} q_{\infty} C_{\infty} \gamma_{\pm NaCeTr}^2}{C_{NO_3} \gamma_{\pm NaNO_3}^2 + K_{LMAL} C_{\infty} \gamma_{\pm NaCeTr}^2}$	$\frac{1}{q} = \frac{1}{q_{\infty}} + \frac{1}{K_{LMAL} q_{\infty}} \frac{C_{NO_3} \gamma_{\pm NaNO_3}^2}{C_{\infty} \gamma_{\pm NaCeTr}^2}$	$\frac{1}{q} = f(C)$	K_{LMAL}, q_{∞}

Notes: 1. ε – Dubinin – Radushkevich constant, $\varepsilon = RT \ln\left(1 + \frac{1}{C_{\infty}}\right)$. 2. θ – surface coverage, $\theta = q/q_{\max}$, q_{\max} – maximum adsorption, for anion resin EV009 $q_{\max} = 2$ eq/kg. 3. C_{NO_3} – concentration of nitrate ions, in the form of which anion resin occurs, mol/kg. 4. $\gamma_{\pm NaNO_3}$, $\gamma_{\pm NaCeTr}$ – average ion coefficients of electrolyte activity, providing salt background (ionic strength) of the solution.

According to data from thermodynamic models equations (Table 2), linear forms of sorption isotherms have been plotted for EDTA cerate ion on anion resin EV009 in nitrate form under temperature 298 K and pH = 3. Results are presented in Figure 2. Values of threshold sorption and constants of ion-exchange equilibrium have been calculated using two-parameter models: Langmuir, Freundlich, Dubinin – Radushkevich, Temkin, Flory – Huggins.

Two-parameter linear equations have the form of $y = kx + b$. Coefficients k and b serve to calculate basic thermodynamic parameters of sorption equilibrium for nitrate and EDTA cerate ions:

- for Langmuir model: $q_{\infty} = \frac{1}{k}$ and $K_L = \frac{1}{b q_{\infty}}$;
- for Freundlich model: $q_{\infty} = \frac{1}{k}$ and $K_F = 10^b$;
- for Dubinin – Radushkevich model: $q_{\infty} = e^b$ and $K_{D-R} = -k$;
- for Temkin model: $q_{\infty} = e^{\frac{RTb}{K_T}}$ and $K_T = \frac{RT}{k}$;
- for Flory – Huggins model: $q_{\infty} = k$ and $K_{F-H} = 10^b$;
- for LMAL model: $q_{\infty} = \frac{1}{b}$ and $K_{LMAL} = \frac{1}{k q_{\infty}}$.

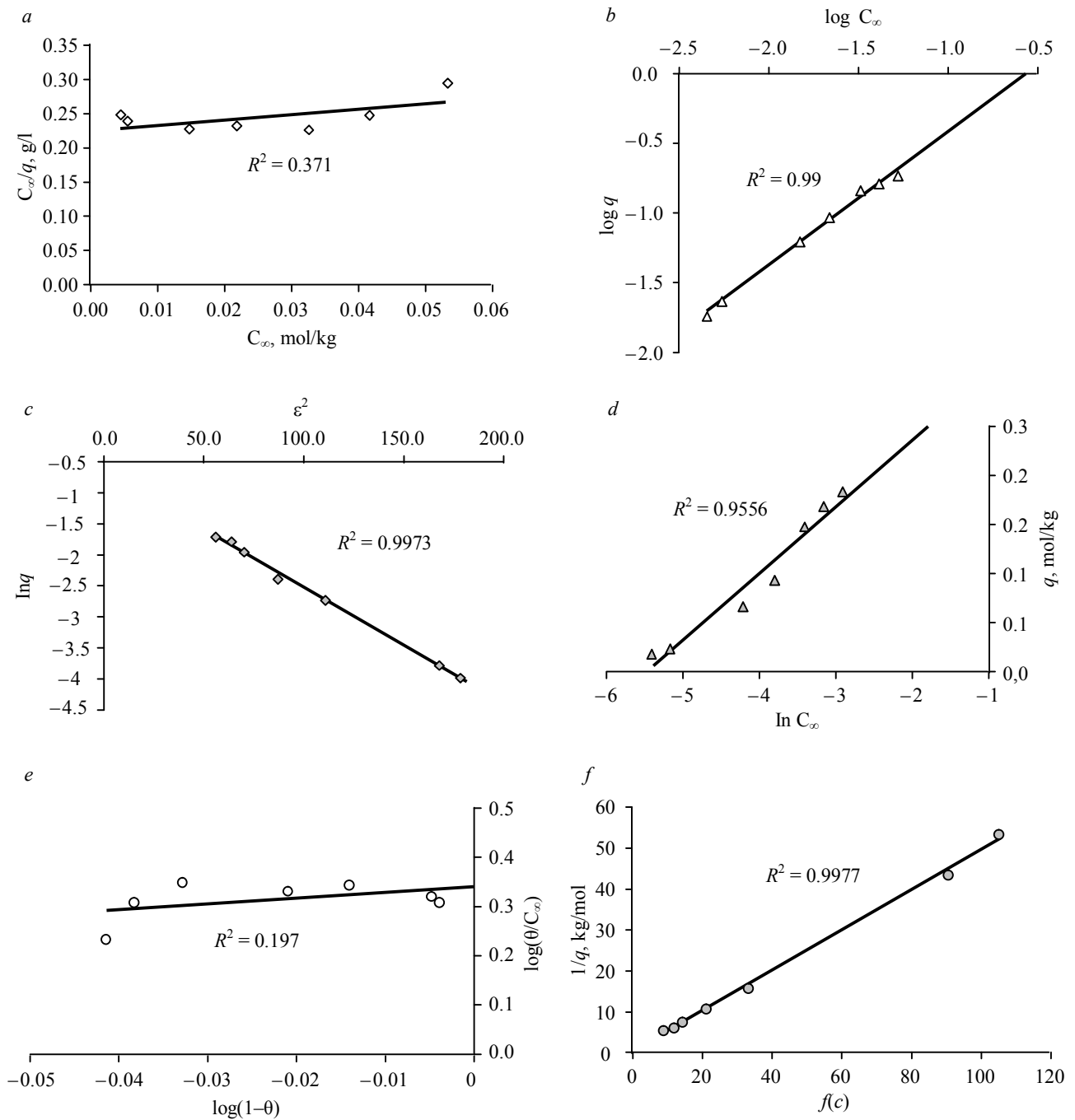


Fig.2. Linear form of sorption isotherm for Langmuir (a), Freundlich (b), Dubinin – Radushkevich (c), Temkin (d), Flory – Huggins (e); modified LMAL equation (f)

Obtained approximating equations, correlation values of linear dependencies and calculated thermodynamic data are all presented in Table 3.

Table 3

Mathematical description of sorption isotherm using various thermodynamic models

Model	Approximating equation	Correlation of linear dependency R^2	q_{∞} , mol/kg	K	$\Delta_r G_{298}^0$, kJ/mol
Langmuir	$y = 0.651x + 0.235$	0.371	1.54 ± 0.08	2.76 ± 0.14	-2.52 ± 0.13
Freundlich	$y = 0.97x + 0.590$	0.995	1.03 ± 0.05	3.63 ± 0.18	-3.19 ± 0.16
Dubinin – Radushkevich	$y = -0.018x - 0.652$	0.997	1.91 ± 0.09	0.018 ± 0.009	9.95 ± 0.49
Temkin	$y = 0.068x + 0.374$	0.932	1.03 ± 0.05	36434 ± 1821	-26.0 ± 1.3
Flory – Huggins	$y = 1.120x + 0.338$	0.197	1.12 ± 0.06	2.18 ± 0.11	-1.93 ± 0.09
LMAL	$y = 0.495x + 0.055$	0.997	2.00 ± 0.10	9.00 ± 0.50	-5.54 ± 0.27

Discussion of experimental results. Basing on calculated data, one can draw a conclusion that low correlation values of linear dependencies do not permit to describe sorption isotherms with Langmuir ($R^2 = 0.371$), Flory – Huggins ($R^2 = 0.197$) and Temkin models ($R^2 = 0.932$). Remaining models have sufficiently high determination factors to be used for thermodynamic data calculations.

However, Dubinin – Radushkevich model, despite its high determination factor $R^2 = 0.997$, demonstrates the following data: constant of ion-exchange equilibrium $K = 0.018 \pm 0.009$, Gibbs energy of ion exchange $\Delta_r G_{298}^0 = 9.95 \pm 0.49$ kJ/mole. These numbers demonstrate that spontaneous occurrence of the process is impossible – positive Gibbs energy implies process direction, which is opposite to sorption extraction of cerium in the system. If we use Dubinin – Radushkevich equation to determine the nature of sorption process using the value of free adsorption energy $E = (-2k)^{-0.5}$, calculated value E (5.27 ± 0.26 kJ/mol) less than 8 kJ/mol characterizes physical nature of ion-exchange process.

The calculation based on Temkin equation provided an ion-exchange constant $K = 36434 \pm 1821$, the value of which is uncharacteristic for chemical processes and ion-exchange reactions. Obtained total capacity of anion resin $q_\infty = 1.03 \pm 0.05$ mol/kg is not equal to certificate capacity (2 mol/kg), which is another sign that the model cannot be used to describe the sorption of anion cerium complexes by a weak-base anion resin.

Application of the proposed model, based on linearized mass action law, modified for ion-exchange equation, is the most optimal option from the viewpoint of obtained thermodynamic parameters: Gibbs energy $\Delta_r G_{298}^0 = -5.54 \pm 0.27$ kJ/mol and ion exchange constant $K = 9.0 \pm 0.5$ point to a spontaneous sorption of cerium ions. Total capacity of anion resin 2.0 ± 0.1 mol/kg, calculated using a modified equation of ion-exchange and accurately fitting certificate capacity of anion resin EV009 (2 mol/kg) and the sorption of hydroxy ions by solid phase resin, characterizes relevance of the applied thermodynamic model for ion-exchange equilibrium description in complex solutions.

Proposed LMAL model is universally applicable and is an optimal fit for the description of sorption processes. It takes into account characteristics of the salt background, determined by the activity of solution components. Strict stoichiometry of ion-exchange process, which allows to obtain the most accurate results of substance sorption by ion exchange, has also been taken into account.

Conclusion. The authors have carried out an analysis of literary sources describing thermodynamic models of sorption processes.

The sorption of EDTA cerate ions on anion resin Cybber EV009 in the nitrate form under $\text{pH} = 3$, temperature 298 K, 1:5 liquid-to-solid ratio has been investigated. Experimental sorption isotherm has been plotted.

To obtain thermodynamic data, the following models of sorption isotherms have been used: Langmuir, Freundlich, Dubini – Radushkevich, Temkin, Flory – Huggins and proposed by the authors thermodynamic model of ion-exchange equilibrium description, based on linearization of mass action law, the final form of which is a modified equation of ion-exchange equation.

Correlation of linear function, strict reaction stoichiometry, concordance of the obtained capacity of ion-exchange resin to the certificate value and identified sorption forms of anion cerium complexes by the solid phase of ion-exchange resin confirm the accuracy of thermodynamic description of ion-exchange equilibrium based on mass action law. Obtained values of Gibbs energy $\Delta_r G_{298}^0 = -5.54 \pm 0.27$ kJ/mol and ion exchange constant $K = 9.0 \pm 0.5$ characterize a spontaneous sorption process.



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