SOLVATION EXCESSES OF IONS OF HEAVY METALS IN WATER SOLUTIONS SATURATED WITH HUMIC ACID

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Abstract
Increase of solubility of stock and mechano chemical dispersed samples of humic acid from brown coal in water solutions of ions of heavy metals has been determined.
Solvation excesses of ions of heavy metals over water on molecular ensemble of humic acid in liquid phase have been calculated.
Anti cooperative binding of ions of heavy metals on two reaction centers of poly electrolyte has been determined. Size effect of metallic complex of molecular ensemble of humic acid in water solution has been estimated.

Key words: Molecular ensemble of humic acid, ions of heavy metals, solvation excess, size effect of humic acid metallic complex.

Introduction
Solubility of humic acid in water – electrolyte solutions is one of its important characteristics. Establishment of heterogeneous equilibrium is accompanied by two conjugated processes – ions adsorption on humic acid in solid phase and ions binding on molecular ensemble of humic acid in liquid phase. Surface and solvation excesses are quantity characteristics of these processes under conditions of heterogeneous equilibrium [1, 2].

This research carries on with works [3, 4]. This work is devoted to the calculation of solvation excesses of ions of heavy metal on humic acid in liquid phase, numbers of humic acid reaction centers binding ions of heavy metals in solution and size effect of polyelectrolyte metallic complexes.

A.A. Pendin’s basis equation (1) was used for solving of problems mentioned above [1]:

\[ \Gamma_{M^{2+}(W)}^{HA} = \frac{1}{2} \left( \frac{\partial \ln Y_{HA}^0}{\partial a_{\pm}} \right)_{T,P,o_{xy}} \] (1),

where \( \Gamma_{M^{2+}(W)}^{HA} \) is the solvation excess of two-charged ions over water on molecular ensemble of humic acid; \( Y_{HA}^0 \) - zero coefficient of activity of humic acid in water-electrolyte solution; \( a_{\pm} \) - average activity of electrolyte.

In equation (1) zero coefficients of activity [1] are free energy of transfer of molecular ensemble of humic acid from standard water solution in standard water-electrolyte solution. These values are calculated according with equation (2):

1-67
\[
\lg Y_{HA}^0 = \lg \left(\frac{C_{HA}^{sat}(w)}{C_{HA}^{sat}(w-e)}\right)
\]  
\[ (2), \]

Where \( Y_{HA}^0 \) - zero coefficient of activity of humic acid in water-electrolyte solution; \( C_{HA}^{sat}(w) \) - solubility of humic acid in water (gr./l); \( C_{HA}^{sat}(w-e) \) - solubility of humic acid in water-electrolyte solution (gr./l).

**Experiment**

Stock (HA) and dispersed (HA\(_d\)) samples of humic acid (HA) were used in this work. Stock sample of humic acid was extracted from analytical sample of brown coal (Kara-Keche deposit, Kyrgyzstan). Dispersed sample of humic acid was obtained by mechano-chemical treatment of stock sample in grinding mill. Grinding balls and glass of agate were used to avoid the pollution of dispersed objects by metals. Grinding was made at 300 rotations in minute during 3 minutes. Physico-chemical characteristic of stock and mechano-chemical dispersed samples of humic acid from Kara-Keche coal has been presented at the work [5].

Heterogeneous equilibrium in the systems: humic acid – water solution of copper chloride (II), humic acid – water solution of nickel chloride (II), humic acid – water solution of cadmium chloride (II) was establishing during 24 hours under temperature \( T=298^0\text{K} \) and continuous agitation in dry-air thermostat. Saturated water-electrolyte solutions of humic acid were separated from sediment using centrifugation and syringe filters with size pore of 5 micron. Concentration of humic acid in saturated water – electrolyte solution was determined by method of spectrophotometry at the wave length \( \lambda = 340 \text{ nm} \), thickness of tray \( l = 1\text{ cm} \), extinction coefficient \( \varepsilon=18,9\pm0,1 \) (l/gr.-sm).

Zero coefficients of activity of humic acid molecular ensemble in water – electrolyte solutions were calculated according with equation (2) and solubility data of stock and dispersed samples of humic acid in water solutions of copper (II), nickel (II) and cadmium chlorides. Results of calculations are presented in tabl. 1. Average activities of research electrolytes (tabl.2) were calculated according with second approximation of Deby – Hukkel theory in form of Gunterberg equation.

**Table 1**

Zero coefficients of activity of molecular ensemble of humic acid of Kara-Keche coal in water – electrolyte solutions under 298\(^0\text{K}\)

<table>
<thead>
<tr>
<th>(C_{MCl_2}) mole/l</th>
<th>( \lg \gamma_\pm )</th>
<th>( \lg a_\pm )</th>
<th>( \text{CuCl}_2 )</th>
<th>( \text{NiCl}_2 )</th>
<th>( \text{CdCl}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \lg \gamma^0_{na} )</td>
<td>( \lg \gamma^0_{nQ} )</td>
<td>( \lg \gamma^0_{na} )</td>
<td>( \lg \gamma^0_{nQ} )</td>
<td>( \lg \gamma^0_{na} )</td>
</tr>
<tr>
<td>0,0010</td>
<td>-0,053</td>
<td>-2,852</td>
<td>0,325</td>
<td>0,232</td>
<td>0,301</td>
</tr>
<tr>
<td>0,0050</td>
<td>-0,132</td>
<td>-2,211</td>
<td>0,376</td>
<td>0,232</td>
<td>0,204</td>
</tr>
<tr>
<td>0,0100</td>
<td>-0,177</td>
<td>-1,949</td>
<td>0,165</td>
<td>0,110</td>
<td>0,058</td>
</tr>
<tr>
<td>0,0200</td>
<td>-0,199</td>
<td>-1,698</td>
<td>0,103</td>
<td>0,015</td>
<td>-0,211</td>
</tr>
<tr>
<td>0,0300</td>
<td>-0,234</td>
<td>-1,556</td>
<td>0,075</td>
<td>-0,075</td>
<td>0,000</td>
</tr>
<tr>
<td>0,0400</td>
<td>-0,261</td>
<td>-1,458</td>
<td>-0,022</td>
<td>-0,134</td>
<td>-0,097</td>
</tr>
</tbody>
</table>
As seen from table 1, zero coefficients of activity decrease as the concentration of electrolyte grows. Consequently, stabilization of molecular ensemble of humic acid increases in water – electrolyte solution in comparison with pure water. This result testifies effects of preferential solvation of heavy metal ions over water on molecular ensemble of humic acid.

Data of tabl. 1 are basis of subsequent calculations of solvation excesses of ions of heavy metals on molecular ensemble of humic acid in water – electrolyte solutions.

**Results and discussion**

According with equation (1) dependences of \( \lg Y_{HA}^0 \) from \( \lg a_\pm \) were described by nonlinear regression method using polynoms of defined degree of expansion presented at Fig.1.

![Fig.1 Dependences of \( \lg Y_{HA}^0 \) from \( \lg a_\pm \) in water-electrolyte solutions saturated by stock and dispersed samples of humic acid of Kara-Keche coal under 298°K](image)

\[
\begin{align*}
\lg Y_{HA}^0 (CuCl_2) &= -1.50 - 1.42 \cdot \lg a_\pm - 0.27 \cdot (\lg a_\pm)^2 \\
\lg Y_{HA}^0 (NiCl_2) &= -1.08 - 0.90 \cdot \lg a_\pm - 0.15 \cdot (\lg a_\pm)^2 \\
\lg Y_{HA}^0 (CdCl_2) &= 0.001 - 0.46 \cdot \lg a_\pm - 0.12 \cdot (\lg a_\pm)^2
\end{align*}
\]

Solvation excesses of ions of heavy metals in research water-electrolyte solutions on humic acid were calculated by analytic differentiation of polynoms presented in Fig.1. Results of calculation are presented in Fig.2.
Fig. 2  Solvation excesses of ions of heavy metals over water on molecular ensemble of stock and dispersed samples of humic acid of Kara-Keche coal in water electrolyte solutions

As seen from Fig. 2 solvation excesses values are positive and grow as concentration of electrolyte increases.

This result testifies solvation excess of ions of heavy metals over water on reaction centers of humic acid molecular ensemble. Notice, water-electrolyte solutions saturated with stock and dispersed samples of Kara-Keche humic acid are discussed in this work.

Solvation excesses of ions of heavy metals over water on molecular ensemble of humic acid in water – electrolyte solutions can be arranged in raw (I):

$$
\Gamma_{\text{HA}}^{\text{Cu}^{2+}} - \Gamma_{\text{HA}}^{\text{Cd}^{2+}} = \frac{\alpha_{\text{M}} \cdot \lg X}{\alpha_{\text{H}}^2} \cdot \lg K
$$

(N)

Notice, the raw of solvation excesses (I) corresponds to the raw of adsorption values of research ions on humic acid surface [4]. This fact indicates similar mechanisms of ions of heavy metal binding by reaction centers of humic acid in solid phase and liquid phase in water – electrolyte solutions.

Hill’s equation was used for calculation of numbers of reaction centers of molecular ensemble of humic acid of Kara-Keche coal binding heavy metal ions in water – electrolyte solution. Hill’s equation can be written in terms of solvation excess:

$$
\alpha_{\text{H}} \cdot \lg X - \alpha_{\text{M}} \cdot \lg K = \frac{\alpha_{\text{M}} \cdot \ln X}{\alpha_{\text{H}}^2}
$$

(3)

where $K$ - constant of binding of two-charged ions on two reaction centers of molecular ensemble of humic acid of Kara-Keche coal in water solutions; $\alpha_{\text{H}}$ - Hill’s cooperative coefficient [6]; $X$ - mole part of ion in water solution.
Analysis of solvation excesses in Hill's graph coordinates is presented in the Fig. 3.

<table>
<thead>
<tr>
<th>stock sample</th>
<th>Liner regression equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lg \left( \frac{\Gamma_{M^{2+}}^{HA}}{2 - \Gamma_{M^{2+}}^{HA}} \right) )</td>
<td>( \lg \left( \frac{\Gamma_{Ni^{2+}}^{HA}}{2 - \Gamma_{Ni^{2+}}^{HA}} \right) = 0.32 + 0.37 \cdot \lg X_{Ni^{2+}} )</td>
</tr>
<tr>
<td>( \lg \left( \frac{\Gamma_{Cu^{2+}}^{HA}}{2 - \Gamma_{Cu^{2+}}^{HA}} \right) = 1.06 + 0.56 \cdot \lg X_{Cu^{2+}} )</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mechanochemical dispersed sample</th>
<th>Liner regression equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lg \left( \frac{\Gamma_{M^{2+}}^{HA}}{2 - \Gamma_{M^{2+}}^{HA}} \right) )</td>
<td>( \lg \left( \frac{\Gamma_{Ni^{2+}}^{HA}}{2 - \Gamma_{Ni^{2+}}^{HA}} \right) = 1.32 + 0.62 \cdot \lg X_{Ni^{2+}} )</td>
</tr>
<tr>
<td>( \lg \left( \frac{\Gamma_{Cu^{2+}}^{HA}}{2 - \Gamma_{Cu^{2+}}^{HA}} \right) = 1.54 + 0.69 \cdot \lg X_{Ni^{2+}} )</td>
<td></td>
</tr>
<tr>
<td>( \lg \left( \frac{\Gamma_{Cd^{2+}}^{HA}}{2 - \Gamma_{Cd^{2+}}^{HA}} \right) = 0.77 + 0.75 \cdot \lg X_{Cd^{2+}} )</td>
<td></td>
</tr>
</tbody>
</table>

Fig.3. Hill's graph for dependence of solvation excesses of two-charged ions over water on molecular ensemble of humic acid of Kara-Keche coal in water-electrolyte solutions.

As seen from Fig.3 Hill’s cooperative coefficient (\( \alpha_H \)) for all research ions is less than one. This result shows anti cooperative binding of heavy metal ions on two reaction centers of molecular ensemble of humic acid in water - electrolyte solutions. Notice, that anti cooperative binding of ions on humic acid molecular ensemble, obtained by saturation of water electrolyte solution with dispersed sample of humic acid is expressed less than on molecular ensemble of humic acid, obtained by saturation of water-electrolyte solution with stock sample of humic acid.

One of the important parts of this work is estimation of size of molecular ensemble of humic acid binding ions of heavy metals on two reaction centers.

Equation (4) can be obtained using phenomenological linkage of solvent and surface excesses [7]:

\[
\begin{align*}
    r_{HA(Ad)} & = \sqrt{\frac{S_{\infty}^{HA,HA(Ad)} \cdot \Gamma_{M^{2+}}^{HA}}{4\pi N_a a_{\infty}^{M^{2+}}^{(HA,HA(Ad))}}} \quad (4),
\end{align*}
\]
where \( r_{HA(HAd)} \) - radius of stock and mechanochemical dispersed samples of humic acid in water-electrolyte solution; \( S_{specific}^{HA,HAd} \) - specific area of surface of humic acid defined using ferriceniy cation \[5\]; \( \alpha_{HA}^{M^{2+}} (HA,HAd) \) - limit adsorption of ions on stock and dispersed samples of humic acid in solid phase \[4\]; \( r_{HA_{M^{2+}}}^{HA} = 2 \) – limit solvation excess of metal ions on molecular ensemble of humic acid in solution.

Results of calculation on equation (4) are presented in tabl. 2

<table>
<thead>
<tr>
<th>ion</th>
<th>( r_{HAM^{2+}} ) (nm)</th>
<th>( r_{HAdM^{2+}} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(^{2+})</td>
<td>0,4</td>
<td>1,2</td>
</tr>
<tr>
<td>Ni(^{2+})</td>
<td>0,6</td>
<td>1,2</td>
</tr>
<tr>
<td>Cd(^{2+})</td>
<td>0,7</td>
<td>1,3</td>
</tr>
</tbody>
</table>

As seen from table true solutions of metallic complexes of humic acid with heavy metal ions \( (r_{HA^{2+}} < 1) \) form under saturation of water-electrolyte solution with stock sample of humic acid. At the same time, ultra dispersed particles form under saturation of water-electrolyte solution with mechanochemical dispersed sample of humic acid in liquid phase. These particles are metallic complexes of humic acid with ions of heavy metals \( (r_{HAdM^{2+}} > 1) \).

Conclusion

Nano size metallic complexes of molecular ensemble of humic acid with ions of heavy metal as a result of preferential solvation effects form in liquid phase under condition of establishment of equilibrium “humic acid in solid phase - water solution of electrolyte”.

This result motivates one of the mechanisms of migration of non organic eco toxicants with surface moisture in polluted soils.

In connection with it, using of humic acid for soils purification from ions of heavy metals is not always reasonable. At the same time formation of nanosize metallic complexes of humic acid in liquid phase promotes theirs useful biosphere regulator functions.

References

3. S. Karabaev, I. Gainullina, A. Djunushalieva, A. Akmatalieva, S. Lugovskoy, A. Pendin / Adsorption of ions of heavy metals from water solutions on humic acid and humine of brown