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ARTICLE TYPE

Anion Transfer across “Anion Channels” of Liquid/Liquid Interface Modified by Anion-Exchange Membrane

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To mimic the anion channels in biomembrane, a novel strategy based on the membrane-modified liquid/liquid interface using anion-exchange membranes was firstly proposed to study simple ion transfer processes of highly hydrophilic anions at the modified liquid/liquid interface by employing voltammetric methods. Significantly, fascinating ion transfer phenomena were observed at the water/1,2-dichloroethane (W/DCE) interface modified by a homogeneous anion-exchange membrane, including the remarkable extension of polarization window; well-defined transfer waves of some highly hydrophilic anions, such as sulfate and nitrite; and the amazing positive-shift of their transfer potentials. According to both ion-exchange membrane models, a new mechanism based on the sieving effect and pre-dehydration in combination with electrostatic effects dominantly induced by the gel phase of anion-exchange membrane on ion transfer reactions were preliminarily proposed to explain those fascinating ion transfer phenomena.

Introduction

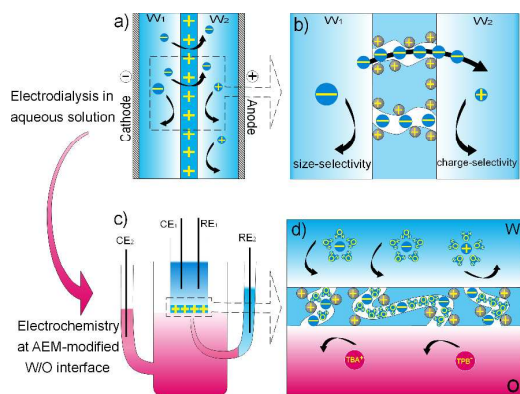
Anion transfer (AT) across biomembrane through the pathway provided by some proteins embedded within membrane bilayer, namely “anion channels”, is one of the significant biological transmembrane processes because it is closely related to numerous crucial physiological phenomena, such as the maintenance of salt and water balance of cells etc.¹ The process of AT is extremely significant; therefore, extensive research efforts have been devoted to study the simple ion-transfer (IT) reactions including AT at the liquid/liquid (L/L) interface, or called as water/oil (W/O) interface. The study has proven to be helpful and effective to understand the IT processes across biomembrane because L/L interface is considered as a simple model to mimic semi-biomembrane.²

However, it is still a challenging task to investigate the AT processes of some highly hydrophilic anions, such as sulfate (SO_4^{2-}), chloride (Cl^-), acetate (Ac^-), and nitrate (NO_3^-), at the L/L interface mainly owing to their extremely high Gibbs transfer free energy (G_{tr}),^{3a-c} the restriction of potential window,^{3d,e} and the interference of coupling IT.^{3f} Until now, besides the facilitated anion transfer (FAT) based on the addition of an ionophore into the organic phase for lowering the G_{tr} of few anions,^{3a-c} several methods focusing on the micro-L/L interface electrochemistry^{3g} have been developed to study the AT processes which are impossible to be observed at the conventional L/L interface (mm-sized). For example, a generation/collection (G/C) technique employing a micro-sized dual pipette^{3f} or nanopipette voltammetry method^{3d,e,h} can solve the above mentioned problems to a certain extent. Recently, as reviewed by Shao et al.,^{3g} membrane-modification has become one of normal methods to build micro-L/L interface. So far,

various porous membranes including inorganic,^{4a-f} organic,^{4g-k} or organic/inorganic hybrid membranes,^{4l} have been used to support and modify L/L interface. Compared to the conventional L/L interface, the integration of micro-L/L interface arrays using porous membranes can not only enhance mass transfer^{3g} and amplify electrochemical signal,^{2c} but also mimic “ion channels” of biomembrane.^{4b} In particular, inconceivable IT phenomena can be observed at the membrane-modified L/L interface, which are often closely related to the unique microstructure and property of employed membranes. For instance, the modification of L/L interface using zeolite membrane can extend the potential window and exclude ITs of anions from cations due to the sieving effect and charge-selectivity of zeolite.^{4c-e} Therefore, above mentioned studies inspired us to design a modified L/L interface by using a membrane with permeability of anions, such as anion exchange membranes (AEMs), to study the transfer reactions of highly hydrophilic anions at the membrane-modified L/L interface.

Commercial ion exchange membranes (IEMs) including AEMs have been extensively used in numerous industrial fields, in general, related to water-treatment, including the electrodialytic desalination of saline water or seawater.^{5a-d} Amount of work focused on electro dialysis (ED) has revealed the excellent permselectivities of AEMs based on the simplest capillary model, which views IEMs as ideal porous medium containing micropores of identical radius with fixed-charge groups,^{5e} as represented in Scheme 1a and b. The charge-relative permselectivity of AEMs refers to the fact that the fixed positive groups (mostly quaternary ammonium type) in AEMs can partially or completely exclude cations from anions to permeate through membranes.^{5a-d} The other is the size-relative permselectivity, that is the micropores in AEMs can repel the

anions with larger size than them.^{5f,g} In general, the average pore diameter of commercial IEMs is around or even less than 10 Å.^{5b,g,h} In view of all the above mentioned attractive characteristics of AEMs, it is expected that the AEM-modified L/L interface may be able to introduce desirable “anion channels” into L/L interface for the transfer of some highly hydrophilic anions across “semi-biomembrane” after one of the aqueous phases (W) in a ED cell using AEMs is replaced by an organic phase (O), as illustrated in Scheme 1c and d.



Scheme.1 Schematic illustration of (a and b) the permselectivities of AEMs in a ED cell based on the capillary model of IEMs, and (c and d) AT across the AEM-modified W/O interface in a four-electrode electrochemical cell.

Herein, first, we explored the feasibility of electrochemical study toward AT processes at the L/L interface modified by commercial heterogeneous or homogeneous AEM (hetero-AEM or homo-AEM, respectively) containing quaternary ammonium group (Table S1 in ESI†). Significantly, fascinating IT phenomena were observed using a homo-AEM, including the remarkable extension of polarization window, well-defined transfer waves of highly hydrophilic anions, and the amazing positive-shift of their transfer potentials. According to the simplest capillary model and the two-phase structural model of IEMs (gel and interstitial phases),⁵ⁱ⁻¹ a new mechanism based on the sieving effect and pre-dehydration in combination with electrostatic effects dominantly induced by the gel phase of AEMs was proposed to attribute the change in energy barrier of IT reactions which led to the corresponding inconceivable IT phenomena occurring at the AEM-modified L/L interface. Water/1,2-dichloroethane (W/DCE) interface with extensive studies in the field of L/L interface electrochemistry^{4b-f,h,i,k,l} was adopted in this pioneering work on the IT across AEM-modified L/L interface. The ITs of SO_4^{2-} , Cl^- , NO_2^- , Ac^- , and NO_3^- were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The entire cell setups employed for voltammetric IT studies were described in the experimental section (see ESI†), where it should be emphasized that all the AEMs used in this study had been equilibrated in pure water before they were utilized to construct the cells.

Results and discussion

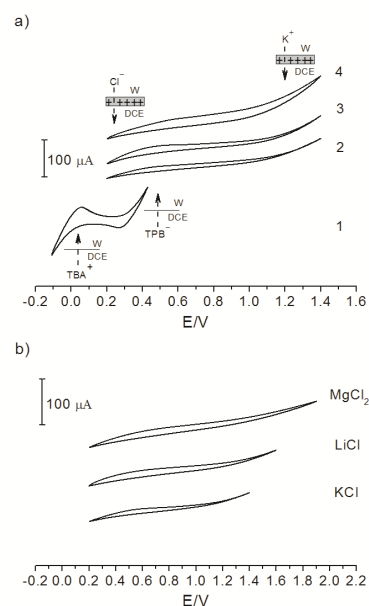


Fig.1 Cyclic voltammograms for the background responses obtained by using cell 1 (a) in the absence (curve 1) and presence of AEM with $x=0$, (curves 2–4, respectively employing TBATPB, BTTPATPB (cell 2), and TBATPBCl (cell 3) as the organic electrolyte; however KCl was employed as the aqueous electrolyte); and the background responses obtained (b) in the presence of AEM by respectively, using KCl (cell 1), LiCl (cell 4), and MgCl_2 (cell 5) as the aqueous electrolytes; however, TBATPB was employed as the organic electrolyte). The scan rate was 50 mV s^{-1} .

Curves 1 and 2 in Fig 1 exhibit the potential windows obtained on the basis of Cell 1 in the absence and the presence of a homo-AEM, respectively. As the most common organic electrolyte, tetrabutylammonium tetraphenylborate (TBATPB) normally provides extremely narrow potential window respectively limited by the ITs of TPB^- and TBA^+ at the positive and negative ends as shown in the curve 1 (-0.1 – 0.4 V). Surprisingly, the potential window shifts to 0.2 – 1.4 V (curve 2) after a homo-AEM was used to modify W/DCE interface, which results in a remarkable extension of potential window by about 700 mV . Although the increase in potential window has been observed at the zeolite-modified W/DCE interface due to the sieving effect of zeolite on supporting electrolyte ions, the maximum extension caused by zeolite was $\sim 300 \text{ mV}$,^{4c} which is much smaller than the value obtained herein. Dryfe et al. demonstrated that the increase in potential window always reflected the fact that small and extremely hydrophilic ions with higher G_{tr} become the ions determining the positive and negative ends of potential window owing to the size-exclusion of organic ions with lower G_{tr} but possessing larger size compared to the micropores in zeolite.^{4c-e} Therefore, the positive and the negative sides of curve 2 are assigned to the ITs of electrolyte ions in aqueous solution, K^+ and Cl^- , due to the similar sieving effect of homo-AEM^{5f,g} to zeolite membrane on TPB^- and TBA^+ (for bare or hydration diameters of all the ions involved in this study see Table S2 in ESI†). However, when a hetero-AEM is used to modify W/DCE interface, the obtained potential window presents the same range as that observed at bare W/DCE interface (Fig. S2 in ESI†). According to the previous reports on the structural difference between

hetero-AEM and homo-AEM,⁶ the distinct potential windows obtained by using different AEMs should be ascribed to the compactness of employed membranes. In addition to the larger pore size of hetero-AEM than homo-AEM,^{6b} some pinholes^{5d} can be observed on the surface of hetero-AEM according to their scanning electron microscopy (SEM) images (Fig. S1 in ESI†). Therefore, it is possible for TPB⁻ and TBA⁺ to transfer across the hetero-AEM-modified W/DCE interface resulting in the similar potential window as shown in curve 1, which in turn indicates that structural homogeneity and integrity of AEMs is crucial for their potential applications in the L/L interface electrochemistry. Indeed, the existence of pinholes in zeolite membranes can also affect the potential windows obtained at the zeolite-modified L/L interface.^{4e} Thus, the following study focused only on homo-AEM without obvious structural defects.

The sieving effect of homo-AEM on ITs is comprehensible as discussed above; however, it is still ambiguous that the overall potential window of curve 2 dramatically shifts to more positive potential relative to curve 1. Therefore, to further confirm the ions determining the potential window and to evaluate the increase and positive-shift of potential window (curve 2), a series of different organic and aqueous electrolytes instead of TBATPB and potassium chloride (KCl), respectively were investigated. When the organic electrolyte in cell 1 was changed to tetrabutylammonium tetrakis(4-chlorophenyl)borate (TBATPBCl) or bis(triphenylphosphoranylidene)ammonium tetraphenylborate (BTPPATPB), as shown in curves 3 and 4, respectively, the potential windows almost maintain the same range (0.2–1.4 V), which not only illuminates that the sieving effect of homo-AEM plays the same role of size-exclusion of TPBCl⁻ and BTPPA⁺ from the micropores in homo-AEM, but also indicates that the potential windows should be limited by the ITs of K⁺ and Cl⁻ because the aqueous electrolyte was always KCl. When the aqueous electrolyte in cell 1 was altered to lithium chloride (LiCl) or magnesium chloride (MgCl₂), the potential windows become progressively broader (Fig. 1b), that is 0.2–1.4 V for KCl, 0.2–1.6 V for LiCl, and 0.2–1.8 V for MgCl₂. The negative end always appears at the same range; however, the positive end changes with the variation of cations in aqueous phase, which confirms that the negative and positive ends of the potential windows obtained by using homo-AEM should be determined by the ITs of Cl⁻ and cations from W to DCE. Interestingly, chloride could transfer across the homo-AEM-modified W/DCE interface at the negative end of potential window; therefore, there is possibility of other highly hydrophilic anions to exhibit the similar behavior.

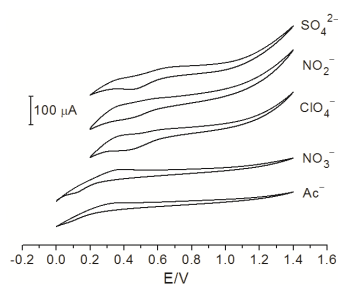


Fig. 2 Cyclic voltammograms for transfers of SO₄²⁻, NO₂⁻, ClO₄⁻, NO₃⁻, and Ac⁻ at the homo-AEM-modified W/DCE interface using Cell 1 with *x* of 10, 20, 10, 30, and 30, respectively. The scan rate was 50 mV s⁻¹ for SO₄²⁻, NO₂⁻, and ClO₄⁻, and 5 mV s⁻¹ for NO₃⁻ and Ac⁻.

Fig. 2 shows the CVs for the ITs of SO₄²⁻, nitrite (NO₂⁻), NO₃⁻, Ac⁻, and perchlorate (ClO₄⁻) in the presence of homo-AEM. Obviously, most of CVs present well-defined transfer waves within the potential window with the involvement of highly hydrophilic anions except ClO₄⁻. In particular, well-defined transfer wave of IT of SO₄²⁻ is observed first time at the W/DCE interface, although its transfer can be observed at the water/ neat DCE interface.^{3e} Furthermore, the dependence of peak currents in Fig. 2 on the concentration of the anions in aqueous phase present good linear correlation (Fig. S3 in ESI†), indicating that all the transfer waves appearing in Fig. 2 should correspond to their IT processes. Moreover, well-defined CVs are almost asymmetrically-shaped under different scan rates (Fig. S4 in ESI†), which is similar to that obtained by micropipette^{3g} or organic/inorganic hybrid membrane with low porosity.⁴ⁱ As reported previously,^{4c-f} CVs of IT obtained at the membrane-modified L/L interface are symmetrically peak-shaped which is mainly ascribed to two factors. First, is the location of L/L interface inside the membrane, or the possible formation of mm-sized L/L interface at membrane surface,^{4f} both of which result in symmetrical peak-shaped CVs. Second, is the well-known overlap of diffusion field due to high porosity of employed membranes,^{4d,h} which also leads to the appearance of peak-shaped CVs. Considering the fact that the AEMs were initially equilibrated with water, it is reasonable that the W/DCE interface could be formed near the mouth of micropores of homo-AEM; and the overlap of diffusion field as mentioned above could be ignored herein, which is similar to our previous report on porous membrane with low porosity.⁴ⁱ Thus, the homo-AEM-modified W/DCE interface tends to be the characteristic of asymmetric diffusion field, where the egress transfer of anions out of homo-AEM, dominated by linear diffusion, produces a peak-shaped CV response due to the confinement of micropores in homo-AEM; however, the ingress transfer of anions into homo-AEM controlled by radial diffusion leads to a steady wave.

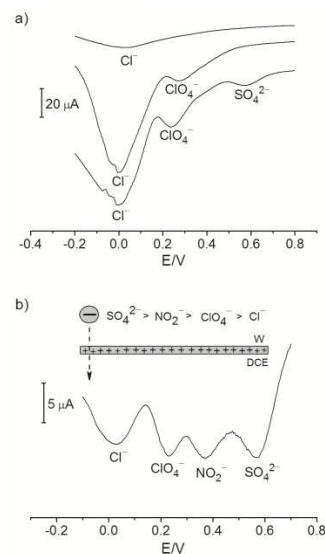


Fig. 3 DPVs for transfer of anions at the homo-AEM-modified W/DCE interface using Cell 1 after (a) successive addition of ClO₄⁻ (10 mM) and SO₄²⁻ (5 mM) into aqueous phase (the pulse amplitude was 50 mV), and (b) simultaneous addition of SO₄²⁻ (5 mM), NO₂⁻ (10 mM), and ClO₄⁻ (10 mM) into aqueous phase (the pulse amplitude was 30 mV).

In addition to the asymmetric shape, the most noticeable feature of all the CVs in Fig. 2 is that the transfer waves corresponding to ITs of the anions almost appear in the region of positive potential. It is easily-understood that the transfer wave of ClO_4^- should appear in this region because of its relatively low G_{tr} .^{3f} However, it is surprising that for other highly hydrophilic anions, their transfer waves also shift to the positive region. To verify that those transfer waves indeed correspond to the IT processes of different anions, another voltammetric method with better resolution than CV, that is DPV, was employed to monitor the transfer waves of the anions at the homo-AEM-modified W/DCE interface by using cell 1. Fig. 3a shows that the transfer wave of Cl^- appears at the negative end of potential window; however, the transfer waves of ClO_4^- and SO_4^{2-} across the modified water/DCE interface appear sequentially at the different potential after successive addition of ClO_4^- and SO_4^{2-} into aqueous phase. Addition of targeted anions into the aqueous phase at the same time, leads to the generation of the well-separated transfer waves of anions at different potentials (Fig. 3b). Considering that E_{tr} is based on the preference of different ITs at the same L/L interface, it can be deduced from CVs and DPVs shown in Fig. 2 and 3 that the preferential order of ATs at the homo-modified W/DCE interface is $\text{Cl}^- < \text{Ac}^- < \text{NO}_3^- < \text{ClO}_4^- < \text{NO}_2^- < \text{SO}_4^{2-}$ according to their different E_{tr} ($w \rightarrow 0$) (Table S2 in ESI†). The above mentioned order is different from the normal IT preferential order of anions obtained at bare W/DCE interface ($\text{Cl}^- < \text{NO}_2^- < \text{NO}_3^- < \text{ClO}_4^-$).^{3f} The positive-shift of potential window and the extraordinary preferential order of anions obtained herein indicate that the mechanism of IT reactions occurring at the homo-AEM-modified W/DCE interface was distinct from those of conventional ITs at bare W/DCE interface.

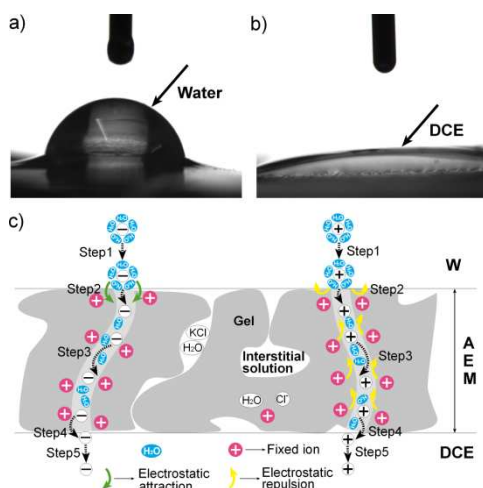


Fig. 4 Photographs of (a) water droplet and (b) DCE droplet on the external surface of homogeneous AEM; (c) Pre-dehydration in combination with electrostatic effects on IT at the homo-AEM-modified W/DCE interface based on two-phase structural model of IEMs (gel phase and interstitial phase).

In general, a simple or direct IT reaction at bare W/DCE interface obeys the conventional one-step mechanism^{2b} or a shuttling mechanism, recently proposed by Mirkin et al.^{3e,h} However, the IT mechanisms are not completely suitable to expound all the above mentioned abnormal IT phenomena because as-built W/DCE interface is not bare, or W/neat-oil,

which is not only supported but also modified by a homo-AEM containing extremely narrow micropores with size almost identical to those of hydrated ions. Therefore, the dehydration process induced by narrow pores, as revealed in the studies on ion transport through artificial nanochannels⁷ and biological channels,⁸ is given significant importance in this study. Normally, the dehydration process induced by narrow pores is ignored at the micro-L/L interface supported even by nanopipettes mainly because of their large pore-size (a few to hundreds of nanometers)^{3d,e,g,h} relative to ionic size. It is well-known that ion dehydration is vital for the membrane-based desalination.^{7a} Since this study is derived from the application of AEMs in ED as shown in Scheme 1, after taking the processes of ion transport through AEMs into account,^{9a} the entire IT processes across the AEM-modified W/DCE interface should involve with not on one-step, but at least five steps (Fig. 4c) based on two-phase structural model of IEMs: first, is the diffusion process of ion from bulk aqueous phase to the AEMs surface; second, is the partition process of ion into AEMs; third, is the transport process of ion through the membrane matrix; fourth, is the transfer of ion at the W/DCE interface; and fifth, is the diffusion of ion into the bulk DCE phase. The results of the investigation indicated that steps two and three are the key steps during ED process and the preferential permeation order of anions tested in this study through a hydrophobic AEM is $\text{Ac}^- < \text{Cl}^- < \text{NO}_2^- < \text{NO}_3^- < \text{SO}_4^{2-}$,^{9a,b} mainly depending on the membrane hydrophobicity (or ionic Gibbs hydration energy),⁹ which is partially similar to the preferential-order of those ATs, implying that the underlying steps two and three would also be the key steps for the entire IT processes.

Besides the simplest capillary model, two-phase structural model of IEMs has acquired remarkable popularity for explaining the complicated processes of ion transport through IEMs,⁵ⁱ⁻¹ which is more helpful to understand the above mentioned extraordinary IT phenomena. According to the model, homogeneous IEMs is considered as a microheterogeneous multiphase system containing at least two phases, namely gel phase and interstitial phase.^{5j} Usually, the gel phase has the main volume fraction in IEMs ($\geq 90\%$) and the interstitial phase does not noticeably affect the permselectivity of IEMs, which are mainly determined by the hydrophobic gel phase composed of polymer matrix with fixed positive groups.⁵ⁱ The homo-AEM employed in this study is also characteristic of relative hydrophobicity, exhibiting better affinity for DCE than water according to the higher contact angle of water ($\sim 76.5^\circ$) than that of DCE ($\sim 10^\circ$) with membrane surface as shown in Fig. 4a and b. Therefore, the narrow pores and the fixed positive groups in gel phase are expected to play the key roles in the above mentioned IT reactions based on the assumption that steps two and three are the key steps for the entire IT processes, as shown in Fig. 4c. As far as anions are concerned, in addition to the sieving effect as discussed above, ion dehydration can also be induced by the narrow pores in gel phase during steps two and three.¹⁰ Moreover, the electrostatic-attraction between fixed positive groups and anions not only favors the partition of anions during step two, but also plays the similar role as the groups in ion-channels^{8c} to compensate for the energetic cost of dehydration. Both of the above mentioned effects lower their transfer energy barrier at the

modified-W/DCE interface, leading to final potential positive-shift of hydrophilic anions. In contrast, as a performance indicator on charge-relative permselectivity of IEMs, high transport number (~ 0.95) of homo-AEM (Table S1 in ESI†) indicates that some cations can get transported across it, but the electrostatic-exclusive effect of fixed positive groups on cation could hinder the partition and transport of cations during steps two and three, which would produce additional energy barrier except the energetic cost of dehydration for the entire IT reactions of cations, resulting in the corresponding potential-shift to more positive level.

Moreover, the transfer waves corresponding to the ITs of TMA⁺ and TEA⁺, readily appearing at bare W/DCE interface,^{3d,g,f} are not observed at the homo-AEM-modified-W/DCE interface (Fig. S5 in ESI†), which indicates that electrostatic-exclusive effect of AEMs on cations is strengthened with the increase in their diameter, leading to the generation of significantly large energy barrier for TMA⁺ and TEA⁺ to overcome at the modified L/L interface, although they are more hydrophobic. Also, the progressively broader potential windows as observed in Fig. 1b can be explained by such an electrostatic-exclusive effect on cation transfer, that is the increase in the hydrated diameters of electrolyte cations (K⁺ ~ 0.424 nm, Li⁺ ~ 0.482 nm and Mg²⁺ ~ 0.598 nm)¹¹ in aqueous phase results in the increase of energy barrier of their IT reactions occurring at the homo-AEM-modified L/L interface and the corresponding shift of positive ends of those potential windows to more and more positive region (Fig. 1b). As for some extremely hydrophilic anions, such as F⁻ and OH⁻, it is still impossible to observe their corresponding transfer waves within the potential window (Fig. S6 in ESI†), which is possibly due to their extremely weak affinity toward the hydrophobic membrane surface.⁹ Even so, the well-defined transfer waves of other highly hydrophilic anions indicate that the dehydration process during steps two and three prior to IT during step four lowers the energy barriers of some AT reactions at the modified L/L interface. This process can be somewhat considered as another type of solvent-effect, or called as pre-dehydration effect induced by a relatively hydrophobic membrane containing narrow pores, playing the similar roles as organic solvent¹² or water clusters^{3h} to lower the energy barriers of ITs. Moreover, according to the literatures, dehydration process definitely affects the energy barriers for ion transport through artificial⁷ or biological membranes⁸ containing narrow pores, on the basis of molecular dynamics (MD) simulations. Thus, as-proposed pre-dehydration in combination with electrostatic effects dominantly induced by the gel phase of AEMs is significant for further mechanistic understanding of the dehydration effect on the membrane-based desalination and the ion transport in biological channels from a new standpoint derived from the change in energy barrier of IT reactions at the L/L interface induced by narrow pores.

Conclusions

In this study, first, we have demonstrated that the AEM-modified L/L interface provided a novel platform to investigate AT processes at the L/L interface even with the involvement of highly hydrophilic anions. Modification of W/DCE interface by a homo-AEM led to the significant extension of the polarization

window. Moreover, well-defined and positively-shifted transfer waves of some highly hydrophilic anions dramatically appeared within the extended potential window. Based on both IEMs models, the sieving effect and pre-dehydration in combination with electrostatic effects dominantly induced by the gel phase of AEMs on IT reactions were preliminarily proposed to explain the extraordinary IT phenomena. This multidisciplinary study not only enriches the investigation of ITs at the L/L interface, but also offers new insight into a number of transport processes of hydrated ions through IEMs in desalination or across biomembrane in bioscience.

Acknowledgments

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Notes and references

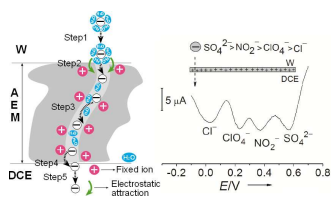
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† Electronic Supplementary Information (ESI) available: the supplementary information mainly contains the experimental procedures, the main characteristic parameters and the SEM images of two kinds of commercial AEMs, the potential window obtained at the hetero-AEM-modified-W/DCE interface, the diameters and thermodynamic data of all ions involved in this study, as well as the CVs for the transfers of some targeted anions obtained under different scan rates or concentrations and the CVs for the transfers of TMA⁺, TEA⁺, F⁻ and OH⁻ at the homo-AEM-modified-W/DCE interface. See DOI: 10.1039/b000000x/

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Table of contents entry



A novel strategy is proposed to mimic anion channels and study anion transfer reactions at the water/1,2-dichloroethane (W/DCE) interface modified by a homogeneous anion-exchange membrane (AEM).