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# Thermodynamic functions of metal–sericin complexation in ultrafiltration study



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## ABSTRACT

A scientific attempt was made to exclusively bridge the gap between theoretical modeling and experimental evaluation of thermodynamic parameters exhibiting the removal efficiency of biopolymer in membrane supported ultrafiltration. The d-electron deficient metal ions are chelated by naturally occurring biopolymer sericin containing polypeptides of several amino acids. Thermodynamically, an equilibrium is established between chelated metal ions in retentate on one side and escaped metal ions in permeate solution on other side of membrane due to metal–sericin complexation in ultrafiltration cell. The amount of metal ions entrapped on account of metal–sericin complexation (MSC) is the function of rejection percentage  $R\%$  in polymer supported ultrafiltration. A novel theoretical model or relationship between  $R\%$  and metal–sericin complexation constant  $K^f$  was developed at Donnan equilibrium followed by the evaluation of thermodynamic functions such as  $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$  in sericin-facilitated ultrafiltration. High rejection percentage ( $R > 90\%$ ) of Cu(II) and Zn(II) implies the significant stability of MSC for these metal ions at three different temperatures 293 K, 303 K and 313 K. Greater values of  $R\%$  were observed at lower concentration of each metal ion on account of enhanced chelating power of applied biopolymer sericin which is susceptible to concentration of metal ions. In addition, rejection data were statistically elaborated to support the argument based on developed novel model.

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## 1. Introduction

Sericin and fibroin are two major proteins of silk derived from the silk worm *Bombyx mori*. Fibroin with fibrous nature is a delicate thread linked by disulfide bonds and surrounded by successive sticky layers of sericin which are supportive to form cocoon. Sericin or silk glue is a globular protein that constitutes 25–30% silk [1–3]. Molecular weight of sericin is not exactly known because it is mixture of proteins with different molecular properties, and thus it exists in a wide range of molecular weight approximately from 1 to over 410 kDa [4,5] depending on methods of extraction, temperature, pH and processing time [6–8]. Sericin with low molecular weight of approximately 20 kDa is soluble in cold water and high molecular sericin is soluble in hot water [9]. Sericin is a polypeptide biomacromolecule with around 18 kinds of amino acids which have strong polar side chains such as hydroxyl, carboxyl and amino groups [6]. High contents of serine and aspartic acid in sericin confer the hydrophilic character of functional groups carrying lone pairs of electrons which could

potentially be donated to d-electron deficient metal ions via chelation [6,10–14]. The small metal ions are trapped in the macromolecules of polypeptides and subsequently rejected by an ultrafiltration membrane effectively [15–17]. High permeate flux is obtained at a reasonable rejection rate by employing the polypeptide-facilitated ultrafiltration [18,19]. This is interpreted in terms of large molecular sizes of the polypeptides and their strong capacities to chelate with electron deficient species for instance, positively charged metal ions [20,21]. The separation performance of this novel approach is measured in terms of rejection percentage of the metals at transmembrane pressure (TMP) [22–24]. An ultrafiltration process works on the principle of osmotic equilibrium across the semipermeable membrane which is impermeable to metal–sericin complex and permeable to un-trapped metal ions in metal and polymeric solution. Applied solution possesses metal ions on both sides of porous barriers such as membrane at equilibrium with unequal concentration because of metal–sericin complexation in retentate. The retentive phase keeps trapped metal ions as many as possible depending on chelating efficiency of biopolymer or the level of substrate saturation. Whereas, the some un-trapped metal ions can escape through the membrane pores in the permeate solution. Membrane supported ultrafiltration comprises two phases such as retentate

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with metal–sericin complex (MSC) and permeate carrying untrapped metal ions (UM). There are assumingly two components in our system MSC and UM. In ultrafiltration solution, MSC acts as polyelectrolyte ions ( $P^{z-}$ ) and metals are also in ionic forms. Under such conditions, theoretically Donnan equilibrium across the membrane or porous barrier takes place. Thermodynamically, Gibbs free energy ( $G$ ) is the chemical potential ( $\mu$ ) with respect to components MSC and UM at constant pressure and temperature in treatment of multicomponent phase equilibria [25] as follows:

$$\mu_{MSC} = \left( \frac{\partial G}{\partial n_{MSC}} \right)_{T,P,UM}, \quad \mu_{UM} = \left( \frac{\partial G}{\partial n_{UM}} \right)_{T,P,MSC} \quad (1)$$

With two components in ultrafiltration system, for convenience we take

$$n_i = n_{MSC, UM}$$

Given system permits that the number of moles of any component may increase or decrease, but the total number of moles must remain constant. A change in the overall Gibbs free energy of the system might be expressed as a sum of the following contributions [26].

System contains phases of retentate and permeate solutions on either side of membrane; so thermodynamically:

$$\Delta G = \Delta G_{retentate} + \Delta G_{permeate} \quad (2)$$

At equilibrium,

$$\Delta G = 0 \quad (3)$$

Since there are two components MSC and UM, Eq. (2) can be rewritten as

$$\Delta G = \mu_{MSC} dn_{MSC} + \mu_{UM} dn_{UM} = 0 \quad (4)$$

The equilibrium between the two phases means that

$$\Delta G = 0 = \Delta G_{retentate} + \Delta G_{permeate} = \sum \mu_{i(retentate)} dn_{i(retentate)} + \sum \mu_{i(permeate)} dn_{i(permeate)} \quad (5)$$

For each component, the following holds:

$$\mu_{i(retentate)} dn_{i(retentate)} + \mu_{i(permeate)} dn_{i(permeate)} = 0 \quad (6)$$

According to law of conservation of matter, any substance lost from one phase must appear in the other phase in multiphase equilibria, therefore

$$dn_{i(retentate)} = -dn_{i(permeate)} \quad (7)$$

By substituting Eq. (7) into (6), it can be concluded that at the phase equilibrium (i.e., multi-component equilibrium with retentate and permeate phases) at constant temperature and pressure

$$\mu_{i(retentate)} = \mu_{i(permeate)} \quad (8)$$

That is for each component in two-phase system, so

$$\mu_{MSC(retentate)} = \mu_{MSC(permeate)} \quad \text{OR} \quad \mu_{UM(retentate)} = \mu_{UM(permeate)} \quad (9)$$

At Donnan equilibrium, chemical potential in Eq. (9) of each component remains the same in two phases in spite of its different values in multi-components phase equilibria and the following relationship holds kinetically:

$$MSC_{retentate} \xrightleftharpoons[k_2]{k_1} UM_{permeate} \quad (10)$$

where  $k_1$  and  $k_2$  are kinetic constants for formation and dissociation of sericin–metal complex, thus

$$k_1[MSC_{retentate}] = k_2[UM_{permeate}] \quad (11)$$

If  $K$  is equilibrium constant at Donnan equilibrium between metal sericin complex in retentate and escaped metal ions in permeate solution, then we can write

$$\frac{k_2}{k_1} = K = \frac{MSC_{retentate}}{UM_{permeate}} \quad (12)$$

If we suppose that there is only metal sericin complex in retentate solution and permeate solution only consists of very small amount of escaped metal ions under ideal condition, then value of  $R$  (rejection percent) and  $(100-R)$  in sericin supported ultrafiltration depends on  $MSC_{retentate}$  and  $UM_{permeate}$  respectively, so Eq. (12) changes into

$$K = \frac{R}{(100-R)} \quad (13)$$

Nevertheless, in terms of metal concentration to be bound or unbound with biopolymer, a correlation of rejection percent  $R(\%)$  to metal sericin complex constant ( $K^f$ ) is evaluated at Donnan equilibrium if permeate solution after ultrafiltration contains only unbound concentration of each metal ( $C_{un}$ ) and retentate solution consists of bound metal concentration ( $C_b$ ) after the formation of MSC in aqueous solution. Under such conditions, we can determine size of binding sites ( $s$ ) per hypothetical  $NH_2-$  group of PDL-S which is mainly responsible for chelation in applied biopolymer sericin and binding or metal sericin complex formation constant ( $K^f$ ) using Carter et al.'s expression [27] in the following form:

$$\frac{C_b}{C_{un}} = \frac{K^f [Sericin]}{2s} - K^f C_b \quad (14)$$

The  $R\%$  values of five metals in aqueous solution were determined at  $2.0 \times 10^5$  Pa TMP and variable temperatures of 293 K, 303 K, and 313 K by using the following empirical equation:

$$R\% = \left[ 1 - \frac{C^p}{C^f} \right] \times 100 \quad (15)$$

where  $C^p$  and  $C^f$  stand for metal concentration in permeate and feed solutions respectively.

We substituted values of  $C_b$  and  $C_{un}$  from Eq. (14) for  $R\%$  (rejection percent value) and  $100-R\%$  respectively as obtained from empirical Eq. (15) because these concentration values (i.e.  $C_b$  and  $C_{un}$ ) of bound and unbound metals to scavenger control rejection percentage ( $R\%$ ) in ultrafiltration study. Thus we can say that  $MSC$  is the function of  $R\%$  or mathematically  $MSC=f(R\%)$  operating in retentate side and  $UM$  is the function of  $(100-R)$  or  $UM=f(100-R)$  in permeate solution of membrane supported ultrafiltration cell. Now Eq. (14) assumes the following form after substitution:

$$\frac{R}{100-R} = \frac{K^f [Sericin]}{2s} - K^f R \quad (16)$$

A plot of  $R/(100-R)$  versus  $R$  gives straight line equation with slope  $K^f$  and intercept  $K^f [Sericin]/2s$  for MSC in ultrafiltration of heavy metals facilitated by membrane for fixed concentration of 0.05 (W/V)% sericin and 50–130 mg L<sup>-1</sup> concentration range of metal ions at  $2.0 \times 10^5$  Pa pressure and variable temperatures. Knowing the values of  $K^f$ , the values of  $\Delta G^0$  for each metal–sericin interaction are evaluated using the fundamental relationship in thermodynamics:

$$\Delta G^0 = -R^*T \ln K^f \quad (17)$$

where  $\Delta G^0$  is the standard Gibbs energy,  $R^*$  is the universal gas constant with value 8.314 J K<sup>-1</sup> mol<sup>-1</sup> and  $T$  is the temperature in

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