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Membrane potential across a cation-exchange membrane separating solutions with a common electrolyte but two different solvents

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ABSTRACT

In the present study, we measured the membrane potential across a cation-exchange membrane separating two solutions with a common electrolyte but two different solvents. Effects of both solvent and electrolyte on the membrane potential were presented respectively. The following results have been obtained: i) membrane potential increases with the electrolyte concentration ratio between two compartments, no matter what the solvent, electrolyte and the weight percentage of organic solvent are; ii) membrane potential decreases with the weight percentage of organic solvent, and the minimum reaches when the weight percentage equals 100%; iii) membrane potentials for different organic solvents gradually decrease in the order of ethylene glycol > methanol > ethanol; iv) membrane potentials for various electrolytes follow such an order: LiCl > NaCl > $MgCl_2$ > $AlCl_3$.

Keywords: Membrane potential; Cation exchange membrane; Electrolyte; Solvent

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1. Introduction

A neutral membrane separates solutes generally by sieving effect, that is, the solutes whose molecule radius is less than the membrane pore can permeate, but the solutes with molecule radius larger than the membrane pore is rejected. However, besides the sieving effect, the charge also plays an important role for a charged membrane. Electrostatic attraction or repulsion between the membrane and the solute can affect the separation process, which makes it possible that the charged membrane with wide pores can separate the components with narrow molecular radius. Moreover, such a charged membrane can separate the components with similar radius but different charge.

In order to further enlarge the usage of existing charged membranes, design novel charged membranes with more excellent performance, and choose more suitable operation module, it is necessary to get the information of the ion-transport behavior across charged membranes. The measure of membrane potential is just a significant method for characterizing such ion-transport phenomena [1,2].

Up to now, the membrane potential across a charged membrane has been extensively studied for several kinds of aqueous solutions [3–10], a few organic-aqueous solutions [11–14], etc. Especially, based on the research achievement of Wstermann-Clark and Christoforou [15], both influence of steric, electric and dielectric effects on membrane potential [16] and membrane potential in multi-ionic mixtures [17] have also been further investigated. In addition, another kind of membrane potential

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called bi-counterionic membrane [18,19] or bi-co-ionic potential [20] has been also of interest in some special practical applications. However, almost all literatures about membrane potential do not take the difference between the solvents of the solutions at both sides of the charged membrane into account. Namely, previous membrane potential measurements have been carried out with the same solvent at both sides of the membrane. In fact, the membrane potential across a charged membrane separating two solutions with a common electrolyte but two different solvents is quite different from that of previous studies. Moreover, such a membrane potential seems interesting, since the solvent at both sides of the ion-exchange membrane in two-phase electrodialysis [21,22] is just such a case. Thus, in this work membrane potential across a cation-exchange membrane separating two solutions with a common electrolyte but two different solvents is studied, and the effects of both the solvent (including its species and weight percentage (W)) and the electrolyte (including its species and concentration ratio between two compartments (C^{II}/C^{I})) are experimentally probed respectively.

2. Experimental

2.1. Materials

A rather stable cation-exchange membrane of homogeneous perfluorinated sulfonic acid type was supplied by Golden Energy Fuel Cell Co., Ltd, China. The thickness, water content and ion-exchange capacity of this membrane are given in Table 1. In order to avoid the perturbation of the impurities in the membrane, before membrane potential measurements were carried out, the membrane was pretreated in 1mol/l NaOH and HCl aqueous solutions in an alternating manner, so that the membrane was inverted to a hydrogen type.

All electrolytes including LiCl, NaCl, $MgCl_2$ and $AlCl_3$ are of analytical grade, and so are solvents such as methanol, ethanol, ethylene glycol, etc.

2.2. Measurement of membrane potential

A cation-membrane was installed at the center of the measuring cell, which had two compartments, one on either side of the membrane. The volume of each compartment was 120 cm^3 and the membrane area was 4.91 cm^2. Electrolyte solutions with different solvents were poured into these compartments: the electrolyte concentration (concentration in brief) in left compartment C^{II} was varied from 0.001 mol/l to 0.1 mol/l, and the corresponding solvent was always fixed to be water during all measurements; the concentration in right compartment C^{I} was kept constant at 0.001 mol/1 for all experiments, and the corresponding solvent was variable as organic solvent or organic-aqueous mixture. During all membrane potential measurements the electrolytes at both sides of the membrane were kept the same, such as LiCl, NaCl, etc. An electrometer (DT9209, Shenzhen Binjiang Electronic Science and Technology Co., Ltd, China) connected to Ag-AgCl electrodes was used for measurements of the electrical potential. Two Ag-AgCl electrodes were placed in saturated KCl solutions, which were connected to compartments by salt bridges. Two self-made electric stirrers to minimize the effect of boundary layers on the membrane potential stirred the solutions in both compartments.

With other conditions unchanged, effects of the weight percentage of organic solvent (W), the species of both organic solvent and electrolyte were determined respectively. The membrane potential measurements were carried out in the following order:

1) LiCl was chosen as the sample electrolyte, the solvent in right compartment was ethylene glycol–aqueous mixed one. The variable is the weight percentage of ethylene glycol (W), which is ranged from 0 to 100%. For each W, the concentration in left compartment (C^{II}) was changed from 0.001 mol/l to 0.1 mol/l respectively.
2) LiCl was still chosen as the sample electrolyte, the weight percentage of organic solvent (W) was fixed as 100% (namely, the solvent in right compartment here is pure organic one). The organic solvents were changed as methanol, ethanol and ethylene glycol. For each kind of organic solvent, the concentration in left compartment (C^{II}) was also changed from 0.001 mol/l to 0.1 mol/l.
3) The solvent in right compartment was pure methanol, namely, the weight percentage of methanol (W) was fixed as 100%. The electrolyte was changed as LiCl, NaCl, $MgCl_2$ and $AlCl_3$. For each kind of electrolyte, the concentration in left compartment (C^{II}) was changed from 0.001 mol/l to 0.1 mol/l, and other experimental conditions were kept unchanged, similar measurements were made again.

All measurements were carried out for three times at constant temperature (20±0.5°C) in a temperature and humidity chambers, and their mean value was taken as the final result. The estimated error is about ±5%.

Table 1
Physicochemical properties of the studied cation-exchange membrane

Thickness, mm	0.17–0.20
Water content, wt%	20–21
Ion-exchange capacity, meg/g,dry	1.8–2.0

3. Results and discussion

3.1. *Effect of the weight percentage of organic solvent* (W)

Ethylene glycol-water was chosen as the mixed solvent in right compartment, among which the weight percentage of ethylene glycol (*W*) ranged from 0 to 100%. For each *W*, the concentration in left compartment (C^{II}) was changed from 0.001 mol/l to 0.1 mol/l respectively. The solvent in the left compartment was fixed as water, and LiCl was the electrolyte.

Variation of the membrane potential (Δϕ) with C^{II} for different *W*s is shown in Fig. 1. Obviously, Δϕ increases with C^{II} whatever *W* is. Such a trend seems plausible, similar experimental result can be also found for charged membranes in aqueous solutions or methanol–water solutions in both compartments presented by Chou et al. [4,7,11]. Theoretically, the membrane potential in the aqueous solution/charged membrane/aqueous solution system developed by Teorell [23], Meyer and Sievers [24] (TMS) can be treated by Donnan equilibrium theory and Nernst–Planck equation, if it is assumed that the fixed charge groups are homogeneously distributed in the membrane [25] and the effect of the mean activity coefficient of the electrolyte in the external solution is negligible. Similarly, such a theoretical method can be also used to calculate the membrane potential in the organic-aqueous solution/charged membrane/organic–aqueous solution system and aqueous solution/charged membrane/organic–aqueous solution system. In fact, all three potentials including two Donnan potentials and a diffusion potential in above theoretical calculation are related with the concentration of outer solutions. Here, the concentration in right compartment C^{I} is fixed to be 0.001 mol/l, thus, the only changeable concentration is the concentration in left compartment C^{II}. Generally, within relatively lower concentration range of the external solutions, the larger the concentration in left compartment C^{II}, the larger the concentration ratio between two compartments C^{II}/C^{I}, the higher the membrane potential is. Therefore, it is easy to understand above relationship between Δϕ and C^{II}.

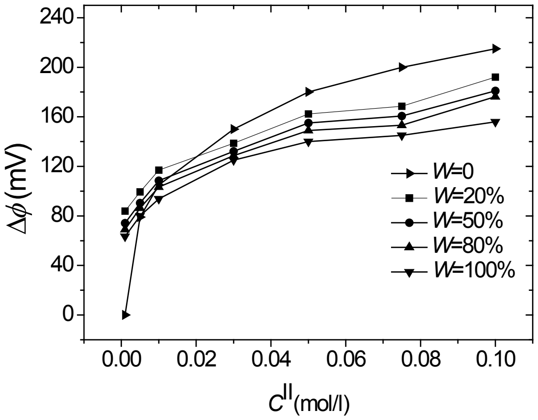

Fig. 1. Membrane potential (Δϕ) as a function of the concentration in the left compartment (C^{II}) for different weight percentages of ethylene glycol (*W*s).

In addition, Δϕ decreases with *W* for the same C^{II}. That is to say, the larger the weight percentage of the ethylene glycol, the lower the membrane potential is. Why can existence of the organic solvent affect the membrane potential? It seems that non electrolyte concentration difference would not originate an electric potential difference. In fact, organic solvent itself cannot affect the membrane potential. However, its lower relative dielectric constant can significantly affect the electrolyte activity and effective membrane charge density due to ion pairing, which can further change the membrane potential. As listed in Table 2, the relative dielectric constant of ethylene glycol is less than water. On the one hand, a decrease of relative dielectric constant leads to an increase of ion-pair between the fixed charge group in the membrane and the counterion in the external solution, which can undoubtedly result in the decrease of the effective membrane charge density. With other conditions fixed, the membrane potential increases with the effective membrane charge density. On the other hand, a decrease in relative dielectric constant of solution in the right compartment results in a decrease in its electrolyte activity due to ion pairing, and further the ion-concentration ratio between the two compartments increases. It is reasonable that the increase in the ion-concentration ratio between two compartments should result in a corresponding increase of the experimental membrane potential Δϕ. However, it can be found from the experimental results that the effective membrane charge density should play a more important role than the ion-concentration ratio between two compartments in our membrane–solution system. That is, the effect of the decrease in relative dielectric constant of the solution on the effective membrane charge density is larger than on the ion-concentration ratio between two compartments. Therefore, the membrane potential decreases with the

Table 2
Relative dielectric constants of various organic solvents and water

Species of organic solvent	Methanol	Ethanol	Ethylene glycol	Water
Relative dielectric constant	33.7	25.8	41.2	81.5

relative dielectric constant of external solution. Such an experimental result coincides with Chou and Tanioka's studies [11,12]. Consequently, when *W* increases from 0 to 100%, the effective charge membrane density becomes less and less, which causes the membrane potential lower and lower too.

3.2. Effect of the species of organic solvent

In this section, pure organic solvents in the right compartment (the weight percentage of organic solvent is equal to 100%) were methanol, ethanol and ethylene glycol. LiCl was chosen as the electrolyte. Similarly, the concentration of aqueous solution in the left compartment C^{II} was changed from 0.001 mol/l to 0.1 mol/l, and that of the organic solution in the right compartment C^{I} was fixed to be 0.001 mol/l. For different organic solvents, results of the membrane potential are schematically shown in Fig. 2.

Obviously, a similar experimental trend that the membrane potential $\Delta\phi$ increases with the solution concentration in the left compartment C^{II} for the cation-exchange membrane can be also obtained. This implies that such an experimental tendency is independent of solvent species. That is to say, no matter the solvents at both sides of the cation-exchange membrane is organic–aqueous/organic–-aqueous [4,7,11,12] or organic–aqueous/aqueous, the membrane potential always increases with the electrolyte concentration in left compartment for the cation exchange membrane within a certain range of C^{II}s.

In addition, for the same electrolyte concentration in the left compartment C^{II}, the membrane potential $\Delta\phi$ gradually decreases in the following order: ethylene glycol > methanol > ethanol. Such a result is also due to the relative dielectric constant difference of various organic solvents. As mentioned in section 3.1, the less the relative dielectric constant, the more the ion-pair between the fixed charge group in the membrane and the counter-ion in the external solution forms. Thereby, the effective membrane charge density becomes lower if the relative dielectric constant decreases, which causes the decline of membrane potential inevitably. As a matter of fact, as indicated in Table 2, the relative dielectric constant for various organic solvents just decreases with the same order: ethylene glycol > methanol > ethanol. Consequently, the above experimental results can be also easily understood.

3.3. Effect of the species of electrolyte

In this part, the organic solvent in right compartment is chosen as methanol, the weight percentage of methanol (*W*) is fixed to 100%. Similarly, the concentration of aqueous solution in the left compartment C^{II} was changed from 0.001 mol/l to 0.1 mol/l, and that of the organic solution in the right compartment C^{I} was fixed to be 0.001 mol/l. Several kinds of electrolyte including LiCl, NaCl, $MgCl_2$ and $AlCl_3$ were used to determine the effect of the species of electrolyte, among which LiCl and NaCl were to examine the effect of the mobility of counter ion with the same valence, and NaCl, $MgCl_2$ and $AlCl_3$ for determining the effect of counter-ionic valence. The results of the membrane potential for different electrolyte species are schematically shown in Fig. 3.

Undoubtedly, the relationship that $\Delta\phi$ increases with C^{II} also exists for all five kinds of studied electrolytes. However, for the same electrolyte concentration in the left compartment C^{II}, membrane potentials for various electrolytes show rather large difference, and they obey the following order: LiCl > NaCl > $MgCl_2$ > $AlCl_3$. Such an interesting phenomenon can be explained from two aspects. On the one hand, for the electrolytes with counter-ions of the same valence, such as LiCl and NaCl, their membrane potential difference is mainly due to their different mobilities of corresponding counter-ions, namely,

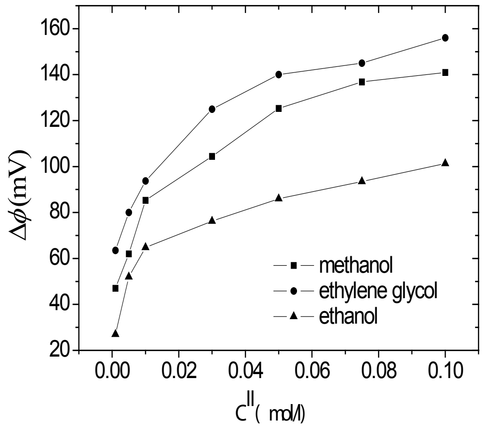

Fig. 2. Membrane potential ($\Delta\phi$) as a function of the concentration in the left compartment (C^{II}) for different species of organic solvent.

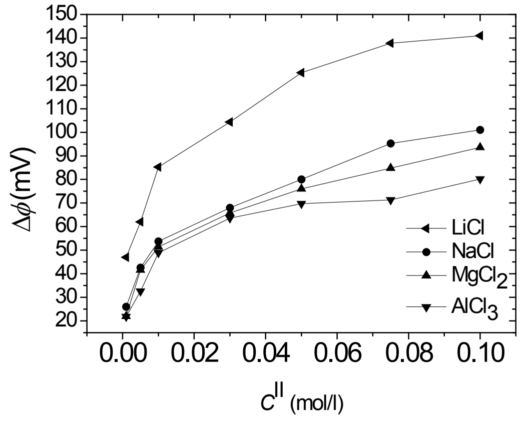

Fig. 3. Membrane potential ($\Delta\phi$) as a function of the concentration in the left compartment (C^{II}) for different species of electrolyte.

Li^+ and Na^+. In fact, just as mentioned by Weirun [26] and Fievet et al. [27], for the electrolytes (LiCl and NaCl here) with the same valence and different cations or anions, the larger the transport number of ions (Cl^- here) in aqueous solution, the higher the membrane potential will be. The transport number of ion is closely linked to its mobility. The mobility of Li^+ and Na^+ gradually increases, and the transport number of Cl^- for LiCl and NaCl decreases little by little. Thus, the membrane potential for LiCl and NaCl solution with equal C^{II} also increasingly goes down. On the other hand, for the electrolytes with counter-ions of different valences, such as NaCl, $MgCl_2$ and $AlCl_3$, the membrane potential difference is mainly due to their effective membrane charge density. As a matter of fact, all of the fixed-charge groups in the membrane do not function perfectly due to the neutralization by the counter-ion. Because of the ion-pair effect, the electrostatic interaction between a fixed-charge group and a counter-ion depends on the valence of counter-ions [9], the effective membrane charge density in a trivalent counter-ion system ($AlCl_3$) is sharply lower than that in a divalent counter-ion system ($MgCl_2$), and it is even much lower than that in a monovalent counter-ion system (LiCl and NaCl). The larger the effective membrane charge density, the higher the membrane potential is. Thereby, the membrane potential must follow such an order: LiCl (or NaCl) > $MgCl_2$ > $AlCl_3$. Taking above two aspects into account, it is reasonable to accept all experimental results of membrane potential for different species of electrolyte.

4. Conclusions

In the present work, the membrane potential across a cation exchange membrane separating two solutions with a common electrolyte but two different solvents was experimentally studied. The results show that the electrolyte concentration ratio between two compartments (C^{II}/C^{I}), the weight percentage of organic solvent (W), and the species of both solvent and electrolyte can all affect the ultimate membrane potential. And the following conclusions can be obtained:

- The membrane potential ($\Delta\phi$) increases with the electrolyte concentration ratio between two compartments (C^{II}/C^{I}) within a certain range of C^{II}, no matter what the solvent, electrolyte and the weight percentage of organic solvent (W) are;
- The membrane potential ($\Delta\phi$) decreases with the weight percentage of organic solvent (W) rising, and the minimum reaches when W equals 100%; which verifies the existence of ion pairs between the fixed charge groups in the membrane and the counter-ions in the mixed solvent systems.
- The relative dielectric constant of the solvent affects the membrane potential significantly. The larger the relative dielectric constant, the higher the membrane potential. Thus, the membrane potentials ($\Delta\phi$) for different organic solvents gradually decrease in the following order: ethylene glycol > methanol > ethanol;
- Because of the mobility and valence difference of counter-ions, the membrane potentials for various electrolytes obey the following order: LiCl > NaCl > $MgCl_2$ > $AlCl_3$.

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