

반투막을 통한 수화된 이온의 투과속도 탈수화율 및 완화시간에 관한 연구

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Ion Permeability, Dehydration and Relaxation Times of Hydrated Ions Through Membranes

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요 약. 간단한 통계역학적 방법을 사용 수화된 이온의 완화시간, 탈수화시의 활성화, 에너지, 탈수화율 등을 계산하였다. 구상한 model에 의하면 수화된 물과 탈수화된 물 간의 평형상수, 물-이온간 에너지 항, 각종 species 간의 혼합 factor들이 들어있다.

이론과 실험은 잘 맞는 결과를 보이고 있다.

또한 이온이 탈수화시의 압력의 영향도 아울러 논의하였다.

ABSTRACT. A simplified statistical mechanical method was developed for the calculation of the dehydration fraction, activation free energy of dehydration, and the relaxation times of hydrated ions.

The model used includes the equilibrium constant between hydrated and dehydrated water, a water-ion interaction potential energy term, and a mixing factor for the species present. The agreement between theory and experiment is good.

The pressure dependence of ion dehydration is also discussed.

INTRODUCTION

There have been a number of papers which indicate that the dehydration of hydrated ions

plays a significant role in ionic diffusion through biological membranes, porous networks, and the specific adsorption of ions at the metal-solution surface¹⁻³. Recently Kim and Rubin⁴ evaluated the theoretical free energy of activation for dehydration of hydrated ions using an early partition function similar to that of Eley and

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In our study, a simplified method is used for the calculation of the dehydration of hydrated ions in terms of the equilibrium constant between hydrated water and free water (i.e., dehydrated water), since liquid partition functions for ionic solutions are not well developed^{6,7}.

We also discuss the correlations between the activation energy for ion dehydration and the relaxation times of hydrated ions ranging from several seconds to 10^{-11} seconds. The pressure dependence on the dehydration of hydrated ions is explicitly included in this paper and evaluated for certain systems.

THEORY

Assuming that the partial dehydration of ions at the membrane/solution interface is the rate determining step in ion diffusion through membranes, the partition function of the initial state, f , which consists of N_i ions with N_{bw} hydrated water molecules, is written as follows:

$$f = (f_{bw})^{N_{bw}} (f_{ion})^{N_i} \frac{N!}{N_i! N_{bw}!}, \quad (1)$$

where f_{bw} and f_{ion} are the partition functions of hydrated or bound water and that of ion, respectively, and $N = N_i + N_{bw}$. Similarly, the partition function of the activation state for dehydration f^* , which consists of N_i ions, N_{bw}^* hydrated water molecules and N_{fw}^* free water molecules is given by

$$f^* = (f_{bw})^{N_{bw}^*} (f_{fw})^{N_{fw}^*} (f_{ion})^{N_i} \frac{N!}{N_i! N_{bw}^*! N_{fw}^*!} \quad (2)$$

where f_{fw} is the partition function of free water. Since the total number of water molecules for the initial and activated states are the same, $N_{bw} = N_{bw}^* + N_{fw}^*$. Therefore, the equilibrium constant K^* between initial and activated state is given by

$$K^* = (f^*/f) (e^{-V_0/kT})^N, \quad (3)$$

where V_0 is the activation energy barrier for the hydration, k is the Boltzmann constant, and T the absolute temperature. With the use of Equations (1) and (2), Equation (3) can be rearranged as:

$$K^* = \frac{N_{bw}!}{N_{bw}^*! N_{fw}^*!} \frac{(f_{bw})^{N_{bw}^*} (f_{fw})^{N_{fw}^*}}{(f_{bw})^{N_{bw}}} \cdot (e^{-V_0/kT})^N. \quad (4)$$

To simplify Equation (4) by eliminating the explicit expression for partition functions, the following procedures were considered. Let x_b and x_f be the probability of water molecule bound to water molecules and onto the ions at the interface. Then, $N_{bw}^* = x_b N_{bw}$, $N_{fw}^* = x_f N_{bw}$, and $x_f + x_b = 1$. The equilibrium constant K between the free water state and the hydrated state is:

$$K = x_f/x_b = f_{fw}/f_{bw} \quad (5a)$$

and

$$x_b = 1/1+K, \quad x_f = K/1+K. \quad (5b)$$

Combining (5a), (5b), and (4), one obtains

$$K^* = \frac{N_{bw}!}{N_{bw}^*! N_{fw}^*!} \frac{(f_{bw})^{1/1+K} (f_{bw}K)^{K/1+K} N_{fw}}{(f_{bw})^{N_{bw}}} (e^{-V_0/kT})^N. \quad (6)$$

Rearranging Equation (6), K^* is given by:

$$K^* = \frac{N_{bw}!}{N_{bw}^*! N_{fw}^*!} (K^{K/1+K})^{N_{bw}} (e^{-V_0/kT})^N \quad (7)$$

The standard free energy of activation for having N_{fw}^* free water from hydrated ions is $\Delta G^* = -KT \ln K^*$. (8)

The relaxation lifetime, τ , of a hydrated water molecule for ions is also written as (4)

$$\tau = \frac{h}{kT} e^{\Delta G^*/kT} \quad (9)$$

ΔG^* and τ can be obtained if the values of K ,

V_0 and the mixing factors in Equation (7) are known.

We take N as Avogadro's number; N is given by:

$$N = N_{ion} + N_{bw} = N_{ion} \div (N_{ion} \times n_{bw}). \quad (10)$$

Here, n_{bw} is the hydration number of ions in the bulk solution and can be obtained from experiment, literature or theory⁸⁻¹⁰. The mixing factor in Equation (7) can be obtained; i.e., N_{bw} from Equation (10) and N_{bw}^* and N_{fw}^* from Equation (5).

Since experimental values for K are not available, best fit values are used, i.e., 0.155 for K^+ , 0.084 for Na^+ , 0.047 for Li^+ , 0.014 for Ca^{2+} , 0.010 for Mg^{2+} , and 0.017 for Al^{3+} at 25 °C. The potential energy barrier V_0 can be obtained from the following relationship:

$$V_0 = n_{bw}^* U_0 - n_{bw} U_0, \quad \text{where} \quad n_{bw}^* = \frac{1}{1+K} n_{bw}. \quad (11)$$

Equation (11) indicates the total potential energy difference of the hydrated ion cluster in the activated and initial states. In the activated state, the potential energy of interaction of free water with hydrated ion clusters is assumed to be zero. The same potential energy of interaction, U_0 , between water-ion pair is assumed for both the initial and activated states.

Then, the total potential energy of interaction, U_0 , between the ion and one water molecule about the Z axis is:

$$U_0 = -\frac{Ze\mu\cos\theta}{r^2} + \frac{Ze\theta_z(3\cos^2\theta-1)}{2r^3} - \frac{(Ze)^2\alpha_w}{2r^4} - \frac{3}{2} \frac{\alpha_i\alpha_w}{r^6} - \frac{I_i I_w}{I_i + I_w} + Ar^{-12}. \quad (12)$$

Here, Z, r, θ, e and I are the sign of the ion, the equilibrium distance between center of the ion and that of water, the angle between Ze and r axis, the electronic charge and ionization

potential, respectively; μ, θ_z and α are the dipole moment of water, quadrupole moment of water, and isotropic polarizability, respectively. The subscripts i and w denote ion and water, respectively. The repulsive constant A can be obtained using the condition $\left(\frac{\partial U_0}{\partial r}\right)_{r=r_i+r_w} = 0$, which is given as

$$\frac{2Ze\mu\cos\theta}{r^3} - \frac{3Ze\theta_z(3\cos^2\theta-1)}{2r^4} + \frac{2(Ze)^2\alpha_w}{r^5} - 9\frac{\alpha_i\alpha_w}{r^7} - \frac{I_i I_w}{I_i + I_w} - 12Ar^{-13} = 0. \quad (13)$$

To relate the pressure dependence of hydrated ions on dehydration, one must know the expression for K from Equation (11). The equilibrium constant can be written as

$$K = e^{-\Delta H/RT} e^{\Delta S/R} e^{-P\Delta V/RT} = K_0 e^{-P\Delta V/RT}, \quad (14)$$

where $\Delta H, \Delta S$ and ΔV are the molar enthalpy change, the molar entropy change and the molar volume difference between hydrated and bulk water, respectively. If $P=1$ atm, the effect in the last term in Equation (14) is neglected.

RESULTS AND DISCUSSION

Using the equations presented, the activation free energy for the dehydration of hydrated ions, the dehydration fraction, the relaxation lifetime, and the pressure dependence of the dehydration of the hydrated ion were calculated at the membrane interface. Table 1 lists the input physical data for the calculations.

In this paper, we discussed the dehydration processes using data for ionic diffusion through a biological membrane such as the squid axon membrane, which is assumed to form a restricted opening to the primary hydrated ions. The present treatment can be extended to other ions in water, and porous networks which involve dehydration effects.

Table 1. Input physical data used in the calculation.

	K ⁺	Na ⁺	Li ⁺	Ca ²⁺	Mg ²⁺	Al ³⁺	H ₂ O
$r, \text{\AA}^a$	1.38	0.95	0.60	0.99	0.65	0.50	1.38
$\alpha \times 10^{24} \text{cm}^{3b}$	1.39	0.156	0.0288	0.918	0.0859	0.0557	1.44
I, eV^c	31.81	47.29	75.62	51.21	80.14	119.96	8.65
n_{bw}^d	3	4	5	10	13	6 ^(e)	

^a R. M. Noyes, *J. Amer. Chem. Soc.*, **84**, 513 (1962).

^b E. Paschalis and W. Weiss, *Theoret. Chim. Acta(Berl.)* **13**, 381(1969).

^c Handbook of Chemistry and Physics, 51st Ed., The Chemical Rubber Co., 1970.

^d See reference (8).

^e See reference (9).

Table 2. Calculated values of ΔG^* , Δn and U_0 .

	K ⁺	Na ⁺	Li ⁺	Ca ²⁺	Mg ²⁺	Al ³⁺
$\Delta G^*, \text{Kcal/mole}$	7.08	7.45	7.93	8.16	11.12	19.77
Δn	0.4	0.31	0.23	0.14	0.13	0.1
$-U_0, \text{Kcal/mole}$	17.50	24.15	35.43	58.52	85.62	197.8

A. The Activation Free Energy of the Dehydration of Hydrated Ions, ΔG^* . Applying Equations (7) and (8), and also using Equations (10) through (13), one can evaluate ΔG^* and $\Delta n = n_{bw} - n_{tw}$. The results are summarized in Table 2.

It is of interest in Table 2 that the values of ΔG^* are in the order $\text{Al}^{3+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Li}^{+} > \text{Na}^{+} > \text{K}^{+}$. Some available experimental values of Li^{+} , Na^{+} and K^{+} ions for the squid axon in the resting state are in the order $P_K > P_{Na} > P_{Li}$ (11), and Δn values are in the order of $\text{K}^{+} > \text{Na}^{+} > \text{Li}^{+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Al}^{3+}$. It is quite likely that the degree of dehydration is related with the order of magnitude of ΔG^* for ions. It is a little discouraging to see that the theory and experimental data are in qualitative agreement.

B. Relaxation Time of Dehydration of Hydrated Ions, τ . There are several papers on the relaxation lifetime of hydrated ions¹²⁻¹⁶. The observed values are in the range of 10^{-9} seconds to several seconds. However, very few experimental data are available for the relaxa-

tion time of hydrated water at an interface^{17,18}. Using Equation (9), the relaxation time of a hydrated ion, τ , at the interface is obtained and compared with experimental values of τ in bulk liquid in Table 3.

Our results for alkali ions are about 10^{-8} sec, which is in the range of upper limit values observed at the mercury/electrolyte solution interface^{17,18} and is comparable with 10^{-9} sec of bulk solution. Again, one sees that our simplified procedures provide a good prediction of the wide range of τ values.

C. Pressure Dependence of the Dehydration of Hydrated Ions. Since we have an explicit functional expression for pressure dependence on equilibrium constant, K , and the hydration number of an ion at an interface, n_{bw} , one can evaluate these values at different pressures. Table 4 list the calculated values of n_{bw} and K values for K^{+} ion with change in pressure up to the 10^5 atm. For these calculations, the ΔV value was assumed to be -2cc .¹⁹

In Table 4, one sees that dehydration of hydrated ions is quite slow up to 10^3 atm, but

Table 3. Relaxation times of hydrated water.

	K ⁺	Na ⁺	Li ⁺	Ca ²⁺	Mg ²⁺	Al ³⁺
τ sec (calc.)	1.3×10^{-8}	2.4×10^{-8}	5.3×10^{-8}	7.8×10^{-8}	1.1×10^{-5}	25
τ sec ^a	10^{-9}	10^{-9}	10^{-9}	10^{-9}	10^{-6}	7.5

^a I. M. Klotz, "Membrane and Ion Transport", Vol. I, P. 106, Ed. E. Edward Bitter, Wiley Interscience, New York 1970.

Table 4. Calculated values of K at 25 °C and n_{hw} for K⁺ ions vs. pressure.

P_{atm}	K	n_{hw}
10^2	0.156	2.60
10^3	0.168	2.56
10^4	0.350	1.32
10^5	547	0.005

above this pressure, increases rapidly and finally at 10^5 atm, very few water molecules exist in the hydrated state.

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