

## Partition Equilibrium Between Charged Membrane and Single Electrolyte Aqueous Solution\*

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**Abstract** Ionic partition equilibrium in charged membrane immersed in solution of single electrolyte with mono-valence or multi-valence is systematically investigated and several expressions are established for determination of partition coefficients. On this basis, the effects of the ratio of membrane charge density to bulk electrolyte solution concentration, the charge sign and valence of electrolyte ions and the type of membrane on the partition equilibrium were analyzed and simulated within chosen parameters. It is revealed that ion partition is not related solely with the respective concentrations but also definitely with the concentration ratio of fixed group to bulk solution in addition to the charge sign and the valence. For a counterion, the partition coefficient increases with this ratio and the valence; while for a coion, the partition coefficient decreases with this ratio and the valence. The theoretical calculations were compared with the experimental data and a good agreement was observed.

**Keywords** partition coefficient, Donnan equilibrium, electrolyte, charged membrane

### 1 INTRODUCTION

Recently, one of the most significant achievements in membrane science and technology is the development and application of charged membrane, which may act as antifouling membrane for ultrafiltration or nanofiltration membrane for low biased-reversed osmosis and thus allow many applications in industrial areas, such as chemical processing, waste proposal, biochemical separation, water treatment, etc.<sup>[1-3]</sup>. To optimize these industrial processes, transport mechanism of electrolytes through the charged membrane receives more attention in recent years<sup>[4-8]</sup>. As far as transport phenomena of electrolyte in this kind of membrane is concerned, the first important thing may be the partition relationship of electrolytes at the membrane-solution interface. Only when the partition is clarified, can the transport be thoroughly interpreted because the partition behavior will provide preliminary information for ion transport. Unlike the distribution of an electrolyte at the solution-neutral membrane interface, the partition at solution-charged membrane will not only vary with the sign and valence of electrolyte ions in the solution but with the membrane properties as well<sup>[9-13]</sup>. In the present study, ionic partition equilibrium in the charged membrane immersed in the solution of a single electrolyte with mono-valence or multi-valence is systematically inves-

tigated. Expressions for partition coefficient were derived based on Donnan equilibrium for single electrolyte systems. On the basis of theoretical expressions, the effects of membrane fixed group concentration and solution concentration on the partition were analyzed in detail. To confirm the expressions, the partition data at various solution concentrations and various charged membrane concentrations were determined and fitted to the above-cited theoretical expressions.

### 2 THEORETICAL

The concentration of ions in charged membrane and in external aqueous solution obeys the Donnan equilibrium relationship

$$K = \left( \frac{c_i^m}{c_i^b} \right)^{1/z_i} \quad (1)$$

$i = +$  for cation ions, and  $i = -$  for anion ions

where  $z_i$  is the valence of ion  $i$  and  $K$  is the Donnan equilibrium constant having nothing to do with the ions existing in the solution.  $K$  can be obtained from equation of electroneutrality in the membrane

$$\sum z_i K^{z_i} c_i + \omega X_M = 0 \quad (2)$$

Here,  $\omega = +1$  for positively charged membrane, while

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$\omega = -1$  for negatively charged membrane. Then,  $K_i$ , the partition coefficient of ion  $i$ , which is defined by the ratio of concentration in the membrane to that in external solution<sup>[10]</sup>,  $K_i = c_i^m/c_i^b = K^{z_i}$  ( $i = +, -$ ), can be obtained.

### 2.1 1-1 (AB) type electrolyte system

In this case,  $z_+ = 1$  and  $z_- = -1$ . Substituting these values into Eq. (2) yields following quadratic equation

$$K^2 + \frac{\omega X_M}{c_a^b} K - 1 = 0 \quad (3)$$

where  $c_a^b$  is the bulk electrolyte concentration. Obviously, this equation has only one meaningful solution and the partition expressions in this case are

$$K_+ = \frac{-\omega X_M}{2c_a^b} + \sqrt{1 + \left(\frac{\omega X_M}{2c_a^b}\right)^2} \quad (4)$$

$$K_- = \frac{\omega X_M}{2c_a^b} + \sqrt{1 + \left(\frac{\omega X_M}{2c_a^b}\right)^2} \quad (5)$$

### 2.2 Electrolyte system type $n-j$ ( $A_jB_n$ )

For a more general case, in which the electrolyte is composed of  $j$ -valence anions and  $n$ -valence cations, the equation for  $K$  is

$$nj(K^n - K^{-j})C_a^b + \omega X_M = 0 \quad (6)$$

Eq. (6) has the following generalized form if the partition coefficients of both anion and cation are incorporated into

$$K_+ + \frac{\omega \lambda}{nj} = K_- \quad (7)$$

where  $\lambda$  is the concentration ratio of fixed group to bulk electrolyte. Obviously, 1-1 electrolyte system satisfies this equation based on Eqs. (4) and (5). It is a very general formula that reveals that the partition coefficient is directly related with concentration ratio other than the respective concentration in addition to the sign and valence of electrolyte ions and the membrane charge sign.

## 3 EXPERIMENTAL

### 3.1 Membrane

The membranes used here are a series of dense and negative membranes with different fixed group concentrations ranging from about 0.3 to 4 mol·L<sup>-1</sup>. They were prepared from engineering plastics poly(phenylene oxide) (PPO) in our lab<sup>[3,4]</sup>. The charge density is controlled by the degree of sulfonation. Table 1 shows the main properties of membranes used in this job. Before experiments, the membranes were conditioned with 1 mol·L<sup>-1</sup> HCl or NaOH alternately twice for 2 h and then soaked in 1 mol·L<sup>-1</sup> NaCl solution or 0.5 mol·L<sup>-1</sup> CaCl<sub>2</sub> overnight to ensure that all of the membrane sites were in the sodium form or the calcium form before use.

### 3.2 Partition equilibrium

The above-treated membranes in the sodium form with various fixed concentration were accurately cut into proper squares of about 30 × 30 mm<sup>2</sup>. These pieces of membrane were separately soaked in beakers containing 25 ml NaCl solution with known concentration. The solution was vibrated in a thermostatic vibrator at the constant temperature of (25 ± 0.5)°C. After at least 24 h, the membranes were taken out of the beakers and the concentration of solution in equilibrium was determined using a conductivity meter (Model SC51 pocket conductivity meter, Yokogawa Hokushin Electric, Tokyo, Japan). The salt concentration in the membrane was calculated from the initial and the equilibrium concentration of the solution. The above procedures were repeated when the initial concentration of NaCl solution was changed. CaCl<sub>2</sub> solution with different concentrations was used as a model electrolyte for the trend examination of a multi-valence system. The experimental procedures are the same as those of the NaCl system except that the membrane samples were transferred into the calcium form before experiments. The reproducibility for the partition measurements was less than 2% for replicate runs with the same membrane piece and less than 5% between different membrane pieces.

Table 1 Properties of the negatively charged membrane series\*

Number	Ion exchange capacity mmol·g <sup>-1</sup>	Water content g·g <sup>-1</sup>	Fixed group concentration mol·L <sup>-1</sup>	Thickness mm	Area resistance Ω·cm <sup>-2</sup>	Transport number	Burst strength MPa
1	0.04	0.11	0.36	0.18	< 1.5	> 0.95	> 5.0
2	0.25	0.204	1.24	0.17	< 1.5	> 0.95	> 5.0
3	1.01	0.248	4.055	0.18	< 1.5	> 0.95	> 5.0
4	1.2	0.317	3.827	0.20	< 1.5	> 0.95	> 5.0
5	1.38	0.365	3.77	0.18	< 1.5	0.95	> 5.0
6	1.23	0.369	3.324	0.18	< 1.5	> 0.95	> 5.0
7	1.66	0.521	3.187	0.21	< 1.5	> 0.95	> 5.0
8	2.39	0.926	2.581	0.20	< 1.5	> 0.95	> 5.0

\* All the measurements were conducted at 25°C.

## 4 RESULTS AND DISCUSSION

### 4.1 Calculated partition coefficients

#### 4.1.1 Univalent electrolyte system ( $AB$ type)

The theoretical trends for partition coefficient can be demonstrated based on Eqs. (4) and (5) in this case. Taking electrolyte contacting with negatively charged membrane ( $\omega = -1$ ) as an example, the partition coefficient of both cation and anion will vary with concentration ratio of fixed group to bulk electrolyte and the results were shown in Fig. 1. Obviously, when the concentration ratio increases (bulk concentration decrease or fixed group concentration increase),  $K_+$  will increase for negatively charge membrane (NCM) and at the same time  $K_-$  decreases. The opposite trends will be observed in positively charged membrane (PCM). Because when concentration ratio increases, the coion exclusion due to Donnan effect increases, membranes tend to absorb less coions and thus  $K_+$  in PCM and  $K_-$  in NCM, with cation A or anion B being the respective coion, is decreased. It is derived from Eqs. (4) and (5) that  $K_+$  and  $K_-$  in PCM or NCM change in opposite directions. Both curves approach unity when the concentration ratio is small enough (approaching zero) at large enough salt concentration or much less fixed group concentration.

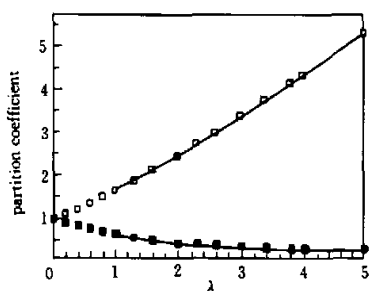


Figure 1 Partition coefficient versus the concentration ratio of fixed group to bulk electrolyte in univalent ion system

—■—  $K_+$  in PCM or  $K_-$  in NCM;  
—□—  $K_+$  in NCM or  $K_-$  in PCM

#### 4.1.2 Multi-valent electrolyte system type $n-j$ ( $A_jB_n$ type)

Figure 2 demonstrates the case of  $A_jB$  type electrolytes ( $j=1,2,3$ , A univalent) contacting with a positively charged membrane. Obviously, the partition coefficients of all the anions with different valence will increase with the increase in concentration ratio of fixed group to bulk solution. Because an anion is a counterion in regard to PCM and an increase in concentration ratio means that the charged density in the membrane increases, more anions are to be absorbed into the membrane, giving rise to an increase in partition coefficient for anions. It can be similarly elu-

cidated that the partition coefficient of a cation will decrease with concentration ratio in PCM. At a given concentration ratio, the partition coefficients for counterions (anions here) will decrease with the valence when the concentration ratio is the same. This is because that when the concentrations of all the considered electrolytes are the same, the equivalent concentration of an anion is proportional to the valence it carries, giving rise to a decrease in equivalent concentration ratio. And therefore, following the analysis in section 4.1.1, the partition coefficient for an anion in PCM will decrease with an increase in valence. In fact, from the theoretical point of view, for same equivalent concentration, the partition coefficient of a counterion will increase with the valence due to an increase in electrostatic attractive force. For  $K_+$ , the analyses are the same as the above.

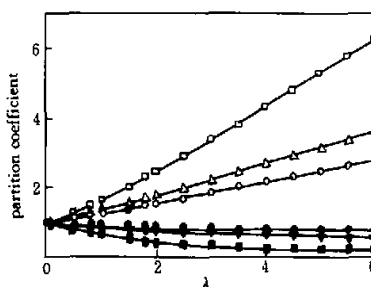


Figure 2 Partition equilibrium of  $A_jB$  type electrolyte systems in a PCM

—□—  $K_-$ ,  $j=1$ ; —■—  $K_+$ ,  $j=1$ ; —△—  $K_-$ ,  $j=2$ ;  
—▽—  $K_+$ ,  $j=2$ ; —○—  $K_-$ ,  $j=3$ ; —●—  $K_+$ ,  $j=3$

Figure 3 demonstrates the case of  $A_jB$  type electrolytes ( $j=1,2,3$ ) contacting with negatively charged membrane. It is observed in this case that partition coefficient of cation A (counterion) increases with the concentration ratio and decrease with the valence of the anion. This trends are attributed to the same reason as the above. However, partition coefficient of anion B (coion) keeps approximately unchanged with the valence due to the increase of both electrostatic repulsion force (a negative effect) and equivalent concentration (a positive effect) with the valence.

For  $AB_j$  type electrolyte system, it can be discussed in a manner analogous to the above and the results are not shown for space saving.

Figure 4 demonstrates the cases of  $A_jB_n$  electrolyte systems. Based on the conventional electrolytes, only  $A_2B_3$  and  $A_3B_2$  type electrolytes equilibrated with positively charged membrane are considered here. The results are mostly the same as the above multivalent system. It is clearly observed that the partition coefficients for both cation and anion in the  $A_3B_2$  type electrolyte system are larger than those

in  $A_2B_3$  type electrolyte system, respectively. This is because that anion (counterion in PCM) in the former system carries more valence than that in the latter system; while cation (coion corresponding to PCM) in the former system carries less valence than that in the latter. So the PCM exerts larger attractive force to anions and less repulsive force to cations in the former system. If NCM is considered, it is not difficult to conjecture that the behavior of  $A_2B_3$  type electrolyte in PCM is the same as  $A_3B_2$  type electrolyte in NCM, while the behavior  $A_3B_2$  type electrolyte in PCM is the same as  $A_2B_3$  type electrolyte in NCM. Because in these two systems, both the coion and counterion have equal valence in regards to the respective membrane.

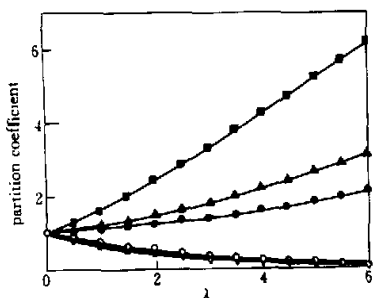


Figure 3 Partition equilibrium of  $A_jB$  type electrolyte systems in NCM

—■—  $K_+$ ,  $j = 1$ ; —□—  $K_-$ ,  $j = 1$ ; —▲—  $K_+$ ,  $j = 2$ ;  
—▽—  $K_-$ ,  $j = 2$ ; —●—  $K_+$ ,  $j = 3$ ; —○—  $K_-$ ,  $j = 3$

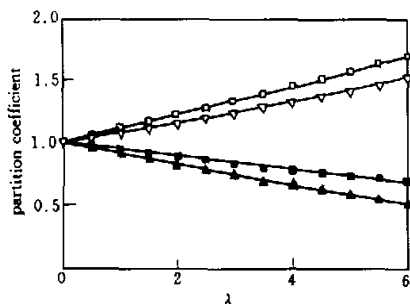


Figure 4 Partition equilibrium of  $A_jB_n$  type electrolyte systems in PCM

—■—  $K_+$ ,  $A_3B_2$  type; —□—  $K_-$ ,  $A_3B_2$  type;  
—▲—  $K_+$ ,  $A_2B_3$  type; —▽—  $K_-$ ,  $A_2B_3$  type

4.2 Experimental confirmation

To check the validity of the theoretical analyses, the partition coefficients for model electrolytes—NaCl and  $CaCl_2$  solutions contacting with a series of negative membranes with a fixed concentration range of  $0.3\text{--}4.0\text{ mol}\cdot\text{L}^{-1}$  were experimentally determined. Fig. 5 shows the results of mono-valence electrolyte NaCl solution contacting with these membranes. Only the partition coefficient of the cation (sodium ion) is shown here. Obviously, from the whole concentration

range in the bulk solution and the fixed group concentration of membrane, all the calculated values are in good agreement with the experimental observations. Especially, the better agreement is found in the middle range of fixed group concentration. Since the partition coefficient of a coion ( $Cl^-$ ) is just a reciprocal to that of a cation, it is not difficult to deduce that same agreement can be obtained for partition coefficients of the chloride ion, though the results are not demonstrated for simplicity.

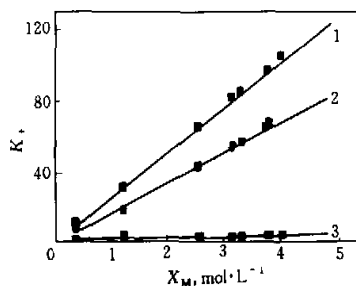


Figure 5 Experimental confirmation for the equilibrium partition in the system of monovalence ions contacted with NCM

[NaCl],  $\text{mol}\cdot\text{L}^{-1}$ : 1—0.04; 2—0.06; 3—1.0  
— theoretical; ■ experimental

The results of a multi-valence system are shown in Fig. 6. For simplicity, only  $CaCl_2$  is used as the model electrolyte. It is observed that the experimental partition coefficients for coions in the considered concentration range decrease slightly with fixed group concentrations, just as predicted by the theoretical calculations. As far as the partition coefficient of cation ( $Ca^{2+}$ ) is considered, good agreement can also be observed from Fig. 6 between the theory and the experiments.

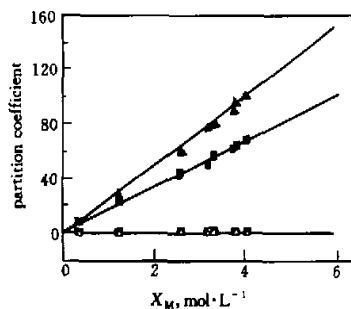


Figure 6 Comparison between theory and experiment for the  $CaCl_2$  aqueous partitioned in NCM

experimental: ■  $K_+$ ,  $0.03\text{ mol}\cdot\text{L}^{-1}$ ; □  $K_-$ ,  $0.03\text{ mol}\cdot\text{L}^{-1}$ ;  
▲  $K_+$ ,  $0.02\text{ mol}\cdot\text{L}^{-1}$ ; △  $K_-$ ,  $0.02\text{ mol}\cdot\text{L}^{-1}$   
theoretical: solidlines

It should be noted that the above comparisons are based on external solution with the concentration be-

low  $1 \text{ mol}\cdot\text{L}^{-1}$ . If the concentration of external solution is too high, for example,  $2 \text{ mol}\cdot\text{L}^{-1}$ , an error as high as 10% between the experiment and calculation has been observed. This is mainly caused by an error detection of solution concentration by the conductivity method when the concentration is high.

## NOMENCLATURE

- c electrolyte concentration,  $\text{mol}\cdot\text{L}^{-1}$   
 K Donnan equilibrium constant, defined by Eq. (1)  
 $K_i$  ionic partition coefficient ( $=K^{2i}$ )  
 $j, n$  electrolyte type  $A_jB_n$   
 $X_M$  fixed group concentration,  $\text{mol}\cdot\text{L}^{-1}$   
 z charge of ions  
 $\omega$  membrane charge signal, 1 for PCM and -1 for NCM  
 $\lambda$  concentration ratio of fixed group to bulk electrolyte

## Superscripts

- b bulk external solution  
 m membrane phase

## Subscripts

- s electrolyte  
 + cation  
 - anion

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