

Influence of Salinity and pH of Solution on Partition Coefficient of Ion at Solution-Charged Media Interface

Yoshimi SEIDA¹

Abstract

Influence of salinity and pH of solution on the partition coefficient of cesium; $K_{d,Cs}$ at solid-liquid interface in charged media contacting with the saline solution was investigated based on the equilibrium chemical reaction model with ion-exchange, dissociation of water and dissociation of the fixed charge in the media. The $K_{d,Cs}$ was estimated by the theoretical model simulation to be decreased with the increase of salinity and pH of solution. The $K_{d,Cs}$ shows a constant value in dilute saline and acidic pH solution. When the salinity decreased below $10^{-3}M$, the $K_{d,Cs}$ tends to show a constant value (plateau region appears at small salinity region). The plateau region of the $K_{d,Cs}$ extends to high salinity region with the decrease of solution pH. The $K_{d,Cs}$ increases in each condition of salinity and pH in the media with larger charge density.

Keyword: Ion-exchange, Partition Coefficient, Salinity, pH, Charge media

1. Introduction

In the previous work, a model that described unsteady state transport of ions through a charged media with ion-exchange reaction was constructed (Seida et al., 2009). System of the model is as follows. Suppose a through-diffusion test method configuration for measurement of effective diffusion coefficient, D_e , of target ion (B^+) in a charged media with ion-exchange, as described schematic diagram of the method in Fig.1. Schematic diagram of the system with initial ion and potential distributions is shown in Fig.2. The media is equilibrated with aqueous 1:1 type electrolyte salt (A^+C^-) solution with its concentration, $C_{i,0}$. The model equations describing the system are shown in Eqs. (1) ~ (13). The parameters with overline indicate those in the charged media. The subscript 0 indicates initial value. Transport of ions was considered based on Nernst-Planck model shown by eq. (1). First term of right side of the Eq.(1) indicates diffusion of ion and the second term indicates migration due to electric potential gradient that is produced by the transport of ions. Nernst-Einstein relation was used for electrochemical mobility of ions (Eq.(2)). Eqs.(3) and (4) indicate

¹ Natural Science Laboratory, 5-28-20, Hakusan, Bunkyo-ku, Tokyo 112-8606, Japan

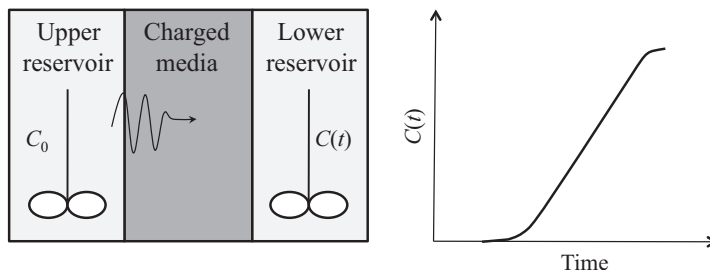


Fig. 1 Through-diffusion test configuration and breakthrough curve for determination of D_e .

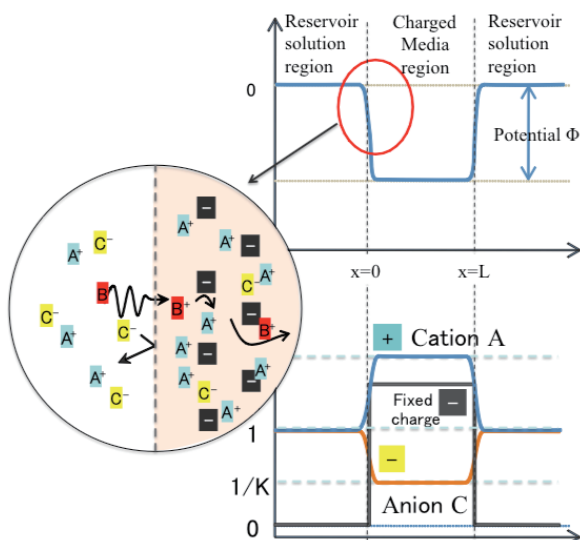


Fig. 2 Schematic diagram of ion and potential distributions of the system at initial condition

electro-neutrality and dissociation of water. Donnan equilibrium was supposed at the interface between outer solution and the charged media. Partition of each ion and difference of electric potential at the interface were determined based on Donnan equilibrium theory (Eqs. (5) and (6)). Electric potential distribution that is produced due to the transport of ions was considered in the model. The counter ion, B^+ diffuses with ion-exchange with original counter ion, A^+ of charged site X in the media. Eq. (7) indicates ion-exchange equilibrium constant for the reaction. Eq. (1) was introduced into net charge balance shown by Eq. (8) in order to obtain the equation for calculation of the electric potential distribution based on the transport of ions. The obtained equation is the same form with the Poisson-Boltzman equation.

$$\frac{\partial \bar{C}_i}{\partial t} = D_{e,i} \frac{\partial^2 \bar{C}_i}{\partial x^2} + u_i \frac{\partial}{\partial x} \left(\bar{C}_i \frac{\partial P}{\partial x} \right) - \rho \frac{\partial q_i}{\partial t} \quad (1)$$

$(i = A^+, B^-, C^+, D^-, H^+, OH^-)$

$$u_i = \frac{z_i e D_{e,i}}{kT} \quad (2)$$

$$\sum_i z_i \bar{C}_i - \bar{C}_X = 0 \quad (3)$$

$$K_w = \bar{C}_{H^+} \bar{C}_{OH^-} \quad (4)$$

$$K^{zi} = \frac{C_{i,x=0,L}}{C_{i,x=0,L}} \quad (5)$$

$$\phi = \frac{kT}{e} \ln K \quad (6)$$

$$K_{A-B} = \frac{C_{A^+} \bar{C}_{X=B}}{C_{X=A} C_{B^+}} \quad (7)$$

$$\sum z_i \frac{\partial q_i}{\partial t} = 0 \quad (8)$$

Initial condition

$$\bar{C}_i = 0 \quad (t=0, 0 \leq x \leq L) \quad (9)$$

Boundary conditions

$$\bar{C}_i = C_{i,0} K^{zi} \quad (i = A^+, C^-, t \geq 0, 0 \leq x \leq L) \quad (10)$$

$$C_i = C_{i,0} \quad (i = A^+, C^-, t \geq 0, x = 0_-, L_+) \quad (11)$$

$$C_{B^+} = C_{B^+,0} \quad (t \geq 0, x = 0_-) \quad (12)$$

$$C_{B^+} = 0 \quad (t \geq 0, x = L_+) \quad (13)$$

Equation for the calculation of D_e in the through-diffusion test method

$$\frac{Q(t)}{A \cdot L \cdot C_{B^+,0}} = \frac{D_e}{L^2} t - \frac{\alpha}{6}, \alpha = \varepsilon + \rho K_d \quad (14)$$

The partition of mobile ions between the charged media and contacting outer solution is defined by Donnan ratio; K^z (concentration ratio of mobile ions between in the outer solution and in the charged media). In the case of 1:1 type electrolyte (A^+C^-) simple system without any competitive counter ions, the Donnan ratio of each ion can be shown in Eq.(15) as the function of concentration of ion in the outer solution C_0 and the concentration of fixed charge \bar{C}_x when the ions in the charged media are mobile irrespective sorbed or not (Hanai, 1979). The electric potential difference produced due to the Donnan equilibrium at the boundary can be shown by Eq.(16). It is also the function of C_0/C_x .

$$K^z = \frac{1}{\sqrt{\left(\frac{\bar{C}_x}{2C_0}\right)^2 + \left(\frac{1}{\bar{C}_x}\right)^2 + \frac{z\bar{C}_x}{2C_0}}} \quad (15)$$

$$\Delta\phi = \frac{RT}{F} \ln \frac{1}{C_0} \left[\sqrt{\left(\frac{\bar{C}_x}{2}\right)^2 + \left(\frac{C_0}{\bar{C}_x}\right)^2} + \frac{\bar{C}_x}{2} \right] \quad (16)$$

The D_e of diffusant B^+ is obtainable based on breakthrough curve in the through-diffusion test under constant concentration in upper reservoir. The equation determining the D_e from the breakthrough curve in the through-diffusion method is shown in Eq.(14). From the slope of breakthrough curve obtained from the model simulation, D_e was determined. One set of the equations was solved numerically using the initial and boundary conditions shown in Eqs.(9) ~ (13) to evaluate transport dynamics and reliability of the D_e obtained by the through-diffusion test method in the previous work. The model simulation gave results that the D_e determined by the breakthrough curve of through-diffusion test method increased monotonically with decreasing salinity in the contacting solution. When the concentration of target is small compared with the concentration of background salt in outer solution, K_d of the target at the solid-liquid interface closes to a constant value. Increase of D_e of target with the decrease of salinity in the contacting solution will occur due to the principle of determination of D_e based on the Eq.(14). However, the D_e obtained by the procedure is not true D_e because it is obtained using concentration gradient determined based on the Donnan equilibrium (influence of boundary condition setting). The D_e value corrected by the Donnan ratio K^z gives true D_e value in the simulation. This unexpected error is induced due to the boundary condition determined based on the Donnan equilibrium theory. Research from viewpoint of influence of pH and salinity of solution on the partition coefficient at the interface will give an important insights into the phenomena that control the partition at the interface.

In the present study, model analysis considering the influence of salinity (1:1 type support

electrolyte) and pH of solution on partition of dilute Cs diffusant ; $K_{d,Cs}$ in charged media contacting with saline solution was performed. The influence on the $K_{d,Cs}$ was examined theoretically based on equilibrium chemical reaction model.

2. APPROXIMATED THEORETICAL MODEL OF Na-Cs-H TERNARY ION-EXCHANGE SYSTEM

Binary model considering Cs-Na ion-exchange was not able to explain the saturation of $K_{d,Cs}$ in dilute salinity condition. The $K_{d,Cs}$ at the solid-solution interface increased monotonically with the decrease of salinity in the binary exchange model. Then, theoretical model for Cs-Na-H ternary ion-exchange system was constructed. The model considers mass balance of each ion, ion-exchange equilibrium between H and Na as well as between Na and Cs, and dissociation (protonation) of charged site as a function of solution pH. The mass balances for Na^+ , Cs^+ and X (fixed anionic charge site in the charged media) are shown in Eqs. (17) ~ (19), respectively.

$$C_{Na^+} + \bar{C}_{NaX} = C_{Na^+,0} + \bar{C}_{NaX,0} \quad (17)$$

$$C_{Cs^+} + \bar{C}_{CsX} = C_{Cs^+,0} + \bar{C}_{CsX,0} = \bar{C}_{Cs^+,0} \quad (18)$$

$$\bar{C}_{NaX} + \bar{C}_{CsX} + \bar{C}_{HX} = Q \quad (19)$$

Equilibrium ion-exchange constants; $K_{A,B}$ for Na-Cs and H-Na exchange system are shown in Eqs. (20) and (21), respectively. Dissociation of water is shown in Eq. (22). Introducing Eqs. (20) and (21) into Eq. (19), Eqs. (23) and (24) are derived using Eqs. (17) and (18). Then, Eq. (25) are derived introducing the Eqs. (23) and (24) into Eq. (20). Eqs. (23) and (24) were calculated using Eq. (25) with given salinity (C_{Na}) and pH (C_H). Finally, $K_{d,Cs}$ was calculated using Eq. (26). When the concentrations of Na^+ , Cs^+ and H^+ (solution pH) were given, the $K_{d,Cs}$ can be determined.

$$K_{Cs-Na} = \frac{K_{Cs}}{K_{Na}} = \frac{\bar{C}_{CsX} C_{Na^+}}{\bar{C}_{NaX} C_{Cs^+}} \quad (20)$$

$$K_{H-Na} = \frac{K_H}{K_{Na}} = \frac{\bar{C}_{HX} C_{Na^+}}{\bar{C}_{NaX} C_{H^+}} \quad (21)$$

$$C_{H^+} C_{OH^-} = K_w \quad (22)$$

$$C_{\text{Cs}^+} = \frac{QC_{\text{Na}^+} - \bar{C}_{\text{NaX}}(C_{\text{Na}^+} + K_{\text{H-Na}}C_{\text{H}^+})}{K_{\text{Cs-Na}}\bar{C}_{\text{NaX}}} \quad (23)$$

$$\begin{aligned} \bar{C}_{\text{CsX}} &= C_{\text{Cs}^+,0} - C_{\text{Cs}^+} \\ &= \frac{-QC_{\text{Na}^+} - \bar{C}_{\text{NaX}}(C_{\text{Na}^+} + K_{\text{H-Na}}C_{\text{H}^+} + K_{\text{Cs-Na}}C_{\text{Cs}^+,0})}{K_{\text{Cs-Na}}\bar{C}_{\text{NaX}}} \end{aligned} \quad (24)$$

$$\begin{aligned} \bar{C}_{\text{NaX}} &= \frac{-b \pm \sqrt{b^2 + 4(C_{\text{Na}^+} + K_{\text{H-Na}}C_{\text{H}^+})K_{\text{Cs-Na}}QC_{\text{Na}^+}^2}}{2(C_{\text{Na}^+} + K_{\text{H-Na}}C_{\text{H}^+})K_{\text{Cs-Na}}} \\ b &= -QC_{\text{Na}^+}K_{\text{Cs-Na}} + C_{\text{Na}^+}^2 + K_{\text{H-Na}}C_{\text{Na}^+}C_{\text{H}^+} + K_{\text{Cs-Na}}C_{\text{Na}^+}C_{\text{Cs}^+,0} \end{aligned} \quad (25)$$

$$\begin{aligned} K_{\text{d,Cs}} &= \frac{\bar{C}_{\text{CsX}}}{C_{\text{Cs}^+}} \frac{1}{\varepsilon/\rho} \\ &= \frac{-QC_{\text{Na}^+} + \bar{C}_{\text{NaX}}(C_{\text{Na}^+} + K_{\text{H-Na}}C_{\text{H}^+} + K_{\text{Cs-Na}}C_{\text{Cs}^+,0})}{K_{\text{Cs-Na}}\bar{C}_{\text{NaX}}} \\ &\quad \times \frac{K_{\text{Cs-Na}}\bar{C}_{\text{NaX}}}{QC_{\text{Na}^+} - \bar{C}_{\text{NaX}}(C_{\text{Na}^+} + K_{\text{H-Na}}C_{\text{H}^+})} \frac{\rho}{\varepsilon} \\ &= \frac{-QC_{\text{Na}^+} + \bar{C}_{\text{NaX}}(C_{\text{Na}^+} + K_{\text{H-Na}}C_{\text{H}^+} + K_{\text{Cs-Na}}C_{\text{Cs}^+,0})}{QC_{\text{Na}^+} - \bar{C}_{\text{NaX}}(C_{\text{Na}^+} + K_{\text{H-Na}}C_{\text{H}^+})} \frac{\rho}{\varepsilon} \end{aligned} \quad (26)$$

Numerical calculation of the ternary ion-exchange model was performed as follows. First, using equilibrium relation of Cs-Na and H-Na ion-exchange reactions, concentration of NaX was calculated as a function of Na (salt) concentration and pH. Then, concentration of Cs was calculated as a function of concentration of proton (pH) and NaX (Eq.(23)). Next, from the mass balance of Cs (Eq.(18)), concentration of CsX was calculated (Eq.(24)). The partition coefficient $K_{\text{d,Cs}}$ at the interface was calculated using the calculated concentration of Cs and CsX. The parameters used in the present simulation are summarized in Table 1.

Table 1 The parameters used in the simulation

parameter	value	unit
Q	60, 30	mol/l
K_{Na}	20	-
K_{Cs}	21.6	-
K_H	21.88	-
$K_{Cs:Na}$	39.810	-
$K_{H:Na}$	75.0	-
ρ	1600	g/l
ϵ	0.4034	-
K_w	10^{-14}	mol ² /l ²

3. Results and Discussion

Fig.3(a) indicates the calculated $K_{d,Cs}$ as the function of salinity and solution pH. The results indicates that the $K_{d,Cs}$ decreased with the increase of concentration of Na (salinity). When the salinity decreased below $10^{-3}M$, the $K_{d,Cs}$ tends to show a constant value (plateau region appears at small salinity region). The plateau region of the $K_{d,Cs}$ extends to high salinity region with the decrease of solution pH. Fig.3(b) indicates the result in the case of half charge density of the media compared with the case in Fig.3(a). The $K_{d,Cs}$ value decreases in the small Q system. The results indicate that the $K_{d,Cs}$ saturates to a constant value in dilute salt salinity and low pH condition.

In the case of measurement of effective diffusion coefficient D_e in charged media by through-diffusion test method, the boundary condition that determines concentration gradient for diffusion of target in the media depends on the partition at the interface between the contacting solution and the charged media. The gradient that should be used in the calculation of the D_e is not a simple concentration difference of target between upper and lower reservoirs. The use of Eq. (14) needs consideration for the treatment of concentration gradient for acceptable D_e determination.

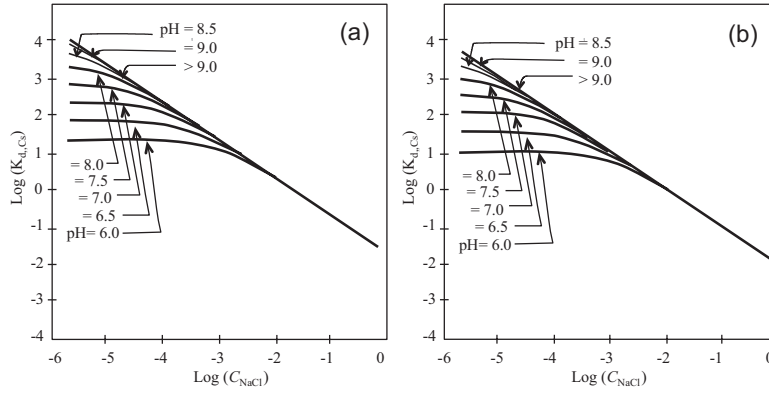


Fig. 3 The simulation results (a) $Q = 60$, (b) $Q = 30$

4. Conclusions

The $K_{d,Cs}$ at the interface between the charged media and the outer solution depends on salinity and pH of contacting solution. At alkaline condition, the $K_{d,Cs}$ increases with decreasing the salinity (concentration of NaCl) monotonically. The $K_{d,Cs}$ shows plateau at small salinity condition depending on solution pH. The plateau region of the $K_{d,Cs}$ extends to high salinity region with the decrease of solution pH. When applying the Donnan equilibrium at the interface between charged media and its outer solution, ternary ion-exchange model gives acceptable results of partition at the interface.

Nomenclature

A :	cross sectional area of media in through-diffusion test method	$[\text{m}^2]$
C_i :	concentration of ion species i	$[\text{mol/L}]$
C_l :	concentration in solution	$[\text{mol/L}]$
$\bar{C}_{X=i}$:	concentration of species i adsorbed to the charge site X	$[\text{mol/L}]$
C_0 :	initial concentration of specie i	$[\text{mol/L}]$
D_e :	effective diffusion coefficient	$[\text{m}^2/\text{s}]$
F :	Faraday's constant	$[\text{C/mol}]$
k :	Boltzman constant	$[\text{m}^2\text{kg/s}^2/\text{K}]$
$K_{d,i}$:	partition (distribution) coefficient of species i at	$[\text{kg/L}]$
K_{A-B} :	ion-exchange equilibrium constant	$[-]$
K_i :	dissociation constant of species i	$[-]$
K_w :	dissociation constant of water	$[\text{mol}^2/\text{l}^2]$

K^z :	Donnan ratio	[-]
L :	thickness of charged media	[m]
ϕ, P :	electric potential	[V]
Q :	mole of charged site	[mol]
$Q(t)$:	amount of target in the lower reservoir	[mol]
R :	gas constant	[J/K/mol]
t :	time	[s]
T :	absolute temperature	[K]
u :	electrochemical mobility	[cm ² /V/s]
x :	coordinate along media thickness	[m]
X :	fixed charge	
z :	valency	[-]
α :	retardation factor	
ε :	porosity	[-]
ρ :	density of charged media	[kg/m ³]
φ :	Donnan potential	[V]

Subscript

0:	initial condition
Cs-Na:	ion-exchange between Cs and Na
H-Na:	ion-exchange between H and Na

References

- [1] Crank, J., *The Mathematics of Diffusion*, Oxford Press, 1979
- [2] Davies, J.T., *Interfacial Phenomena*, Academic Press, 1963
- [3] Hanai, T., *Membrane and ions*, Kagaku Dojin, 1979 Tokyo
- [4] Seida, Y. *et al.*, Influence of boundary condition of diffusion test method on migration parameter in compacted bentonite, *Geochimica et Cosmochimica Acta*, **73** (13), *Goldschmidt Conference Abstracts 2009, Supplement 1191* (2009)

要 旨

荷電体の接液界面における分配係数に及ぼす塩分濃度と pH の影響

清 田 佳 美

塩水溶液に浸した荷電体の接液（固液）界面における分配係数について、化学平衡反応に基づく理論モデルを構築して溶液の塩濃度および pH 依存性を検討した。Cs-Na-H の三

元系イオン交換を考慮した平衡反応理論モデルを構築し、分配係数に及ぼす溶液の塩濃度および pH の影響をシミュレートした。溶液の pH が高い場合には、分配係数は塩濃度の低下と共に大きくなる一方で、溶液 pH が小さい場合には分配係数が変わらなくなる領域が低塩濃度領域に存在し、pH の低下とともにその領域が高塩濃度側に広がることを明らかにした。本結果から、荷電体中のイオンの実効拡散係数を算出する際の境界条件（溶液濃度勾配）の取扱いに注意を要することを示した。through-diffusion 法により拡散係数を算出する場合には、上流側の溶液濃度を用いて破過曲線の傾きから実効拡散係数を算出するのが一般的であるが、実際の拡散の濃度勾配は荷電体の接液界面における濃度で決まる濃度勾配である場合には、実効拡散係数の算出に用いる溶液濃度はこの界面濃度を用いる方が妥当である。