

离子液体缓蚀剂的研究现状

姜志阳¹, 郝 鑫²

(1. 中石化石油工程设计有限公司, 山东 东营 257000;

2. 中国石化胜利油田分公司石油开发中心科研所, 山东 东营 257000)

[摘要] 随着世界范围内生态意识和环保意识的增强,绿色环保的腐蚀防护技术变得越来越重要。离子液体缓蚀剂得到越来越多学者的关注。综述了研究较多的离子液体缓蚀剂的种类、发展历史以及研究现状,介绍了量子化学计算和分子动力学模拟在离子液体缓蚀剂方面的应用,同时总结了离子液体缓蚀剂的缓蚀机理。离子液体缓蚀剂可以抑制腐蚀反应的阳极过程和阴极过程,同时存在物理吸附和化学吸附,但目前模拟方法主要集中在分析分子的活性,以及分子在纯水中的吸附构型,没有考虑缓蚀剂分子与其它粒子间的相互作用,模拟环境与实际环境有较大差异,并没有模拟方法来解释缓蚀剂物理和化学吸附过程。总而言之,离子液体缓蚀剂在绿色环保的基础上向着不断提高缓蚀性能的方向发展,但其机理解释目前还存在一定的局限性。

[关键词] 离子液体; 绿色缓蚀剂; 腐蚀; 吸附机理; 分子动力学; 密度泛函理论

[中图分类号] TG174.42 **[文献标识码]** A **doi:** 10.16577/j.issn.1001-1560.2022.0138

[文章编号] 1001-1560(2022)05-0142-07

Research Status of Ionic Liquid Corrosion Inhibitors

JIANG Zhi-yang¹, HAO Xin²

(1. Sinopec Petroleum Engineering Corporation, Dongying 257000, China;

2. Research Institute of Petroleum Development Center, Sinopec Shengli Oilfield Company, Dongying 257000, China)

Abstract: With the increasing awareness of environmental protection around the world, the green corrosion protection technology is becoming more and more important. Tonic liquid corrosion inhibitors are getting more and more attention from scholars. In this paper, the types, development history and research status of ionic liquid corrosion inhibitors were reviewed. The application of quantum chemical calculation and molecular dynamics simulation in the field of ionic liquid corrosion inhibitor was studied. And the corrosion inhibition mechanisms of such inhibitors were summerized. The ionic liquid corrosion inhibitors can inhibit the anodic and cathodic processes of corrosion reactions, and both physical adsorption and chemisorption occur. However, current simulation methods focus on analyzing the activity of molecules and the adsorption configuration in pure water. The interaction between the corrosion inhibitor molecules and other particles is not considered. The simulated environments are quite different from the actual ones, and there is no simulation method to explain the physical and chemical adsorption processes of corrosion inhibitors. In all, the ionic liquid corrosion inhibitors will develop in the direction of increasing corrosion inhibition performance on the basis of environmental protection, but there are still certain limitations with regard to the explanation of mechanism.

Key words: ionic liquid; green corrosion inhibitor; corrosion; adsorption mechanism; molecular dynamics; density functional theory

0 前言

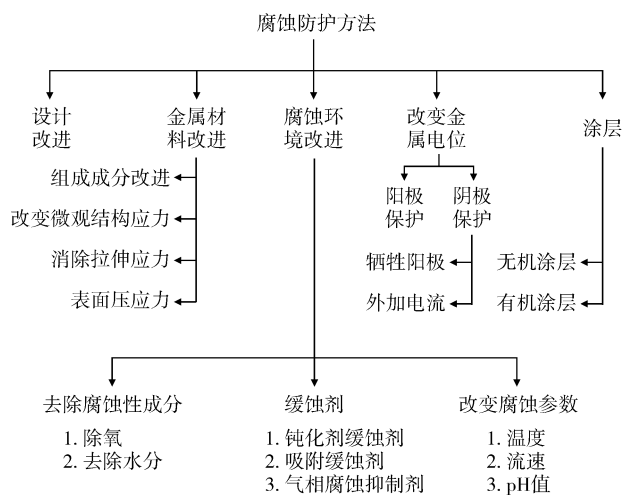
腐蚀是金属在环境中发生化学或电化学反应而导致的不可逆的自发失效^[1]。腐蚀会导致金属材料大量浪费,引起巨大的经济损失。在我国,每年因金属腐蚀而造成的经济损失可达到5 000亿元,世界范围内的经济损失更是高达国民生产总值的3%^[2-4],因而金属腐蚀引起了学术界和工业界的广泛关注^[5-8]。如今为减

少腐蚀所带来的损失,各行业已开发出多种金属腐蚀防护方法^[9,10],当前可用的防腐方法总结如图1所示^[11],其中缓蚀剂因其成本效益和应用方便而成为最佳方法之一^[12-16]。

离子液体因其具有较高的化学稳定性、高热稳定性、低蒸汽压、低可燃性、绿色环保、毒性低、设计灵活等特点,受到各行各业的关注^[11, 17, 18]。近年来,离子液体在特定领域的应用显著增加,尤其是在催化、化学

[收稿日期] 2021-12-11

[通信作者] 姜志阳(1964-),硕士研究生,高级工程师,从事管道材料研究,电话:13589988703, E-mail: sleccjzy@163.com

图1 可用的金属腐蚀防护方法^[11]Fig. 1 Available Metal Corrosion Protection Methods^[11]

转化溶剂、纳米材料合成、分离等领域^[19-25]。根据离子液体的定义,其熔点低于 100 ℃,可设计离子液体的阴离子和阳离子而达到所需要满足的性质,这是离子液体的最大优势^[26]。因此,离子液体被称作 21 世纪最具发展前景的绿色化学材料之一^[27]。因其独特的性质,离子液体也被广泛用于缓蚀剂,据报道称,理论上组合不同的阳离子与阴离子,离子液体缓蚀剂的数量可达 10^{19} 种,具有巨大的研究空间和应用价值^[28]。

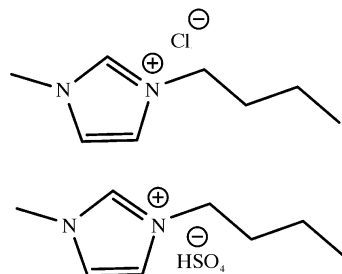
1 离子液体缓蚀剂的分类

目前对离子液体缓蚀剂的研究大多针对阳离子型,按阳离子官能团来分研究最多的为咪唑基离子液体缓蚀剂和吡啶基离子液体缓蚀剂,此外还有季铵盐离子液体缓蚀剂、哌啶离子液体缓蚀剂和吡咯烷离子液体缓蚀剂等。

1.1 咪唑基离子液体缓蚀剂

对于咪唑基离子液体缓蚀剂的研究大都在酸性体系中。Zhang 等^[29]于 2009 年研究了氯化 1-丁基-3-甲基咪唑盐 (BMIC) 和 1-丁基-3-甲基咪唑硫酸盐 ($[BMIM]H_2SO_4$) 在 1 mol/L HCl 中对低碳钢的酸腐蚀抑制作用,结构如图 2 所示,研究表明,2 种缓蚀剂缓蚀效率随着缓蚀剂浓度的增加而增大, $[BMIM]H_2SO_4$ 的缓蚀性能优于 BMIC,通过计算活化焓 (ΔH),计算活化熵 (ΔS),吸附平衡常数 (K_{ads}) 和标准吸附自由能 (ΔG_{ads}) 等明确了 2 种缓蚀剂为混合型缓蚀剂,这是最早对咪唑基离子液体在酸性介质中缓蚀性能的研究。

此外,对缓蚀剂侧链烷基的长度与缓蚀剂性能关系的研究也是一个热门方向,Guzmán-Lucero 等^[30]采

图2 咪唑类离子液体缓蚀剂^[29]Fig. 2 Imidazole Ionic Liquid Corrosion Inhibitors^[29]

用常规合成法和微波合成法,分别得到了 5 种含有 N_1 不饱和链和 N_3 长烷基饱和链阳离子和溴离子的咪唑类离子液体,测试其在 1 mol/L H_2SO_4 水溶液中对碳钢的缓蚀能力,结果表明,其缓蚀效率随缓蚀剂浓度的增加而增大,这取决于与 N_3 相连的烷基链尺寸 ($IL4 > IL3 > IL1 > IL2 > IL5$),同时研究表明,质子化咪唑离子液体缓蚀剂分子在阳极和阴极位点上的吸附,是通过与氢离子竞争吸附以减缓腐蚀。Zheng 等^[31]利用失重法研究了 1-辛基-3-甲基咪唑基溴化物 ($[OMIM]Br$) 和 1-烯丙基-3-辛基咪唑基溴化物 ($[AOIM]Br$) 对低碳钢在 0.5 mol/L H_2SO_4 中的缓蚀性能和机理,结果表明 $[AOIM]Br$ 的缓蚀性能优于 $[OMIM]Br$,模拟分析表明,这是因为丙烯基具有更强的给电子作用所致。Feng 等^[32]合成了 3 种具有不同碳链长度的咪唑基缓蚀剂 $[VMIM]I$ 、 $[VPIM]I$ 和 $[VBIM]I$,测试了它们在 0.5 mol/L H_2SO_4 溶液中对 X70 钢的缓蚀作用,结果表明缓蚀效率的顺序为: $[VMIM]I < [VPIM]I < [VBIM]I$,即随着咪唑环上烷基链长度的增加,缓蚀性能得到了改善,这是由于烷基的供电子作用使得具有长链烷基的缓蚀剂吸附性更强。通过对不同长度烷基对离子液体缓蚀剂的性能影响研究,均表明烷基链越长,缓蚀剂缓蚀性能越好,一方面是因为长烷基链具有更强的给电子能力,另一方面是因为烷基链越长缓蚀剂膜越牢固。

1.2 吡啶类离子液体缓蚀剂

早在 20 世纪 90 年代,就有关于吡啶基离子液体缓蚀剂的报道^[33],对于吡啶基离子液体缓蚀剂的研究也都在酸性体系中。Li 等^[34]利用电化学方法研究了十四烷基溴化吡啶基离子液体缓蚀剂 (TDPB) 在 1 mol/L HCl 溶液中对铝的缓蚀作用,结构如图 3 所示,结果表明,TDPB 在低浓度下具有良好的缓蚀效果,极化曲线显示 TDPB 充当阴极型缓蚀剂,能够抑制腐蚀反应的阴极过程,从而起到缓蚀作用。Dandia 等^[35]利用超声波辐照合成了 4-(2-氯-6-氟苯基)-3-甲基-6-氧代-4,5,6,7-四氢-2H-吡啶并[3,4-b]吡啶-5-腈

(AP-1), 3-甲基-6-氧代-4,5,6,7-四氢-2 H-吡唑并[3,4-b]吡啶-5-腈(AP-2), 3-甲基-6-氧代-4-(对甲基)-4,5,6,7-四氢-2 H-吡唑并[3,4-b]吡啶-5-腈(AP-3), 4-(4-甲氧基苯基)-3-甲基-6-氧代-4,5,6,7-四氢-2 H-吡唑并[3,4-b]吡啶-5-甲腈(AP-4)和3-甲基-6-氧代-4-(3,4,5-三甲氧基苯基)-4,5,6,7-四氢-2 H-吡唑并[3,4-b]吡啶-5-甲腈(AP-5) 5种吡啶衍生物,通过失重法和电化学测试研究其在 1 mol/L HCl 溶液中对低碳钢的缓蚀作用,结果表明 5 种缓蚀剂为混合型缓蚀剂,但其阴极效果更明显,AP-5 缓蚀效果最佳,在 100 mg/L 时的缓蚀效率为 95.2%。Gu 等^[36]合成了 1 种新 N-烷基-2-(4-羟基丁-2-炔基)溴化吡啶基离子液体缓蚀剂,研究其在 5 mol/L HCl 溶液中对 X70 碳钢的缓蚀作用,结果表明反应温度与缓蚀剂浓度在缓蚀过程中起重要作用,通过 XPS 分析表明该缓蚀剂为混合型缓蚀剂,既阻碍了阳极金属的溶解,又阻碍了阴极氢的还原反应。

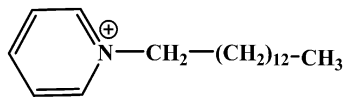


图 3 吡啶类离子液体缓蚀剂结构^[34]

Fig. 3 Structure of pyridine ionic liquid corrosion inhibitor^[34]

目前吡啶类离子液体缓蚀剂大都作为酸化缓蚀剂,研究思路为合成新型缓蚀剂,测试其缓蚀性能,通过 XPS 分析缓蚀剂的类型,通过分子模拟解释其缓蚀机理。

1.3 其它离子液体缓蚀剂

其它类型的离子液体缓蚀剂因其阳离子不同而具有不同的缓蚀性能。汪红梅^[37]合成了 3 种苯并三氮唑缓蚀剂:溴化 1,3-二乙基苯并三氮唑(C2BtEtBr)、溴化 1-丁基-3-乙基苯并三氮唑(C4BtEtBr)和溴化 1,3-二丁基苯并三氮唑(C4BtBuBr),研究了它们在 5% 的 HCl 溶液中对 15Mn 钢的缓蚀作用,结果表明,缓蚀剂的缓蚀效率随其加注浓度的增加而增大,当浓度为 20 mol/L 时,3 种缓蚀剂的缓蚀效率均在 83% 以上,实验表明 3 种缓蚀剂均为混合型缓蚀剂,缓蚀效率依次为 C4BtBuBr > C4BtEtBr > C2BtEtBr,通过计算吉布斯自由能,表明三种离子液体缓蚀剂在金属表面的吸附是自发进行的,以物理吸附为主,但也存在化学吸附。Kowsari 等^[38]合成了 1 种氨基酸衍生的离子液体缓蚀剂,为蛋氨酸四正丁基铵,并使用电化学、量子化学和表面分析研究了该缓蚀剂在 1 mol/L HCl 溶液中对低碳钢的腐蚀防护作用,研究表明,该缓蚀剂为一种混合

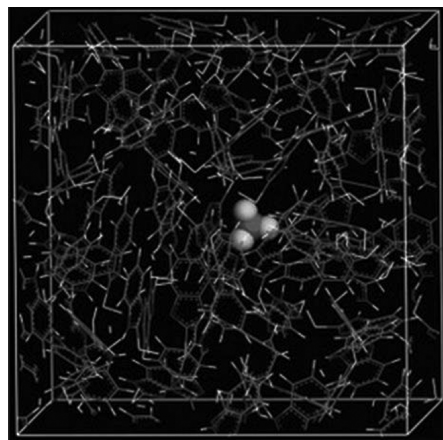
型缓蚀剂,但其对腐蚀反应的阳极过程阻碍作用更强,其缓蚀机理是通过甲硫氨酸基团朝向阳极位点和四正丁基铵基团朝向阴极位点的吸附。El-Shamy 等^[39]合成了一种 1-丁基-1-甲基吡咯烷三氟甲基磺酸盐离子液体缓蚀剂,研究其在 3.5% NaCl 溶液中对低碳钢腐蚀的缓蚀作用,结果表明该缓蚀剂为混合型缓蚀剂,且在 800 mg/L 时缓蚀效率可达 80.2%。

2 离子液体缓蚀剂的分子模拟研究

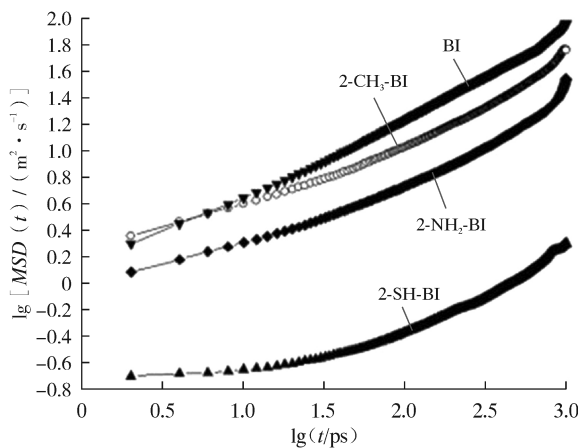
目前对于离子液体缓蚀剂的分子模拟研究主要是量子化学计算和分子动力学模拟研究。尤其是基于密度泛函理论(DFT)的量子化学计算,能够从理论上比较缓蚀剂的缓蚀性能。DFT 计算可提供几个参数来评判缓蚀剂的性能,比如分子的最高占据轨道能量(E_{HOMO})、分子的最低未占据轨道能量(E_{LUMO})、能隙($E_{\text{LUMO}} - E_{\text{HOMO}} = \Delta E$)、分子整体反应活性的化学势 μ 、绝对硬度 η 、全局软度 S 、亲电指数 ω 、原子的 Fukui 指数、Mulliken 电荷分布等,这些参数可以解释缓蚀剂与金属的相互作用强弱。通常来讲,HOMO 能级为缓蚀剂的第一电离能,其值越低,缓蚀剂越容易失去电子;LUMO 能级值越低,缓蚀剂分子越容易得到电子;能隙的大小反映了电子从分子最高占据轨道向最低未占据轨道跃迁的能力,其值越大说明电子越难跃迁,分子相对稳定,难以吸附在金属表面^[40]。分子的电负性 χ 与化学势 μ 互为相反数关系,其值与缓蚀剂的缓蚀效率阶数成反比;此外缓蚀剂分子的缓蚀效率随着硬度(η)的增加和柔软度(S)的降低而降低^[41-43]。分子动力学模拟主要集中在研究缓蚀剂膜与其它粒子的相互作用能、粒子的扩散系数、粒子在缓蚀剂膜中的扩散机理等来比较缓蚀剂的缓蚀性能^[44]。

Manamela 等^[45]通过实验和模拟的方法比较了 2 种缓蚀剂[DMIM][BF₄⁻]和[BMIM][BF₄⁻]的缓蚀性能,通过分析分子的最高占据轨道能量、分子的最低未占据轨道能量、能隙、分子整体反应活性的化学势 μ 、绝对硬度 η 、全局软度 S 、亲电指数 ω 、原子的 Fukui 指数,得到缓蚀剂[DMIM][BF₄⁻]比[BMIM][BF₄⁻]具有更多向金属表面提供电子的位点,这反过来表明[DMIM][BF₄⁻]更易吸附在金属表面,这与实验得到的结果一致。Murulana 等^[46]研究了 4 种咪唑基离子液体的吸附行为,通过对 1-丙基-3-甲基咪唑双(三氟甲基磺酰基)酰亚胺([PMIM][NTf₂])、1-丁基-3-甲基咪唑双(三氟甲基-磺酰基)酰亚胺

([BMIM][NTf2])、1-己基-3-甲基咪唑双(三氟甲基-磺酰基)酰亚胺([HMIM][NTf2])和1-丙基-2,3-甲基咪唑双(三氟甲基-磺酰基)酰亚胺([PDMIM][NTf2])在1 mol/L HCl中的低碳钢腐蚀的实验和量子化学计算,试验证明这些离子液体的缓蚀效率依次为:[PDMIM][NTf2]>[HMIM][NTf2]>[BMIM][NTf2]>[PMIM][NTf2]。 E_{HOMO} 和 E_{LUMO} 的值与实验结果相符。结果表明,[PDMIM][NTf2]的 ΔE 值最低,因此具有最高的化学反应性和缓蚀效率。整体柔软度(S)值再次表明,[PDMIM][NTf2]是被测化合物中最柔软分子,从而具有最高的化学反应性



(a) 分子模型



(b) 均方位移曲线

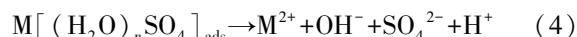
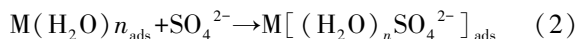
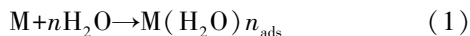
图4 缓蚀剂的模拟机理^[44]Fig. 4 Simulation mechanism of corrosion inhibitor^[44]

3 离子液体缓蚀剂的缓蚀机理

与其它有机缓蚀剂缓蚀机理相似,离子液体缓蚀剂也是通过吸附在金属的阳极和阴极位点来保护金属免受腐蚀。因此离子液体缓蚀剂既能抑制阳极金属腐蚀反应,又能减缓阴极析氢反应^[47,48]。

3.1 阳极反应

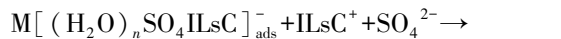
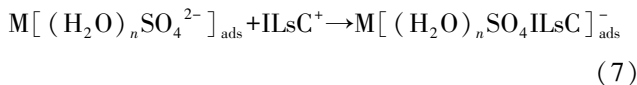
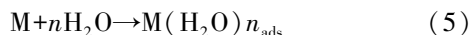
在酸性介质中,以 Atta 等^[48]的研究为例,金属(M)在酸性溶液(以 H_2SO_4 溶液为例)中的腐蚀过程(阳极反应)如下所示:



其它酸性溶液中的腐蚀机理类似,唯一的区别是腐蚀性离子为 Cl^- 、 NO_3^- 等。然而,当有离子液体缓蚀剂(ILs)存在时,金属腐蚀过程如下^[16]:

和缓蚀效率。

Zhang 等^[44]采用分子动力学模拟,研究了2-巯基苯并咪唑(2-SH-BI)、2-氨基苯并咪唑(2-NH₂-BI)、2-甲基苯并咪唑(2-CH₃-BI)、苯并咪唑(BI)缓蚀剂膜内腐蚀粒子的扩散,通过均方位移曲线、径向分布函数和相互作用能等参数研究了腐蚀粒子与膜的相互作用,以及膜的迁移率等微观扩散机理,通过对比不同缓蚀剂的相应参数来比较缓蚀剂的缓蚀性能,明确缓蚀剂结构与其性能的关系,如图4所示。模拟表明缓蚀剂的缓蚀效率顺序为2-SH-BI > 2-NH₂-BI > 2-CH₃-BI > BI,与其实验结果一致。

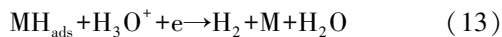
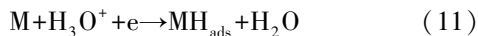


其中 $ILsC^+$ 和 X^- 分别代表离子液体缓蚀剂的有机阳离子和阴离子。有研究表明,在酸性溶液中金属表面形成的 $M[(H_2O)_nSO_4^{2-}]_{\text{ads}}$ 和 $(MX)_{\text{ads}}^-$ 会通过静电吸引力(物理吸附)吸引离子液体阳离子,在金属表面形成单分子复合物层^[49],离子液体阳离子吸附后会改变金属表面的极性变化,进而吸附阴离子形成多分子复合物层^[50]。复合物层的存在使金属与腐蚀介质隔离,保护金属免受腐蚀。

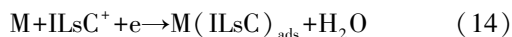
3.2 阴极反应

当缓蚀剂不存在时,阴极的析氢反应可表示为如

下过程^[51,52]:



当缓蚀剂存在时,阴极过程如下^[49]:



离子液体缓蚀剂取代氢离子接受来自金属的电子,形成电中性分子,此后电中性分子将其杂原子上的孤对电子迁移到金属原子的 d 轨道上,从而形成化学键吸附在金属表面^[53,54],由于其分子量较大,可取代金属表面的水分子和腐蚀性离子,从而起到保护金属的作用。

4 总结与展望

与传统缓蚀剂相比,离子液体缓蚀剂具有挥发性低、可燃性低、化学稳定性高、无毒等优点,是一种绿色环保型缓蚀剂。目前对离子液体缓蚀剂比较前沿的研究为不断提高缓蚀剂的缓蚀性能,主要方法为:(1)与其它纳米材料协同构成吸附膜;Liu 等^[55]通过咪唑离子液体与氧化石墨烯的快速接枝反应制备了离子液体氧化石墨烯杂化纳米材料,这种离子液体氧化石墨烯杂化能有效改善环氧基水性涂料的耐腐蚀性能。(2)对缓蚀剂分子结构进行改性,提高其缓蚀性能:第一是增长缓蚀剂的侧链长度^[30-32];第二是修饰缓蚀剂分子活性基团,Yang 等^[56]以咪唑离子液体和柠檬酸基碳点为原料,合成了尺寸为 3.0~5.5 nm 的绿色缓蚀剂,使得缓蚀剂在 1 mol/L HCl 体系中的缓蚀效率高于其在 3.5%NaCl 溶液中;第三种是将缓蚀剂修饰为共轭结构^[57]。对于离子液体缓蚀剂的机理解释方面仅仅局限于前线轨道分布与计算分子的全局反应活性,进行动力学模拟时模型处于真空中或者纯水中,没有考虑缓蚀剂与其它粒子间的相互作用,与实际环境有较大差异。总而言之,离子液体缓蚀剂在绿色环保的基础上不断提高缓蚀性能,但其缓蚀机理目前没有比较有力的证明。

[参 考 文 献]

- [1] REVIE R W, UHLIG H H. Corrosion and corrosion control: an introduction to corrosion science and engineering [M]. New York: John Wiley & Sons, 2008.
- [2] QIAN H C, XU D, DU C W, et al. Dual-action smart coatings with a self-healing superhydrophobic surface and anti-corrosion properties [J]. Journal of Materials Chemistry A, 2017, 5(5): 2 355-2 364.
- [3] YE Y W, ZHANG D W, LI J Y, et al. One-step synthesis

of superhydrophobic polyhedral oligomeric silsesquioxane - graphene oxide and its application in anti - corrosion and anti-wear fields [J]. Corrosion Science, 2019, 147: 9-21.

- [4] KOCH G. Cost of corrosion [M]. Cambridge: Woodhead Publishing, 2017: 3-30.
- [5] 柯 伟. 中国工业与自然环境腐蚀调查的进展 [J]. 腐蚀与防护, 2004, 25(1): 1-8.
- KE W. Progress in public inquiry concerning corrosion in chinese industrial and natural environments [J]. Corrosion and Protection, 2004, 25(1): 1-8.
- [6] MASADEH S. The effect of added carbon black to concrete mix on corrosion of steel in concrete [J]. Journal of Minerals and Materials Characterization and Engineering, 2015, 3(4): 271-276.
- [7] PANCHENKO Y M, MARSHAKOV A I. Long-term prediction of metal corrosion losses in atmosphere using a power-linear function [J]. Corrosion Science, 2016, 109: 217-229.
- [8] WINKLEMAN A, SVEDBERG E B, SCHAFFRIK R E, et al. Preventing corrosion from wearing our future away [J]. Advanced Materials & Processes, 2011, 169(3): 26-32.
- [9] LIU C, REVILLA R I, ZHANG D W, et al. Role of Al_2O_3 inclusions on the localized corrosion of Q460NH weathering steel in marine environment [J]. Corrosion Science, 2018, 138: 96-104.
- [10] LIU Z Y, LI X G, CHENG Y F. Understand the occurrence of pitting corrosion of pipeline carbon steel under cathodic polarization [J]. Electrochimica Acta, 2012, 60: 259-263.
- [11] VERMA C, EBENSO E E, QURAISHI M A. Ionic liquids as green and sustainable corrosion inhibitors for metals and alloys: an overview [J]. Journal of Molecular Liquids, 2017, 233: 403-414.
- [12] Antonijević M M, Milić S M, Petrović M B. Films formed on copper surface in chloride media in the presence of azoles [J]. Corrosion Science, 2009, 51(6): 1 228-1 237.
- [13] NGUYEN THUY D, TO THI XUAN H, NICOLAY A, et al. Corrosion protection of carbon steel by solvent free epoxy coating containing hydrotalcites intercalated with different organic corrosion inhibitors [J]. Progress in Organic Coatings, 2016, 101: 331-341.
- [14] LIU C, REVILLA R I, LIU Z Y, et al. Effect of inclusions modified by rare earth elements (Ce, La) on localized marine corrosion in Q460NH weathering steel [J]. Corrosion Science, 2017, 129: 82-90.
- [15] MERESHT E S, FARAHANI T S, NESHATI J. 2-Butyne-1, 4-diol as a novel corrosion inhibitor for API X65 steel pipeline in carbonate/bicarbonate solution [J]. Corrosion Science, 2012, 54: 36-44.

- [16] WANG X M, YANG H Y, WANG F H. A cationic gemini-surfactant as effective inhibitor for mild steel in HCl solutions[J]. *Corrosion Science*, 2010, 52(14): 1 268–1 276.
- [17] QIANG Y J, ZHANG S J, GUO L, et al. Experimental and theoretical studies of four allyl imidazolium-based ionic liquids as green inhibitors for copper corrosion in sulfuric acid[J]. *Corrosion Science*, 2017, 119: 68–78.
- [18] CIOC R C, RUIJTER E, ORRU R V A. Multicomponent reactions: advanced tools for sustainable organic synthesis[J]. *Green Chemistry*, 2014, 16(6): 2 958–2 975.
- [19] DRIOLI E, MACEDONIO F. Membrane engineering for water engineering[J]. *Industrial & Engineering Chemistry Research*, 2012, 51(30): 10 051–10 056.
- [20] GREAVES T L, DRUMMOND C J. Protic ionic liquids: evolving structure – property relationships and expanding applications[J]. *Chemical Reviews*, 2015, 115(20): 11 379–11 448.
- [21] 赵旭, 邢华斌, 李如龙, 等. 离子液体在气体分离中的应用[J]. *化学进展*, 2011, 23(11): 2 258–2 268.
ZHAO X, XING H B, LI R L, et al. Gas Separation Based on Ionic Liquids[J]. *Progress in Chemistry*, 2011, 23(11): 2 258–2 268.
- [22] 陈旭伟, 毛全兴, 王建华. 离子液体在蛋白质萃取分离中的应用[J]. *化学进展*, 2013, 25(5): 661–668.
CHEN X W, MAO Q X, WANG J H. Ionic Liquids in Extraction/Separation of Proteins[J]. *Progress in Chemistry*, 2013, 25(5): 661–668.
- [23] HOOGERSTRAETE T V, ONGHENA B, BINNEMANS K. Homogeneous liquid – liquid extraction of metal ions with a functionalized ionic liquid[J]. *The Journal of Physical Chemistry Letters*, 2013, 4(10): 1 659–1 663.
- [24] AMARASEKARA A S. Acidic ionic liquids[J]. *Chemical Reviews*, 2016, 116(10): 6 133–6 183.
- [25] XING D Y, DONG W Y, CHUNG T S. Effects of different ionic liquids as green solvents on the formation and ultrafiltration performance of CA hollow fiber membranes[J]. *Industrial & Engineering Chemistry Research*, 2016, 55(27): 7 505–7 513.
- [26] TANG S, LIU S J, GUO Y, et al. Recent advances of ionic liquids and polymeric ionic liquids in capillary electrophoresis and capillary electrochromatography[J]. *Journal of Chromatography A*, 2014, 1 357: 147–157.
- [27] 王军, 杨许召, 吴师德, 等. 离子液体的性能及应用[M]. 北京: 中国纺织出版社, 2007.
WANG J, YANG X Z, WU S D, et al. Properties and applications of ionic liquids[M]. Beijing: China Textile Press, 2007.
- [28] 赵永升, 张香平, 赵继红, 等. 离子液体的定量结构-性质/活性研究[J]. *化学进展*, 2012, 24(7): 1 236–1 244.
ZHAO Y S, ZHANG X P, ZHAO J H, et al. Research of QSPR/QSAR for Ionic Liquids[J]. *Progress in Chemistry*, 2012, 24(7): 1 236–1 244.
- [29] ZHANG Q B, HUA Y X. Corrosion inhibition of mild steel by alkylimidazolium ionic liquids in hydrochloric acid[J]. *Electrochimica Acta*, 2009, 54(6): 1 881–1 887.
- [30] Guzmán-LUCERO D, OLIVARES-XOMETL O, Martínez-PALOU R, et al. Synthesis of selected vinylimidazolium ionic liquids and their effectiveness as corrosion inhibitors for carbon steel in aqueous sulfuric acid[J]. *Industrial & Engineering Chemistry Research*, 2011, 50(12): 7 129–7 140.
- [31] ZHENG X W, ZHANG S T, LI W P, et al. Experimental and theoretical studies of two imidazolium-based ionic liquids as inhibitors for mild steel in sulfuric acid solution[J]. *Corrosion Science*, 2015, 95: 168–179.
- [32] FENG L, ZHANG S T, QIANG Y J, et al. The synergistic corrosion inhibition study of different chain lengths ionic liquids as green inhibitors for X70 steel in acidic medium[J]. *Materials Chemistry and Physics*, 2018, 215: 229–241.
- [33] SUBRAMANIAM G, BALASUBRAMANIAN K, SRIDHAR P. 1, 1'-Alkylene bis-pyridinium compounds as pickling inhibitors[J]. *Corrosion Science*, 1990, 30(10): 1 019–1 023.
- [34] LI X H, DENG S D, FU H. Inhibition by tetradecylpyridinium bromide of the corrosion of aluminium in hydrochloric acid solution[J]. *Corrosion Science*, 2011, 53(4): 1 529–1 536.
- [35] DANDIA A, GUPTA S L, SINGH P, et al. Ultrasound-assisted synthesis of pyrazolo [3, 4-b] pyridines as potential corrosion inhibitors for mild steel in 1.0 M HCl[J]. *ACS Sustainable Chemistry & Engineering*, 2013, 1(10): 1 303–1 310.
- [36] GU T B, CHEN Z J, JIANG X H, et al. Synthesis and inhibition of N-alkyl-2-(4-hydroxybut-2-ynyl) pyridinium bromide for mild steel in acid solution: Box – Behnken design optimization and mechanism probe[J]. *Corrosion Science*, 2015, 90: 118–132.
- [37] 汪红梅. 离子液体的制备及其在锂二次电池和缓蚀剂方面的应用研究[D]. 长沙: 中南大学, 2013.
WANG H M. Preparation of ionic liquids and their application in lithium secondary batteries and corrosion inhibitors[D]. Changsha: Central South University, 2013.
- [38] KOWSARI E, ARMANS Y, SHAHINI M H, et al. In situ synthesis, electrochemical and quantum chemical analysis of an amino acid-derived ionic liquid inhibitor for corrosion protection of mild steel in 1M HCl solution[J]. *Corrosion Science*, 2016, 112: 73–85.

- [39] EL-SHAMY A M, ZAKARIA K, ABBAS M A, et al. Anti-bacterial and anti-corrosion effects of the ionic liquid 1-butyl-1-methylpyrrolidinium trifluoromethylsulfonate[J]. *Journal of Molecular Liquids*, 2015, 211:363-369.
- [40] 吴刚, 郝宁眉, 廉兵杰, 等. 吡啶类缓蚀剂及其在 Al(111)表面吸附行为的密度泛函理论分析[J]. *化工学报*, 2013, 64(7): 2 565-2 572.
- WU G, HAO N M, LIAN B J, et al. Density functional theory analysis on pyridine corrosion inhibitors and adsorption behavior on Al(111) surface[J]. *Chinese Journal of Chemical Industry*, 2013, 64(7): 2 565-2 572.
- [41] VERMA C, QURASHI M A, OLASUNKANMI L O, et al. L-Proline-promoted synthesis of 2-amino-4-arylquinoline-3-carbonitriles as sustainable corrosion inhibitors for mild steel in 1 mol/L HCl: experimental and computational studies[J]. *RSC Advances*, 2015, 5(104): 85 417-85 430.
- [42] VERMA C, OLASUNKANMI L O, EBENSO E E, et al. Adsorption behavior of glucosamine-based, pyrimidine-fused heterocycles as green corrosion inhibitors for mild steel: experimental and theoretical studies[J]. *The Journal of Physical Chemistry C*, 2016, 120(21): 11 598-11 611.
- [43] VERMA C, OLASUNKANMI L O, OBOT I B, et al. 2, 4-Diamino-5-(phenylthio)-5H-chromeno[2,3-b]pyridine-3-carbonitriles as green and effective corrosion inhibitors: gravimetric, electrochemical, surface morphology and theoretical studies[J]. *RSC Advances*, 2016, 6(59): 53 933-53 948.
- [44] ZHANG J, YU W Z, YU L J, et al. Molecular dynamics simulation of corrosive particle diffusion in benzimidazole inhibitor films[J]. *Corrosion Science*, 2011, 53(4): 1 331-1 336.
- [45] MANAMELA K M, MURULANA L C, KABANDA M M, et al. Adsorptive and DFT studies of some imidazolium based ionic liquids as corrosion inhibitors for zinc in acidic medium[J]. *International Journal of Electrochemical Science*, 2014, 9(6): 3 029-3 046.
- [46] MURULANA L C, SINGH A K, SHUKLA S K, et al. Experimental and quantum chemical studies of some bis(trifluoromethyl-sulfonyl) imide imidazolium-based ionic liquids as corrosion inhibitors for mild steel in hydrochloric acid solution[J]. *Industrial & Engineering Chemistry Research*, 2012, 51(40): 13 282-13 299.
- [47] LIKHANOVA N V, Domínguez - AGUILAR M A, OLIVARES-XOMETL O, et al. The effect of ionic liquids with imidazolium and pyridinium cations on the corrosion inhibition of mild steel in acidic environment[J]. *Corrosion Science*, 2010, 52(6): 2 088-2 097.
- [48] ATTA A M, EL-MAHDY G, AL-LOHEDAN H A, et al. Adsorption Characteristics and Corrosion Inhibition Efficiency of Ethoxylated Octadecylamine Ionic Liquid in Aqueous Acid Solution[J]. *International Journal of Electrochemical Science*, 2016, 11(2): 882-898.
- [49] ASHASSI-SORKHABI H, ES'HAGHI M. Corrosion inhibition of mild steel in acidic media by [BMIm] Br Ionic liquid[J]. *Materials Chemistry and Physics*, 2009, 114(1): 267-271.
- [50] ZHANG D S, LI L D, CAO L X, et al. Studies of corrosion inhibitors for zinc-manganese batteries: quinoline quaternary ammonium phenolates[J]. *Corrosion Science*, 2001, 43(9): 1 627-1 636.
- [51] BHARDWAJ M, BALASUBRAMANIAM R. Uncoupled non-linear equations method for determining kinetic parameters in case of hydrogen evolution reaction following Volmer-Heyrovsky-Tafel mechanism and Volmer-Heyrovsky mechanism[J]. *International Journal of Hydrogen Energy*, 2008, 33(9): 2 178-2 188.
- [52] DE CHIALVO M R G, CHIALVO A C. The Tafel-Heyrovsky route in the kinetic mechanism of the hydrogen evolution reaction[J]. *Electrochemistry Communications*, 1999, 1(9): 379-382.
- [53] HAQUE J, SRIVASTAVA V, VERMA C, et al. Experimental and quantum chemical analysis of 2-amino-3-((4-((S)-2-amino-2-carboxyethyl)-1H-imidazol-2-yl)thio)propionic acid as new and green corrosion inhibitor for mild steel in 1 M hydrochloric acid solution[J]. *Journal of Molecular Liquids*, 2017, 225: 848-855.
- [54] VERMA C, EBENSO E E, VISHAL Y, et al. Dendrimers: a new class of corrosion inhibitors for mild steel in 1 mol/L HCl: experimental and quantum chemical studies[J]. *Journal of Molecular Liquids*, 2016, 224: 1 282-1 293.
- [55] LIU C B, QIU S H, DU P, et al. An ionic liquid-graphene oxide hybrid nanomaterial: synthesis and anticorrosive applications[J]. *Nanoscale*, 2018, 10(17): 8 115-8 124.
- [56] YANG D P, YE Y W, SU Y, et al. Functionalization of citric acid-based carbon dots by imidazole toward novel green corrosion inhibitor for carbon steel[J]. *Journal of Cleaner Production*, 2019, 229: 180-192.
- [57] ELGENDY A, ELKHOLY A E, EL BASIONY N M, et al. Monte Carlo simulation for the antiscaling performance of Gemini ionic liquids[J]. *Journal of Molecular Liquids*, 2019, 285: 408-415.