

Electromigration of $[C_6Mim][TFSI]$ from Ionic Liquids Bulk to Aqueous Solutions

WANG Ming-yong^{1,2,3}, SUN Jin-he^{1,2}, ZHANG Peng-rui^{1,2,3}, HUANG Chao-chi^{1,2,3}, ZHANG Qian^{1,2,3},
SHAO Fei^{1,2}, JING Yan^{1,2}, JIA Yong-zhong^{1,2}

(1. Key Laboratory of Comprehensive and Highly Efficient Utilization of Salt Lake Resources, Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining, 810008, China; 2. Qinghai Engineering and Technology Research Center of Comprehensive Utilization of Salt Lake Resources, Xining, 810008, China; 3. University of Chinese Academy of Sciences, Beijing, 100049, China)

Abstract: The ions electromigration of ionic liquids (ILs)/aqueous solution binary system have attracted increasingly attention in many fields. In this work, the effect of acidity-alkalinity, electrolyte concentration of electrode solutions and ILs with $LiN(CF_3SO_2)_2$ on the migration of $[C_6Mim]^+$ ions was investigated systematically by studying the concentration change of ions of ILs in the electrode solutions. Generally, the concentration of $[C_6Mim]^+$ ions increased in cathode solution and decreased in anode solution with increasing current, while the concentration of $N(CF_3SO_2)_2^-$ ions increased in anode solution and decreased in cathode solution. When basic solution was used as electrode solution, the migration of $[C_6Mim]^+$ ions was restrained markedly. $LiN(CF_3SO_2)_2$ solution was used as electrode solution and the dissolution of $LiN(CF_3SO_2)_2$ in ILs could reduce the migration of $[C_6Mim]^+$ ions effectively.

Key words: Ionic liquids; Electromigration; Aqueous electrode solutions; Back-dissolution

CLC number: O645.17

Document code: A

Article ID: 1008-858X(2021)02-0035-09

1 Introduction

ILs, as a new eco-friendly solvent and efficient reaction medium, has the performance advantages of wide electrochemical window and low vapor pressure etc.^[1]. ILs doesn't exist as single phase but mixing system with aqueous solutions when it is used for organic acid separation from biological tissues^[2], lithium recovery from seawater^[3], and interfacial electrochemical synthesis^[4], removal of pharmaceutical

pollutants^[5], wastewater treatment and extraction of organic acid^[6] and so on. The interaction between ILs and aqueous solutions plays an important role in physicochemical properties and application performance of binary system. And the interaction can be affected immensely by the external factors such as light, temperature, pH, CO_2 and so on.

As a typical external factor, electric field can change the interfacial structures, properties and performance of binary systems consisted of ILs and aqueous solutions, in which increasing attention has

Received date: 2019-12-16; **Revised date:** 2020-03-06

Fund projects: Key R&D Program of Qinghai Province (No. 2021-GX-104) and Youth Innovation Promotion Association of CAS (2015351)

First and corresponding author: WANG Ming-yong, Master degree, engaged in lithium isotope separation and photocatalytic degradation of organic pollutants. Email: mywang0202@163.com

Corresponding author: SUN Jin-he, Professor, interested in lithium isotope separation and phase change materials. Email: jhsun@isl.ac.cn

been attracted nowadays. Herrera et al. applied external electric field to amino acid ionic liquids-water mixtures. The hydrogen bonding networks were disrupted and the system properties could be fine-tuned with electric field^[7]. Zhao et al. found that the hydrogen bond network could be destroyed when external electric field reached a critical value and the diffusion coefficient of uncharged solute in the direction of electric field was greatly enhanced^[8]. Merlet et al. observed that small voltages induced changing of the orientation of the anisotropic cations which differed on the two electrodes. The structural transition was associated with a large change in the charge distribution across the interfacial region of the electrolyte^[9]. Sha et al.^[10] demonstrated that hydrophobic ILs can be strikingly tuned to hydrophilic under a strong external electric field. With the increase of electric field strength, the cation-anion and water-water interactions are both attenuated while the ion-water interactions are augmented. This made the water molecules solvate the ILs easily. The cations and anions gradually evolved from an ILs interface to a water medium, leading to surprisingly hydrophilicity with high inter-solvent mixing. Li et al. carried out protein partitioning in ILs-aqueous solutions system. A low-voltage alternating current electric field could shorten the phase splitting time of ILs and aqueous solutions by 2 ~ 3 times^[11]. T. Hoshino et al. separated lithium isotope with PP₁₃[TFSI] ILs/aqueous solutions and found that the loss ratio of ILs after 5 h reached 37%^[12]. The ILs loss was restrained after a cation exchange membrane or nafion324 overcoat was used to cover the ILs impregnated membranes, but the migration of ions from ILs to aqueous solution still existed^[13]. Obviously, the ions of ILs migrated into aqueous solutions inevitably, which caused remarkable loss of ILs bulk. It was an unfavourable factor on the above-mentioned application and the dissolution of ILs into the aqueous solutions meant environmental risk while it didn't get enough attention. The quantitative data of ionic migration from ILs to aqueous solutions was still scarce.

For understanding the process and regularity of ionic migration of ILs in hydrophobic ILs/aqueous solution binary system under an electric field and suppressing the negative effect, the experiment was designed and the setup was fabricated. The ionic electromigration of [C₆MIm][TFSI] from ILs bulk to aqueous solutions under different conditions was investigated. The regularities of ionic electromigration were discussed. It was beneficial to better utilization of binary system of ILs and aqueous solutions and reduce the consumption of ILs and environmental risks.

2 Experimental

2.1 Chemicals

ILs, 1-hexyl-3-methylimidazolium bis (trifluoromethanesulfonyl) imide ([C₆MIm][TFSI]) was purchased from Linzhou Keneng material technology Co., Ltd (Linzhou, China). While other chemicals were analytical grade and purchased from Shanghai Aladdin bio-chemical technology Co., Ltd (Shanghai, China). All the chemicals were used as received.

2.2 Experimental conditions

As seen in Figure 1, the glass U-tube (cross-sectional area is 0.80 cm²) was used as electrophoresis cell and the platinum wires were used as electrode with a diameter of 1 mm. The ILs and aqueous solutions were placed in the bottom and the upper section of U-tube respectively according to the density difference from ILs and aqueous solutions. 4.0 mL ILs was first injected into the U-tube, and then 8.0 mL cathode solutions and 8.0 mL anode solutions (LiOH, HCl, LiCl or LiN(CF₃SO₂)₂ solution) were fed into different branches of U-tube meanwhile. The injecting operation should be careful to avoid violent mixing between ILs and aqueous solutions. Similarly, the sampling operation should also be careful to avoid disturbing the interface of ILs and aqueous so-

lutions. All the experiments were carried out at room temperature. The electric field was supplied by a DC power (DH1766-1, Beijing Dahua radio instrument Co., Ltd, China).

2.3 Samples analysis

Fourier transformation infrared (FT-IR) spectra of samples were recorded by a FT-IR spectrometer (Nicolet Nexus 670, Thermo Nicolet Corporation, USA) and scanned from $4\,000\text{ cm}^{-1}$ to 500 cm^{-1} using KBr pellets

RPP-5000S sulphur Analyzer (Taizhouzhonghuan analysis instrument Co., Ltd, Jiangsu, China)

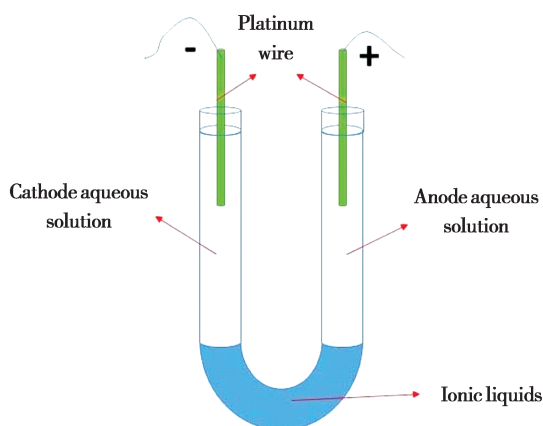


Fig. 1 The schematic diagram of experimental setup

3 Results and discussion

3.1 Effect of acidity-alkalinity of electrode solutions

For confirming the effect of acidity-alkalinity of electrode solutions on the migration of $[\text{C}_6\text{MIm}]^+$ ions under electric field, a series of experiments were designed and carried out. The conditions and results were displayed in Table 1.

According to table 1, the following conclusions can be reached. Firstly, the immigrant concentration of $[\text{C}_6\text{MIm}]^+$ ions in cathode solutions is higher than that in anode solutions under the similar experiments

was used to test sulphur contents of samples. According to the sulphur contents, the concentration of anions was determined. UV-Vis spectrophotometer (UV-2600, Shimadzu, Japan) was used to test the concentration of cations. $[\text{C}_6\text{MIm}]^+$ ions was tested in its maximum absorption wavelength 211.500 nm . And the absorbance-concentration standard curve of $[\text{C}_6\text{MIm}]^+$ ions aqueous solutions was initially established as shown in Figure 2. The value of the ABS (absorbance) was kept between 0.2 and 0.8 by the proper dilution to reduce relative error.

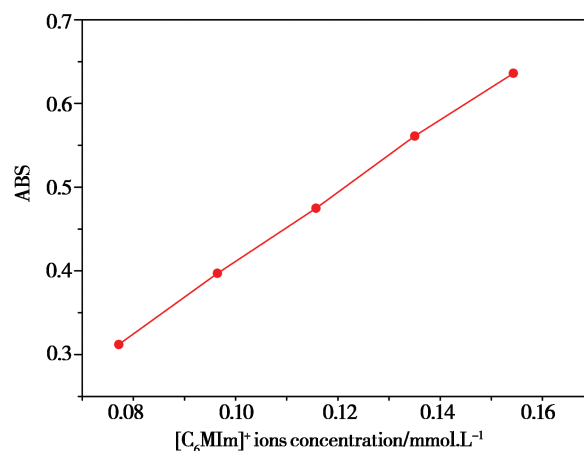


Fig. 2 Standard curve of UV-Vis absorbance-cation concentration of aqueous solutions

(experiments 1-4), which is attributed to oriented electromigration of charged cations to cathode solutions. Secondly, the LiOH solution can restrain the electromigration of $[\text{C}_6\text{MIm}]^+$ ions to electrode solutions, especially the LiOH solution used as cathode solution (experiments 1-4). Thirdly, the immigrant concentration of $[\text{C}_6\text{MIm}]^+$ ions in both HCl solution and LiOH solution are similar when the electric field is replaced by oscillation or standing (experiments 5-8), which is attributed to ionic diffusion through the interface of ILs and aqueous solutions. So it can be concluded that the difference of immigrant concentration of $[\text{C}_6\text{MIm}]^+$ ions of HCl solution and LiOH solution (experiments 1-4) has nothing to do with ionic diffusion.

Table 1 The migration of $[\text{C}_6\text{MIm}]^+$ ions in different electrode solutions from $[\text{C}_6\text{MIm}][\text{TFSI}]$

Experiment	External Field	Electrode	Solute /(0.05 mol/L)	$C_{[\text{C}_6\text{MIm}]} / (\text{mmol/L})$	Time/h
1	5mA current	Cathode	HCl	7.11	0.5
		Anode	HCl	2.18	0.5
2	5mA current	Cathode	LiOH	2.56	0.5
		Anode	LiOH	1.14	0.5
3	5mA current	Cathode	HCl	7.76	0.5
		Anode	LiOH	1.19	0.5
4	5mA current	Cathode	LiOH	2.59	0.5
		Anode	HCl	1.50	0.5
5	oscillation	—	HCl	5.90	0.5
6	oscillation	—	LiOH	6.37	0.5
7	standing	—	HCl	2.17	0.5
8	standing	—	LiOH	1.95	0.5

$C_{[\text{C}_6\text{MIm}]}$ represents the concentration of $[\text{C}_6\text{MIm}]^+$ ions in the aqueous solutions

Here, the FTIR spectra of original ILs and ILs after different experiments are shown in Figure 3. The meaning of the curves are as following: a: original $[\text{C}_6\text{MIm}][\text{TFSI}]$; b: experiment 5, 0.05 mol/L HCl solution, shocked for 0.5 h; c: experiment 6, 0.05 mol/L LiOH solution, shocked for 0.5 h; d: 5 mA current, 0.05 mol/L HCl solution in both electrode, 24 h; e: 5 mA current, 0.05 mol/L HCl solution in anode and 0.05 mol/L LiOH solution in cathode, 24 h; f: 5 mA current, 0.05 mol/L HCl solution in cathode and 0.05 mol/L LiOH solution in anode, 24 h; g: 5 mA current, 0.05 mol/L LiOH solution in both electrode, 24 h. For making the structural variation of ILs more visibility, the electric field was prolonged to 24 h from 0.5 h comparing to experiments 1–4 in Table 1. It is observed that the structures of ILs remain stable when the HCl solutions were used (shown as Figure 3a, 3b and 3d). Two peaks at $1\,621.94\text{ cm}^{-1}$ and $3\,417.30\text{ cm}^{-1}$ appear in Figure 3c, 3e, 3f and 3g which indicate the variation of $[\text{C}_6\text{MIm}][\text{TFSI}]$ structures when the LiOH solutions are used. No matter LiOH solution

was in anode or cathode, the structural variation of ILs always exists. Peaks at $1\,621.94\text{ cm}^{-1}$ and $3\,417.30\text{ cm}^{-1}$ can be attributed to stretching vibration of O-H bonds and imidazole ring respectively, which shows the existence of O-H bonds and variation of groups connecting with imidazole ring. Here it should be pointed out that the shape of peak at $3\,417.30\text{ cm}^{-1}$ is not sharp but broad, which illustrates that the vibration doesn't corresponds to not free hydroxide ions but covalent hydroxyls. And the possibility of vibration of O-H bonds from water molecules is excluded for not finding peaks at $1\,621.94\text{ cm}^{-1}$ and $3\,417.30\text{ cm}^{-1}$ in Figure 3b and 3d even that immigrant concentration of $[\text{C}_6\text{MIm}]^+$ ions in both HCl solution and LiOH solution are similar under oscillation or standing. So it can be inferred that the OH^- ions from LiOH solutions combine with $[\text{C}_6\text{MIm}]^+$ ions to form “neutral” C_6MImOH (Other ILs perhaps) and results in the appearance of both new peaks. And a large amount of “neutral” C_6MImOH is formed at the interface of ILs/LiOH solutions and dissolved back into ILs due to its hydro-

phobicity and density greater than aqueous solution when LiOH solutions are used as cathode solutions. The immobility and back-dissolution of “neutral” C_6MImOH in ILs bulk under electric field makes the

immigrant concentration of $[\text{C}_6\text{MIm}]^+$ ions in cathode solutions reduce significantly (Seen in experiment 2 and 4, Figure 3e and 3g).

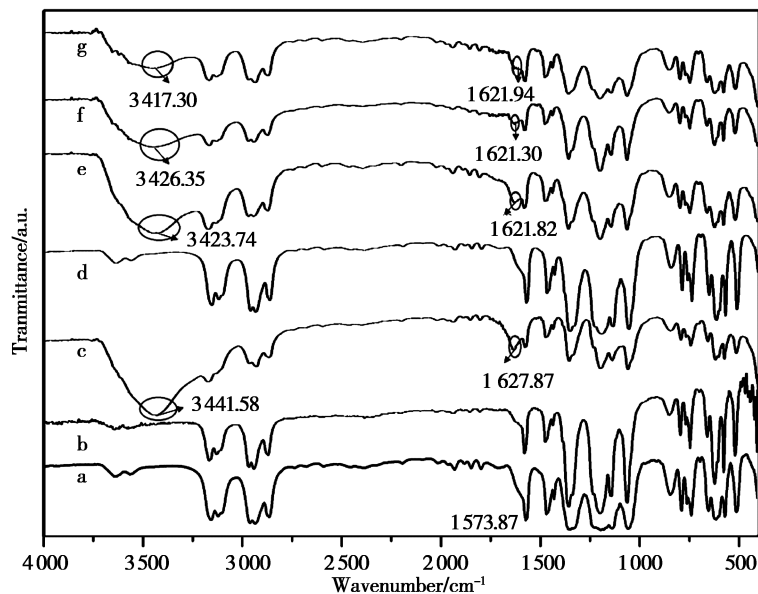


Fig. 3 FTIR spectra for $[\text{C}_6\text{MIm}][\text{TFSI}]$

3.2 Effect of electrolyte concentration of aqueous solutions

A constant voltage of 20 V and LiCl electrolyte solution of 5.0×10^{-4} , 5.0×10^{-3} , 5.0×10^{-2} , 5.0×10^{-1} , 5.0 and 10.0 mol/L were used respectively to investigate the influence of concentration of electrolyte solution. ILs is $[\text{C}_6\text{MIm}][\text{TFSI}]$ and the reaction time is 30 minutes. The concentration of $[\text{C}_6\text{MIm}]^+$ ions in cathode and anode solution with different concentration of LiCl electrolyte as electrode solution is shown in Figure 4.

As the electrolyte concentration increases, concentration of $[\text{C}_6\text{MIm}]^+$ ions increases in cathode solution but decreases in anode solution seen as in Figure 4. The increasing concentration of electrolyte in aqueous solution causes the resistance of the system decrease and the current to increase when the voltage remains unchanged. The increased current requires more ions migration of ILs for charge transfer. The driving forces of ionic migration of ILs can

be divided into two main types; electro-migration and diffusion. Immigrant concentration of $[\text{C}_6\text{MIm}]^+$ ions increases in cathode solution when the direction of ionic diffusion and electro-migration is identical. Immigrant concentration of $[\text{C}_6\text{MIm}]^+$ ions decreases in anode solution when the direction of ionic diffusion and electro-migration is opposite.

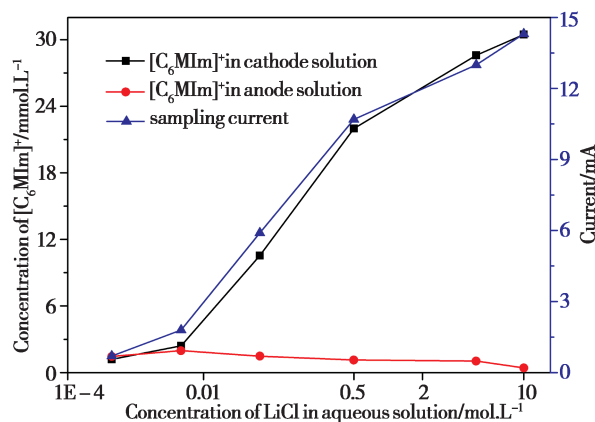


Fig. 4 The effect of concentration of LiCl in aqueous solutions on immigrant concentration of $[\text{C}_6\text{MIm}]^+$ ions in electrode solution

The increase of sampling current and $[\text{C}_6\text{MIm}]^+$ ions concentration in cathode solution is consistent with the increase of concentration of LiCl electrode solution when the voltage remains unchanged, shown in Figure 4. The increase of electrolyte concentration means the decrease of resistance and the increase of current of the total ILs-aqueous solution system. It can be inferred that the voltage on ILs increases with the increase of concentration of LiCl electrode solution. Here, the synchronized increase of sampling current and $[\text{C}_6\text{MIm}]^+$ ions concentration in cathode solution maybe means that the conductive nature of ILs is the oriented migration of $[\text{C}_6\text{MIm}]^+$ and $\text{N}(\text{CF}_3\text{SO}_2)_2^-$ ions.

3.3 Effect of electrolytes of aqueous solutions

Two electrolyte: LiCl (0.05 mol/L) solution and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (0.05 mol/L) solution were used to study the effect of different electrolyte solution on the migration of $[\text{C}_6\text{MIm}]^+$ ions from ILs into aqueous solution under an electric field. Currents of 1.0 mA, 2.0 mA, 3.0 mA, 4.0 mA, and 5.0 mA were used respectively. The reaction time was 30 minutes. The results are shown in Figure 5.

When LiCl solution was used, the immigrant concentration of $[\text{C}_6\text{MIm}]^+$ ions in cathode solution increased and that in anode solution decreased with increasing current (Seen in Figure 5 in LiCl electrolyte). It is easily to understand the migrating varia-

tion of $[\text{C}_6\text{MIm}]^+$ ions with electromigration effect and diffusion effect.

When $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ solution was used as electrode solution, the immigrant concentration of $[\text{C}_6\text{MIm}]^+$ ions into the electrode solution decreased markedly compared to that of LiCl solution (Seen in Figure 5 $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ electrolyte). And the increase margin of immigrant concentration of $[\text{C}_6\text{MIm}]^+$ ions into the cathode solution is apparently easy to understand. In $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ solution anode solution, the variation trend of immigrant concentration of $[\text{C}_6\text{MIm}]^+$ ions was opposite to that of LiCl anode solution. For understanding this phenomenon better, the third force influencing ionic migration: back-dissolution is introduced. Back-dissolution means that the $[\text{C}_6\text{MIm}]^+$ ions migrated into electrode solutions by diffusion and electromigration re-dissolved into ILs after it reacts with OH^- ions or $\text{N}(\text{CF}_3\text{SO}_2)_2^-$ ions to form hydrophobic “neutral” molecules or neutral ionic pairs, which can refer to the preparation process of ILs^[14]. Obviously, back-dissolution would make the immigrant concentration of $[\text{C}_6\text{MIm}]^+$ ions in the electrode solutions reduce. So in $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ solution anode solution, the variation trend of immigrant concentration of $[\text{C}_6\text{MIm}]^+$ ions was opposite to that of LiCl anode solution, which could be thought that strong back-dissolution was responsible for the strange phenomena. For LiCl solution or acidized “LiCl solution” after electric field was applied for a period of time, there was no back-dissolution basically at the interface of ILs/anode solution. While there always existed stronger back-dissolution at the interface of ILs and anode solution or cathode solution for $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ solution due to the formation of neutral ion pairs with $[\text{C}_6\text{MIm}]^+$ ions and $\text{N}(\text{CF}_3\text{SO}_2)_2^-$ ions^[14]. With the increasing current, the increasing electromigration effect made the $[\text{C}_6\text{MIm}]^+$ ions migrate to anode solution would decrease. But, on the one hand, the back-dissolution of $[\text{C}_6\text{MIm}]^+$ ions formed $[\text{C}_6\text{MIm}][\text{TFSI}]$ from anode solution to ILs was always existed with increasing current because the concentration of

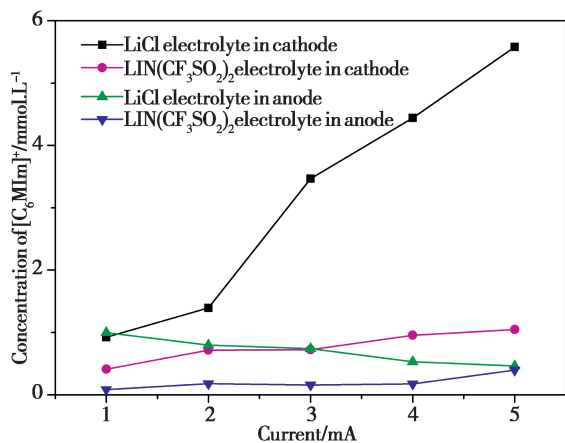


Fig. 5 Effect of different electrolytes on immigrant concentration of $[\text{C}_6\text{MIm}]^+$ ions in electrode solution

$\text{N}(\text{CF}_3\text{SO}_2)_2^-$ ions in anode aqueous solution would not decrease. On the other hand, as the anode electrode reaction continued, the aqueous solution will became more and more acidic, which resulted in the concentration of $[\text{C}_6\text{MIm}]^+$ ions increased as fore-said in 3.1 part. So the back-dissolution and acidification of anode aqueous solution made the immigrant concentration of $[\text{C}_6\text{MIm}]^+$ ions increase in the anode solution with increasing current.

It can be concluded that When $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ solution is used as electrode solution, the solution loss of ILs ($[\text{C}_6\text{MIm}][\text{TFSI}]$) can be reduced under electric filed.

3.4 The effect of $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ dissolved in ILs

Following experiments were designed in order to investigate the effect of $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ dissolved in ILs on the migration of $[\text{C}_6\text{MIm}]^+$ ions from ILs to electrode solutions. $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ was dissolved into ILs to form 0.1 mol/L solutions. 0.05 mol/L LiCl solution was used as electrode solution. Currents of 1.0 mA, 2.0 mA, 3.0 mA, 4.0 mA, and 5.0 mA were used respectively. Reaction time was 30 minutes. The results are shown in Figure 6.

Obviously, the immigrant concentration of $[\text{C}_6\text{MIm}]^+$ ions increased in cathode solution and decreased in anode solution with increasing current with or without $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in ILs. The change of immigrant concentration of $[\text{C}_6\text{MIm}]^+$ ions was mainly depended on the current. Compared with ILs without $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, the immigrant concentration of $[\text{C}_6\text{MIm}]^+$ ions in cathode solutions decreased while $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ was dissolved in ILs under same current. It indicated that the Li^+ ions in ILs undertook the part of charge transfer replaced $[\text{C}_6\text{MIm}]^+$ ions and there existed competition migration between $[\text{C}_6\text{MIm}]^+$ ions and Li^+ ions. It is believed that the introduction of metal ions in ILs is an effective routine of reduction of the consumption of ILs under electric field.

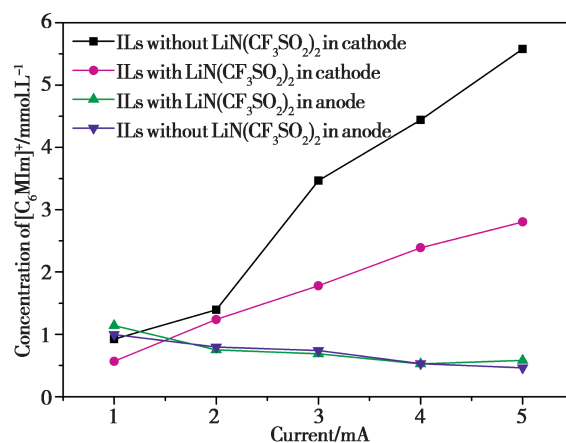


Fig. 6 Effect of ILs with or without $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ on immigrant concentration of $[\text{C}_6\text{MIm}]^+$ ions in electrode solution

3.5 Effect of voltage

The different voltage of 5, 10, 15, 20 and 30 V with LiCl electrolyte solution of 0.05 mol/L was used respectively to study the influence of different voltage on the migration of negative ions of ILs. The results are shown in Figure 7. The immigrant concentration of $\text{N}(\text{CF}_3\text{SO}_2)_2^-$ ions increases in anode solution and decreases in cathode solution with the increasing voltage, which is similar to $[\text{C}_6\text{MIm}]^+$ ions increases in cathode solution and decreases in anode solution with the increasing voltage. The immigrant concentration of $[\text{C}_6\text{MIm}]^+$ ions increases with the increasing voltage more than the immigrant concentration of $\text{N}(\text{CF}_3\text{SO}_2)_2^-$ ions, which may be because other anion takes part in the charge transfer.

It is easily to draw a conclusion that the anions and cations of ILs will migrate to the anode solution and cathode solution respectively under electric field.

4 Conclusions

Here, the effects of acidity-alkalinity, electrolyte concentration of electrode solutions and ILs with or without $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ on the migration of $[\text{C}_6\text{MIm}]^+$ ions was investigated and discussed.

1) When basic solution was used as cathode solution, the migration of $[\text{C}_6\text{MIm}]^+$ ions was restrained markedly. The formation and back-dissolution of

“neutral” C_6MImOH molecules was responsible for this result.

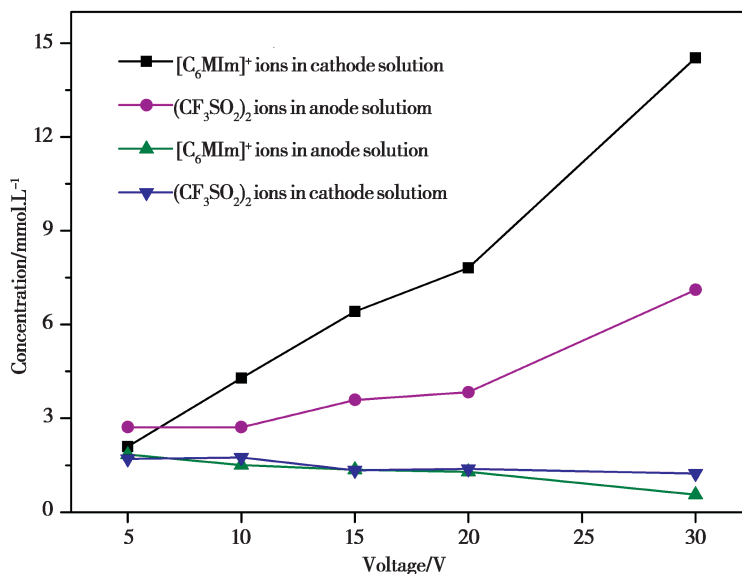


Fig. 7 The effect of voltage on immigrant concentration of ILs ions in electrode solution

2) Back-dissolution was a factor that cannot be ignored for migration of $[\text{C}_6\text{MIm}]^+$ ions from ILs to electrode solution when $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ solution was used as electrode solution. And what $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ solution is used as electrode solution is a way to reduce the solution loss of ILs under electric field.

3) The dissolution of $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in ILs can reduce the migration of $[\text{C}_6\text{MIm}]^+$ ions effectively under electric field.

The results were helpful to better understand the migrating law of ILs cations in ILs/aqueous solutions binary system and presented guideline for application of such systems under electric field.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by Key R&D Program of Qinghai Province (No. 2019 – GX – 169) and Youth Innovation Promotion Association of CAS (2015351). We also acknowledge Mr. Jiancheng Huang and Fengtai Tong, Miss Yanqin Wu and Lulu Fu for assistance in this work.

References:

- [1] Alexandra S, Matthew L H, Shafaq M., *et al.* Proteins in ionic liquids: reactions, applications, and futures [J]. *Frontiers in Chemistry*, 2019(7):347. doi:10.3389/fchem.2019.00347.
- [2] Sun J N, Shi Y P, Chen J. Development of ionic liquid based electromembrane extraction and its application to the enrichment of acidic compounds in pig kidney tissues [J]. *RSC Advances*, 2015(5):37682 – 37690.
- [3] Hoshino T. Preliminary studies of lithium recovery technology from seawater by electrodialysis using ionic liquid membrane [J]. *Desalination*, 2013(317):11 – 16.
- [4] Pringle J M, Ngamna O, Lynam C., *et al.* Conducting polymers with fibrillar morphology synthesized in a biphasic ionic liquid/water system [J]. *Macromolecules*. 2007(40):2702 – 2711.

- [5] Cheng M, Song G F, Zhu G F., *et al.* Reusable ionic liquid-functionalized polystyrene for the highly efficient removal of sulfadiazine sodium [J]. Journal Of Applied Polymer Science, 2019, 136 (38) : DOI:10. 1002/APP. 47981.
- [6] Wang X H, Wang G Y, Hou Y Y., *et al.* Extraction of ferulic acid and vanilla acid by hydrophobic ionic liquid 1-hexyl-3-methylimidazolium hexafluorophosphate [J]. Journal Of Food Science And Technology-Mysore, 2018, 55 (9) : 3508 – 3517.
- [7] Herrera C, Costa L T, Atilhan M., *et al.* Microscopic characterization of amino acid ionic liquids-water mixtures [J]. Journal of Molecular Liquids, 2017 (236) : 81 – 92.
- [8] Zhao Y L, Dong K, Liu X M, Zhang S J., *et al.* Structure of ionic liquids under external electric field; a molecular dynamics simulation [J]. Molecular Simulation, 2012, 38 (3) : 172 – 178.
- [9] Merlet C, Limmer D T, Salanne M., *et al.* The electric double layer has a life of its own [J]. Journal of Physical Chemistry C, 2014 (118) : 18291 – 18298.
- [10] Sha M L, Niu D X, Dou Q., *et al.* Reversible tuning of the hydrophobic-hydrophilic transition of hydrophobic ionic liquids by means of an electric field [J]. Soft Matter, 2011 (7) : 4228 – 4233.
- [11] Li F F, Liu Y, Lin W P. Phase equilibrium and protein partitioning in aqueous two-phase systems containing imidazolium ionic liquids and surfactant at low voltage levels [J]. Journal of Molecular Liquids, 2018 (256) : 372 – 379.
- [12] Tsuyoshi H, Takayuki T. High-efficiency technology for lithium isotope separation using an ionic-liquid impregnated organic membrane [J]. Fusion Engineering and Design, 2011 (86) : 2168 – 2171.
- [13] Tsuyoshi H, Takayuki T. Basic technology for 6Li enrichment using an ionic-liquid impregnated organic membrane [J]. Journal of Nuclear Materials, 2011 (417) : 696 – 699.
- [14] Montaninoa M, Alessandrinia F, Passerinib S., *et al.* Water-based synthesis of hydrophobic ionic liquids for high-energy electrochemical devices Electrochemical Acta [J]. 2013 (96) : 124 – 133.

离子液体 ($[C_6MIm][TFSI]$) 从体相电迁移至水相研究

王明勇^{1,2,3}, 孙进贺^{1,2}, 张鹏瑞^{1,2,3}, 黄超驰^{1,2,3}, 张 茜^{1,2,3},
邵 斐^{1,2}, 景 燕^{1,2}, 贾永忠^{1,2}

- (1. 中国科学院青海盐湖研究所, 中国科学院盐湖资源综合利用重点实验室, 青海 西宁 810008;
2. 青海省盐湖资源综合利用工程技术中心, 青海 西宁 810008; 3. 中国科学院大学, 北京 100049)

摘 要: 离子在离子液体/水溶液二元系统中的电迁移行为在很多领域受到了越来越多的关注。本文通过研究不同条件下离子液体离子在电极液中的浓度变化, 系统地研究了电极溶液酸—碱度, 电极溶液中电解质浓度以及离子液体中溶解 $LiN(CF_3SO_2)_2$ 与否对 $[C_6MIm]^+$ 离子电迁移的影响。总的来说, 随着电流的增加, $[C_6MIm]^+$ 离子向阴极水溶液的迁移量随之增加, 向阳极水溶液的迁移量随之减少; 然而 $N(CF_3SO_2)_2^-$ 离子向阳极水溶液的迁移量随之增加, 向阴极水溶液的迁移量随之减少。当电极溶液为碱性, $[C_6MIm]^+$ 离子的迁移量明显减少。在电极溶液中溶入 $LiN(CF_3SO_2)_2$ 时或者将 $LiN(CF_3SO_2)_2$ 溶入离子液体时, $[C_6MIm]^+$ 离子的迁移量也明显受到抑制。

关键词: 离子液体; 电迁移; 电极水溶液; 回溶