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Thermodynamics of nanoadsorption from solution: Theoretical and experimental research

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ABSTRACT

In this study, the effect of nanoparticle size on adsorption thermodynamics was investigated. The results of theoretical and experimental studies show that particle size significantly affects the equilibrium constant and thermodynamic properties of nanoadsorption. Relationships between the equilibrium constant, thermodynamic properties and particle size were derived using the thermodynamic theory of nanoadsorption. The equilibrium constant and thermodynamic properties were obtained by investigating the adsorption of Cu^{2+} onto different sizes of nano-ZnO and the adsorption of Ag^+ onto different sizes of nano-TiO_2. Good agreement was achieved between results obtained by experiments and predicted by theoretical analyses. The equilibrium constant and the molar Gibbs free energy of nanoadsorption were found to increase with smaller nanoparticle size. However, the effects of particle size on the molar enthalpy and the molar entropy are uncertain. In addition, the molar Gibbs free energy, the molar enthalpy, the molar entropy and the logarithm of the equilibrium constant are linearly related to the reciprocal of the diameter of the nanoparticle. The thermodynamic properties revealed in this study may provide important guidelines for research and application in the field of nanoadsorption.

1. Introduction

Nano-materials, especially nanoparticles, based on their unique adsorption properties compared with corresponding bulk materials, have been widely used as adsorbents and catalyzers [1–7]. The effect of nanoparticle size is not well understood. Therefore, it is essential to study the effect of particle size on the thermodynamics of nanoadsorption. Zhang *et al.* [8] and Lu *et al.* [9] concluded that the equilibrium adsorption constant increases with decreasing material size. Pettibone *et al.* [10] investigated nano-TiO_2 adsorption for organic acids and reported differences in measured Langmuir adsorption constants for 5 and 32 nm-sized particles. Zhou *et al.* [11] showed that the adsorption equilibrium constant decreases with decreasing nanoparticle size.

Most studies have focused on thermodynamic properties of nanoparticle adsorption, in which the particle size was a constant value or a range. However, few studies have investigated the effects of different particle sizes on thermodynamic properties. Venkatesha *et al.* [12] tested the adsorption behavior of MgO over a crystallite size range of 25–30 nm and calculated the standing free energy and entropy. The results showed that the nanoparticle adsorption was spontaneous and exothermic. Sheela *et al.* [13] studied the adsorption of Cd (II) and Pb (II) on 28 nm-sized NiO particles; the standard free energy, enthalpy and entropy calculations indicated that the adsorption was endothermic and spontaneous. Zhang *et al.* [14] determined that the adsorption of selenium ions on 10–15 nm-sized TiO_2 particles was exothermic.

To expand our knowledge of nanoparticle adsorption thermodynamics we must conduct theoretical and experimental research. Here, the thermodynamic theory of nanoadsorption was extended. By studying the adsorption of Cu^{2+} on ZnO nanoparticles of different sizes and the adsorption of Ag^+ on TiO_2 nanoparticles of different sizes, the effects of size on the equilibrium constant, the molar Gibbs free energy, the molar enthalpy and the molar entropy of adsorption were investigated.

2. Theoretical section

Nanoadsorption from solution can be assumed to be a reaction system where all stoichiometric coefficients are unity, which is expressed as:

$$\mathrm{A(sol.)} + \mathrm{N(s)} \rightleftharpoons \mathrm{P(s)}, \tag{1}$$

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where A(sol.) is an adsorbate in solution, N(s) is a pure nano-adsorbent with diameter d and P(s) is an adsorption product formed by adsorbing A onto the surface of N.

2.1. Chemical potential of the adsorbate in solution

From solution thermodynamics, we know

$$\mu_{\mathrm{A}}(\mathrm{l}) = \mu^{\mathrm{o}}_{\mathrm{A}}(\mathrm{l}) + RT\ln a_{\mathrm{A}}, \tag{2}$$

where $\mu_{\mathrm{A}}(\mathrm{l})$ is the chemical potential of the adsorbate in solution, a_{A} is the activity of the adsorbate in solution, $\mu^{\mathrm{o}}_{\mathrm{A}}(\mathrm{l})$ is the standard chemical potential of the adsorbate in solution, R is the universal gas constant ($8.314\,\mathrm{J}\cdot\mathrm{mol}^{-1}\cdot\mathrm{K}^{-1}$), T is the absolute temperature, and the superscript $^{\mathrm{o}}$ denotes the standard state.

2.2. Chemical potential of the nano-adsorbent

From the thermodynamics of a pure condensed phase, the chemical potential of the nano-adsorbent is

$$\mu^{*}_{\mathrm{N}} = \mu^{*\mathrm{o}}_{\mathrm{N}} + RT\ln a^{*}_{\mathrm{N}}, \tag{3}$$

where the superscript * denotes a pure substance, $\mu^{*\mathrm{o}}_{\mathrm{N}}$ is the standard chemical potential of the nano-adsorbent, and a^{*}_{N} is the activity of the nano-adsorbent, which can be calculated by

$$\ln a^{*}_{\mathrm{N}} = \frac{V^{*}_{\mathrm{N}}}{RT}(p - p^{\mathrm{o}}), \tag{4}$$

where V^{*}_{N} is the molar volume of the nano-adsorbent.

When the pressure is not too high, $a^{*}_{\mathrm{N}} \approx 1$. This simplifies equation (3) to

$$\mu_{\mathrm{N}} = \mu^{\mathrm{o}}_{\mathrm{N}}. \tag{5}$$

The adsorbent, at the nanoscale level, can produce a strong surface effect, so the chemical potential for the nano-adsorbent needs to consider both the bulk part and the interfacial part, which can be written as

$$\mu_{\mathrm{N}} = \mu^{\mathrm{bo}}_{\mathrm{N}} + \mu^{\mathrm{so}}_{\mathrm{N}}, \tag{6}$$

where superscripts b and s denote the bulk phase and the interfacial phase, respectively, $\mu^{\mathrm{bo}}_{\mathrm{N}}$ and $\mu^{\mathrm{so}}_{\mathrm{N}}$ are the chemical potentials of the bulk phase and the interfacial phase of the pure nano-adsorbent at standard state, respectively.

For a spherical pure nano-adsorbent, the chemical potential becomes

$$\mu_{N} = \mu^{\mathrm{bo}}_{\mathrm{N}} + \frac{4\sigma^{*}_{\mathrm{N}}V^{*}_{\mathrm{N}}}{\mathrm{d}}, \tag{7}$$

where σ^{*}_{N} and d are the surface tension and the diameter of nano-adsorbent, respectively.

2.3. Chemical potential of the adsorption product

The chemical potential of the adsorption product is related to the amount of adsorption that can be achieved. It is based on the definition of the general chemical potential at constant temperature:

$$d\mu_{\mathrm{P}} = RTd\ln\frac{\Gamma_{\mathrm{A}}}{[\Gamma]}, \tag{8}$$

where Γ_{A} is the absorption capacity of the adsorbate per unit of the nano-adsorbent at a given time, and $[\Gamma]$ is the unit of Γ_{A}.

Integrating the above equation from $\Gamma^{\infty}_{\mathrm{A}}$ to Γ_{A} and from $\mu^{\infty}_{\mathrm{P}}$ to μ_{P}, we get

$$\mu_{\mathrm{P}} = \mu^{\infty}_{\mathrm{P}} + RT\ln\frac{\Gamma_{\mathrm{A}}}{\Gamma^{\infty}_{\mathrm{A}}}, \tag{9}$$

where $\Gamma^{\infty}_{\mathrm{A}}$ is the absorption capacity of adsorbate in a saturated state, $\mu^{\infty}_{\mathrm{P}}$ is the chemical potential of the adsorption product in a saturated state, and the superscript ∞ denotes a saturated state.

Similarly, the chemical potential of the adsorption product in the saturated state is made up of $\mu^{\mathrm{b}\infty}_{\mathrm{P}}$ and $\mu^{\mathrm{s}\infty}_{\mathrm{P}}$:

$$\mu^{\infty}_{\mathrm{P}} = \mu^{\mathrm{b}\infty}_{\mathrm{P}} + \mu^{\mathrm{s}\infty}_{\mathrm{P}}. \tag{10}$$

For the spherical adsorption product, the chemical potential of the interfacial phase in a saturation state can be expressed as

$$\mu^{\mathrm{s}\infty}_{\mathrm{P}} = \frac{4\sigma^{\infty}_{\mathrm{P}}V^{*}_{\mathrm{N}}}{d}, \tag{11}$$

where $\sigma^{\infty}_{\mathrm{P}}$ is the surface tension of the adsorption product in a saturated state. The molar volume and the diameter of the adsorption product are approximately equal to those of the nano-adsorbent because the molecular size of the nano-adsorbent is much greater than that of the adsorbate.

Equation (9) can then be written as

$$\mu_{\mathrm{P}} = \mu^{b\infty}_{\mathrm{P}} + \frac{4\sigma^{\infty}_{P}V^{*}_{\mathrm{N}}}{d} + RT\ln\frac{\Gamma_{A}}{\Gamma^{\infty}_{A}}. \tag{12}$$

The state of nanoparticle-saturated adsorption is defined as the standard state of the nanoadsorption product; therefore, the standard chemical potential of nanoadsorption products can be expressed as

$$\mu^{\mathrm{o}}_{\mathrm{P}} = \mu^{b\infty}_{\mathrm{P}} + \frac{4\sigma^{\infty}_{P}V^{*}_{\mathrm{N}}}{d}. \tag{13}$$

Equation (12) can then be simplified to

$$\mu_{\mathrm{P}} = \mu^{\mathrm{o}}_{\mathrm{P}} + RT\ln\frac{\Gamma_{\mathrm{A}}}{\Gamma^{\infty}_{\mathrm{A}}}. \tag{14}$$

2.4. The molar Gibbs free energy for adsorption

Based on the adsorption process expressed by equation (1), the molar Gibbs free energy is

$$\Delta_{a}G_{\mathrm{m}} = \mu_{\mathrm{P}} - \mu_{\mathrm{A}} - \mu_{\mathrm{N}}. \tag{15}$$

Applying equations (2), (7) and (12) to equation (15), we obtain

$$\Delta_{a}G_{\mathrm{m}} = \Delta_{a}G^{\mathrm{bo}}_{\mathrm{m}} + RT\ln J + (\sigma^{\infty}_{\mathrm{P}} - \sigma^{*}_{\mathrm{N}})\frac{4V^{*}_{\mathrm{N}}}{d} = \Delta_{a}G^{b}_{m} + \Delta_{a}G^{s}_{m}, \tag{16}$$

$$\text{where}\quad \Delta_{a}G^{\mathrm{bo}}_{m} = \mu^{\mathrm{b}\infty}_{\mathrm{P}} - \mu^{\mathrm{o}}_{\mathrm{A}} - \mu^{\mathrm{bo}}_{\mathrm{N}}, \tag{17}$$

$$J = \frac{\Gamma_{\mathrm{A}}/\Gamma^{\infty}_{\mathrm{A}}}{a_{\mathrm{A}}}, \tag{18}$$

$$\Delta_{a}G^{\mathrm{b}}_{m} = \Delta_{a}G^{\mathrm{bo}}_{m} + RT\ln J,\quad \text{and} \tag{19}$$

$$\Delta_{a}G^{\mathrm{s}}_{\mathrm{m}} = (\sigma^{\infty}_{\mathrm{P}} - \sigma^{*}_{\mathrm{N}})\frac{4V^{*}_{\mathrm{N}}}{d}. \tag{20}$$

The standard state of the molar Gibbs free energy of nanoadsorption is defined as follows,

$$\Delta_{a}G^{\mathrm{o}}_{m} = \Delta_{a}G^{\mathrm{bo}}_{m} + (\sigma^{\infty}_{\mathrm{P}} - \sigma^{*}_{\mathrm{N}})\frac{4V^{*}_{\mathrm{N}}}{d}. \tag{21}$$

It can be seen from equation (16) that the molar Gibbs free energy of nanoadsorption is dependent on the bulk and interfacial components. The $\Delta_{a}G^{\mathrm{s}}_{m}$ term can be neglected for a bulk adsorbent because the molar surface area of a bulk adsorbent with a larger diameter is much smaller. However, for a nano-adsorbent, the influence of the surface area on the molar Gibbs free energy is significant; here, $\Delta_{a}G^{\mathrm{s}}_{m}$ cannot be neglected. For equation (16), we know that there is a decrease in the surface tension after adsorp-