Effect of size on dissolution thermodynamics of nanoparticles: A theoretical and experimental research

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HIGHLIGHTS

- The dissolution model of nanoparticles was established.
- The size-dependent dissolution thermodynamics were derived.
- The influence regularities of nano-Cu dissolved in dilute acid were discussed.
- The dissolution behavior of nanoparticles could be explained by the dissolution model.
- It provided guidance for the preparations and applications of the nanomaterials.

GRAPHICAL ABSTRACT
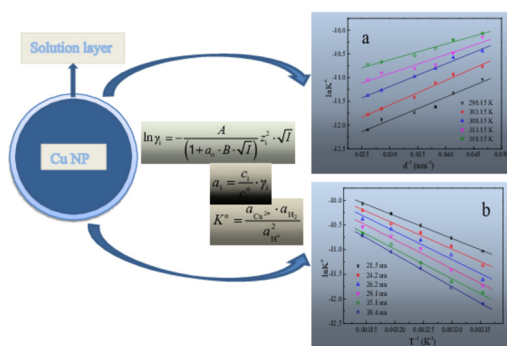
ABSTRACT

Dramatic differences in dissolution thermodynamics between nanoparticles and their bulk counterparts have been observed in which the particle size plays a crucial role. However, the quantitative influences of particle size on the dissolution thermodynamic properties of nanoparticles have not been systematically investigated. In this paper, the relations between dissolution equilibrium constant and dissolution thermodynamic functions with particle size were deduced by introducing the surface variables into the Gibbs function. Then the influence regularities of size on the dissolution equilibrium constant and the dissolution thermodynamic functions were obtained by measuring the solubilities of nano-Cu with different sizes in dilute acid at different temperatures. Theoretical analysis and experimental results reveal that with particle size decreasing, the dissolution equilibrium constant (K^o) increases, while the standard molar dissolution Gibbs energy ($\Delta_r G_m^o$), the standard molar dissolution enthalpy ($\Delta_r H_m^o$) and the standard molar dissolution entropy ($\Delta_r S_m^o$) decrease. Furthermore, when the diameter approaches or exceeds 20 nm, $\ln K^o$, $\Delta_r G_m^o$, $\Delta_r H_m^o$, and $\Delta_r S_m^o$ present linear relations with the reciprocal of diameter, respectively.

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1. Introduction

In the processes of preparation and application of nano-materials, the dissolution of nanoparticles is often involved, such as the preparation of antibacterial agent composite materials [1], and heterogeneous nanocatalysts [2,3], as well as the improvement of

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the solubility for the drug bioavailability [4–6]. Nevertheless, there are remarkable differences in the dissolution thermodynamic properties of nanomaterials compared with those of the corresponding bulk materials, which are caused by the nanometer size effect. So it is essential to investigate the size-dependent dissolution thermodynamics.

Presently, with regard to effect of size on the dissolution of nanoparticles, it has been found that the solubility increases with the decrease of particle size [7–13]. Vogelsberger et al. found that the solubility product of nano-BaSO$_4$ in the water is far greater than that of the bulk [14]. Lubej et al. observed that the solubility product of Cu$_2$Cl(OH)$_3$ increases with the particle size decreasing in the range below 100 nm, and then the molar dissolution Gibbs energy, enthalpy and entropy of Cu$_2$Cl(OH)$_3$ at 298 K were obtained [15]. Fan et al. harvested that the standard molar reaction enthalpy of peanut-like micro/nano CaMoO$_4$ decrease with size decreasing [16]. As a matter of fact, far insufficient theoretical and experimental studies on the dissolution thermodynamics for nanoparticles have been reported, not to mention the quantitative influence regularities of particle size on the dissolution thermodynamic functions.

Herein, the relations of dissolution equilibrium constant and dissolution thermodynamic functions with the particle size were derived. Then nano-Cu was taken as an example, and by measuring the solubilities of nano-Cu with different particle sizes at different temperatures, the effects of size on the equilibrium constant, the molar Gibbs energy, the molar enthalpy and the molar entropy for dissolution were investigated. Subsequently, the experimental results were compared with the theoretical analysis.

2. Theory analysis

2.1. The dissolution thermodynamics of nanoparticles

The dissolution of nanoparticles includes two types, one is the physical dissolution, and the other is the chemical dissolution of nanoparticles. Both of them can be seen as a reaction that can be expressed as follows,

$$0 = \sum \nu_B B \tag{1}$$

where ν_B is the stoichiometric number of component B in the dissolution system.

Assuming that the nanoparticles are the only dispersed phase and introducing the interface variable to the Gibbs energy, the total Gibbs energy G can be seen a function of temperature T, pressure p, amount of substance n for component B and interfacial area for nanoparticles A.

$$G = G(T, p, n, A) \tag{2}$$

When the state has an infinitesimal change, dG can be given as:

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,n,A} dT + \left(\frac{\partial G}{\partial p}\right)_{T,n,A} dp + \sum_B \left(\frac{\partial G}{\partial n}\right)_{T,p,A} dn + \left(\frac{\partial G}{\partial A}\right)_{T,p} dA \tag{3}$$

According to the classical thermodynamic theory, equation (2) can be simplified to the following formula,

$$dG = -SdT + VdP + \sum_B \mu_B^b dn + \sigma dA \tag{4}$$

where μ_B^b is the bulk chemical potential of component B and σ is the specific surface Gibbs function. The superscript b denotes the bulk phase.

The molar dissolution Gibbs energy $\Delta_r G_m$ of nanoparticles at constant temperature and constant pressure can be derived as follows,

$$\Delta_r G_m = \left(\frac{\partial G}{\partial \xi}\right)_{T,p} = \sum_B \mu_B^b \left(\frac{\partial n}{\partial \xi}\right)_{T,p} + \sigma \left(\frac{\partial A}{\partial n}\right)_{T,p} \left(\frac{\partial n}{\partial \xi}\right)_{T,p} \tag{5}$$

where ξ is the extent of reaction expressed as equation (1), and μ_B^b is the chemical potential of bulk phase of component B.

The surface chemical potential μ^s is defined as follows,

$$\mu^s \equiv \sigma \left(\frac{\partial A}{\partial n}\right)_{T,p} \tag{6}$$

where the superscript s denotes the surface phase.

According to the definition of μ^s and the stoichiometric number ν, equation (5) can be changed as follows,

$$\Delta_r G_m = \sum_B \nu_B \mu_B^b + \nu \mu^s = \Delta_r G_m^b + \Delta_r G_m^s \tag{7}$$

where $\Delta_r G_m^b$ and $\Delta_r G_m^s$ are the molar dissolution Gibbs energy of the bulk and surface phases, respectively.

For a spherical nanoparticle without endoporus, μ^s can be expressed as follows,

$$\mu^s = \frac{4\sigma V}{d} \tag{8}$$

where V and d denote the molar volume and the diameter of nanoparticle, respectively.

Substituting equation (8) into equation (7), it becomes

$$\Delta_r G_m = \Delta_r G_m^b + \frac{4\nu\sigma V}{d} \tag{9}$$

As can be seen from equation (9), the molar dissolution Gibbs energy decreases with the decrease of the particle size.

On the base of equation (9) and $[\partial(G/T)/\partial T]_p = -H/T^2$, the molar dissolution enthalpy $\Delta_r H_m$ is gotten,

$$\Delta_r H_m = \Delta_r H_m^b + \Delta_r H_m^s = \Delta_r H_m^b + \frac{4\nu V}{d}\left[\sigma - T\left(\frac{\partial \sigma}{\partial T}\right)_p - \frac{2T\sigma\alpha}{3}\right] \tag{10}$$

where α is the coefficient of thermal expansion, $\Delta_r H_m^b$ and $\Delta_r H_m^s$ are the molar dissolution enthalpy of the bulk and surface phases, respectively.

Similarly, the molar dissolution entropy $\Delta_r S_m$ can be obtained by equation (8) and $(\partial G/\partial T)_p = -S$,

$$\Delta_r S_m = \Delta_r S_m^b + \Delta_r S_m^s = \Delta_r S_m^b - \frac{4\nu V}{d}\left[\left(\frac{\partial \sigma}{\partial T}\right)_p + \frac{2}{3}\sigma\alpha\right] \tag{11}$$

As for metals, the order of magnitudes of σ, T, $(\partial\sigma/\partial T)_P$, and α are 10^0 Jm^{-2}, 10^2 K, 10^{-4} Jm^{-2} K^{-1}, 10^{-5} K^{-1}, respectively [17–20], so the value in the bracket of equations (10) and (11) are positive, and both the molar enthalpy and the molar entropy decrease with the decrease of the particle size. On account of the transformation of the surface energy into the heat energy in dissolution, more heat releases for an exothermic reaction, or less heat absorbs for an endothermic reaction, causing the decrease of molar dissolution enthalpy. As for the decrease of the molar dissolution entropy, it is