COMPARATIVE EVALUATION OF THERMODYNAMIC AND SORPTION PARAMETERS OF ARSENIC AND MERCURY ION COMPLEXES

Inatova Makhsuda Sag'dullayevna
Doctor of Philosophy Chemistry, Associate Professor
Jizzakh State Pedagogical University Uzbekistan
Ubaydullayeva Zilola
Independent researcher

MAQOLA MALUMOTI

MAQOLA TARIXI:
Received: 22.08.2026
Revised: 23.08.2026
Accepted: 24.08.2026

KALIT SO'ZLAR:
arsenic; mercury; complexation; sorption; UV–Vis; thermodynamics; Kd..

ANNOTATSIYA:

The thermodynamic and sorption parameters of As(III), As(V), and Hg(II) systems formed with an organic analytical reagent, R, and an R–sorbent phase were compared. Double-beam UV–Vis measurements were performed over 190–800 nm using 10 mm quartz cells; the thermodynamic series covered 293–313 K. At 293 K, ΔG° values for As(III)–R and Hg(II)–R were −18.40 and −24.10 kJ mol⁻¹ and became −21.70 and −27.35 kJ mol⁻¹ in the sorbent systems. Sorption capacity increased by 59.3% for As(III) and 39.5% for Hg(II). Hg(II)–R–sorbent gave the highest capacity (63.9 mg g⁻¹) and sorption degree (98.8%).

Monitoring arsenic and mercury compounds in water and technogenic samples requires reliable analytical approaches [1]. UV–Vis spectrophotometry monitors complexation through changes in electronic absorption; controlling the blank correction, optical path length, and solution conditions is essential for obtaining quantitative results [2]. The sorption step enables the accumulation of the complex in the solid phase. In this process, the sorption capacity (q), distribution coefficient (Kd), and the degrees of sorption (S) and desorption (D) characterize the interfacial properties of the system. The aim of this study is to comparatively evaluate—using consistent criteria—the thermodynamic and sorption parameters of As(III), As(V), and Hg(II)–R systems, as well as the corresponding pairs involving the sorbent.

Working solutions of metal ions were prepared at each stage by diluting 10.0 mL of the solution to 100 mL. Spectra were recorded against a blank using a double-beam UV–Vis spectrophotometer in the 190–800 nm range, employing quartz cuvettes with a 10 mm optical path length. The temperature was maintained in a thermostat with an accuracy of ±0.5 °C. Contact with the sorbent was maintained at 150–250 rpm, and phase separation was achieved using a 0.45 μm membrane or by centrifugation at 3000–5000 rpm for 5–10 min. Measurements were performed in triplicate, although individual results and dispersion

values were not reported. Verification using the equation $\Delta G° = \Delta H° - T\Delta S°$ confirmed that the Gibbs energy values listed in the table correspond to 293 K. Relative change was calculated using the formula $(X_s - X_r)/X_r \times 100\%$.

Table 1. Thermodynamic parameters of complex systems

Tizim	T, K	$\Delta G°_{293}$, kJ/mol	$\Delta H°$, kJ/mol	$\Delta S°$, J/(mol·K)
As(III)–R	293–313	−18,40	−26,75	−28,49
As(V)–R	293–313	−16,85	−21,60	−16,21
Hg(II)–R	293–313	−24,10	−34,85	−36,69
Hg(II)–R–sorbent	293–313	−27,35	−39,20	−40,44
As(III)–R–sorbent	293–313	−21,70	−30,45	−29,86

Note. R is an organic analytical reagent; the $\Delta G°_{293}$ value was verified using the equation $\Delta G° = \Delta H° - 293\Delta S°$

In all systems, the negative value of $\Delta G°_{293}$ indicates that the process is thermodynamically favorable, while the negative value of $\Delta H°$ indicates that it is exothermic. In the solution phase, the energetic favorability follows the order Hg(II)–R > As(III)–R > As(V)–R. Upon the addition of the sorbent, $\Delta G°$ became more negative by 3.30 kJ/mol in the As(III) system and by 3.25 kJ/mol in the Hg(II) system. The negative values of $\Delta S°$ correspond to the formation of an ordered state during complexation and surface immobilization. As the composition of the sorbent is not specified, these differences cannot be attributed to a specific functional group.

Table 2. Sorption parameters of complex systems.

Tizim	q, mg/g	Kd, mL/g	S, %	k, min^{-1}	D, %
As(III)–R	32,4	$4,8\times10^3$	89,5	0,086	9,8
As(V)–R	28,7	$3,9\times10^3$	84,3	0,071	12,4
Hg(II)–R	45,8	$8,6\times10^3$	95,4	0,118	5,6
As(III)–R–sorbent	51,6	$1,2\times10^4$	97,2	0,136	3,7
Hg(II)–R–sorbent	63,9	$1,8\times10^4$	98,8	0,154	2,5

Note. q – capacity; Kd – distribution coefficient; S – sorption; k – rate constant (model not specified); D – desorption.

In the solution phase, the Hg(II)–R system is characterized by the highest values of q (45.8 mg/g), Kd (8.6×10^3 mL/g), S (95.4%), and k (0.118 min^{-1}). For the As(III) system, the sorbent increased capacity by 59.3%, Kd by a factor of 2.50, and the rate constant by 58.1%,

while desorption decreased by 62.2%. In the Hg(II) system, capacity increased by 39.5%, Kd by a factor of 2.09, and k by 30.5%, with a 55.4% reduction in desorption. The highest overall result was observed for the Hg(II)–R–sorbent system. Selecting between the Langmuir and Freundlich models requires complete isotherm and regression criteria [3–5], while determining the kinetic mechanism requires a computational model for k [6]. Therefore, the tabulated values were compared descriptively; no claims regarding statistical significance were made.

Analytical interpretation of sorption results. Sorption capacity and **Kd** are complementary parameters, though they do not represent the exact same concept: **q** represents the amount retained in the solid phase, whereas **Kd** reflects the tendency of the complex to partition between the solution and the sorbent. In the As(III)–R–sorbent system, **S** increased by 7.7 percentage points compared to its counterpart in the solution phase, while in the Hg(II)–R–sorbent system, it increased by 3.4 percentage points. For both pairs, the increase in **q**, **Kd**, **S**, and **k**, alongside the decrease in **D**, consistently confirms that retention is enhanced in the presence of the sorbent.

Although the relative change is greater in the As(III) system, the absolute sorption values are higher in the Hg(II) system. The As(V)–R system is characterized by the lowest q (28.7 mg/g), Kd (3.9×10^3 mL/g), and S (84.3%) values, as well as the highest D (12.4%). In Chapter II, these differences are explained in terms of coordination bonding, surface complexation, and ion exchange. However, due to the absence of data regarding the quantitative distribution of ionic species as a function of pH and the functional composition of the surface, these mechanisms remain at the level of a working interpretation.

The obtained results demonstrate the feasibility of using the sorbent during the separation and pre-concentration stages prior to photometric detection. However, due to the absence of data regarding the limit of detection, linear range, recovery, selectivity, and performance in real sample matrices, it is not possible to make a definitive quantitative claim regarding the superiority of the proposed analytical method. Further validation should specifically evaluate the calibration model, blank signal, repeatability, spike-recovery experiments, and the influence of interfering ions.

The structure of reagent. R, the composition of the sorbent, primary spectra, calibration equations, and individual replicate measurements were not provided. Consequently, the article relied solely on the specific aggregate values presented and their arithmetic comparison; no isotherm or kinetic model was refitted.

Conclusion. At 293 K, ΔG° was negative for all systems, indicating the thermodynamic feasibility of complexation and sorption–complexation.

The sorbent enhanced energetic favorability, capacity, Kd, and k, while reducing desorption in As(III) and Hg(II) systems.

The Hg(II)–R–sorbent system was characterized by the highest q (63.9 mg/g), Kd (1.8×10^4 mL/g), S (98.8%), and k (0.154 min^{-1}).

Final validation of the methodology requires identification of the reagent and sorbent, primary data, and metrological parameters.

References

1. Alekseev V. G. Analytical Chemistry. Separation and Concentration Methods. Moscow: Khimiya, 2001. pp. 72–85.
2. Kabata-Pendias A. Trace Elements in Soils and Plants. 4th ed. Boca Raton: CRC Press, 2011. pp. 65–102. Marczenko Z. Separation and Spectrophotometric Determination of Elements. Chichester: Ellis Horwood, 1986. pp. 180–220.
3. Skoog D. A., Holler F. J., Crouch S. R. Principles of Instrumental Analysis. 6th ed. Belmont: Thomson Brooks/Cole, 2007. pp. 280–340.
4. World Health Organization (WHO). Guidelines for Drinking-water Quality. 4th ed. Geneva: WHO Press, 2017. pp. 15–
5. Zolotov Yu. A. Sorption Methods in Analytical Chemistry. Moscow: Nauka, 1998. pp. 110–145.