生　态　毒　理　学　报
Asian Journal of Ecotoxicology

Vol. 13, 2018
No.6 69-78

DOI:10.7524/AJE.1673-5897.20170801001

夏一璐, 范慧阳, 刘惠君, 等. 离子液体的水生生态毒理及其毒性影响因素研究进展[J]. 生态毒理学报,2018, 13(6): 69-78

Xia Y L, Fan H Y, Liu H J, et al. Aquatic ecotoxicology of ionic liquids and the factors affecting the toxicity: A review [J]. Asian Journal of Ecotoxicology, 2018, 13(6): 69-78 (in Chinese)

离子液体的水生生态毒理及其毒性影响因素研究进展

夏一璐, 范慧阳, 刘惠君*

浙江工商大学环境科学与工程学院,杭州 310018

收稿日期:2017-08-01　　**录用日期**:2017-10-10

摘要: 离子液体具有极低挥发性等良好理化性质而被公认为是传统有机溶剂的替代品,然而其较强的水溶性对水环境造成的潜在威胁受到关注。本文归纳总结了国内外有关不同类型离子液体对不同营养级水生生物个体、组织器官、细胞、酶等的毒性影响,并对碳链长度、阴阳离子以及环境因子等毒性影响因素的最新研究进展进行了综述,为设计绿色离子液体及合理控制管理水环境提供参考。

关键词: 离子液体;水生生态;毒性效应;构效关系

文章编号: 1673-5897(2018)6-069-10　　**中图分类号**: X171.5　　**文献标识码**: A

Aquatic Ecotoxicology of Ionic Liquids and the Factors Affecting the Toxicity: A Review

Xia Yilu, Fan Huiyang, Liu Huijun*

School of Environmental Science and Engineering, Zhejiang Gongshang University, Hangzhou 310018, China

Received 1 August 2017　　**accepted** 10 October 2017

Abstract: Ionic liquids (ILs), which have good physical and chemical properties such as low volatility, have been recognized as an attractive solvent alternative to organic solvents. Along with the widespread use, ILs gained great attention as their potential threat to the aquatic environment due to their strong solubility. The latest researches regarding the toxic effects of ILs on aquatic organisms within different trophic levels, organs and tissues, cell and enzyme have been concluded in the present paper. Besides, the factors affecting the toxicity of ILs such as carbon chain length, the type of cations and anions, and environmental factors have also been summarized. This paper will help to develop an understanding of the biologically mediated environmental processes of ILs in aquatic environment, providing reference on designing green ILs and management of aquatic environment.

Keywords: ionic liquids; aquatic ecology; toxic effects; the structure-activity relationship

离子液体(ionic liquids, ILs)是指在室温或接近室温下呈现液态的、完全由阴阳离子所组成的盐,也称为室温熔融盐或低温熔融盐。它被认为替代传统挥发性有机溶剂的新型绿色溶剂[1-2],具有极低的蒸汽压、不易燃、导电性强、性质稳定、对许多无机盐和有机物有良好溶解性等诸多优点,在分离过程、有机

基金项目:国家自然科学基金项目(21377115);浙江工商大学研究生科技创新项目

作者简介:夏一璐(1993-),女,硕士,研究方向为生态毒理学,E-mail: 646224082@qq.com

* **通讯作者**(Corresponding author), E-mail: lhj@zjgsu.edu.cn

合成、生物催化、电化学、生物质溶解和转化等领域具有广阔的应用前景。在ILs广泛应用的同时,它的化学和热力学稳定性导致其在环境难以降解,具有潜在环境风险。虽然ILs不易挥发可有效减少大气污染,但由于其较好的水溶性,在实际使用中大量ILs被释放入水环境中[2],其在水中的积累和污染对水环境存在潜在危害。

近年来ILs的环境行为以及生态毒性受到了研究者的广泛关注。有关ILs对水藻、大型溞(*Daphnia magna*)及斑马鱼(*Danio rerio*)等水生生物的影响相继已有研究报导[6-7],研究发现ILs的潜在毒性可能与常用的有机溶剂相当或者更高[8],多种ILs对不同营养级水生生物的毒性影响详见表1与表2。ILs的毒性与其自身的结构有关,包括烷基链长度、阳离子类型与阴离子类型,此外,环境因子也是ILs的毒性影响因素[9]。本文从多角度综述了不同类型ILs对水生生物的毒性作用及其毒性影响因子(图1),为环境友好型ILs结构设计和合理控制水环境中的ILs污染提供参考。

1 离子液体的水生生态毒理研究(Aquatic ecotoxicology of ILs)

1.1 离子液体对水生植物的毒性影响

水生植物研究对象主要包括藻类与浮萍,探讨ILs对其生长、叶绿素含量、抗氧化系统、酶活性、细胞超微结构等的毒性效应。1-辛基-3-甲基咪唑六氟磷酸盐([C_8mim]PF_6)对小球藻(*Chlorella vulgaris*)生长和叶绿素a的抑制作用随浓度增加而增大,高浓度可致死[10]。1-丁基-3-甲基咪唑氯盐([C_4mim]Cl)会导致斜生栅藻(*Scenedesmus obliquus*)叶绿素含量下降,过氧化氢酶(CAT)和超氧化物歧化酶(SOD)活性降低,藻细胞通透性增大且超微结构受到破坏[11]。[$C_n$mim]Cl(n=6、8、10、12、16)对斜生栅藻的毒性随ILs浓度的增加和烷基链的增长而增大[12]。手性1-烷基-3-甲基咪唑酒石酸盐(RMIMT)对斜生栅藻有立体选择性,L构型的毒性比D构型强[13]。Chen等[14]提出手性ILs的立体选择性影响可能是由于活性氧自由基(ROS)和藻细胞膜通透性损伤差异所致。研究表明随着1-辛基-3-甲基咪唑溴盐([C_8mim]Br)浓度增加,三角褐指藻(*Phaeodactylum tricornutum*)的生长受到抑制,SOD活性先微小增加而后被抑制,细胞脂质过氧化产物丙二醛(MDA)含量增加,这可能是由于ROS过量造成的[15]。[C_8mim]Br对浮萍(*Lemna minor*)也有相似的抑制作用[16],有较长烷基链的1-烷基-3-甲基咪唑化合物对浮萍有更强的毒性[17]。Jin等[18]建立了3D定量构效关系模型,通过标准藻类生长抑制实验证实2,3-二硝基酚、2-氯代-4硝基、1,2,3,-三甲基苯和3-溴苯酚这4个取代基的ILs对斜生栅藻有高毒性。

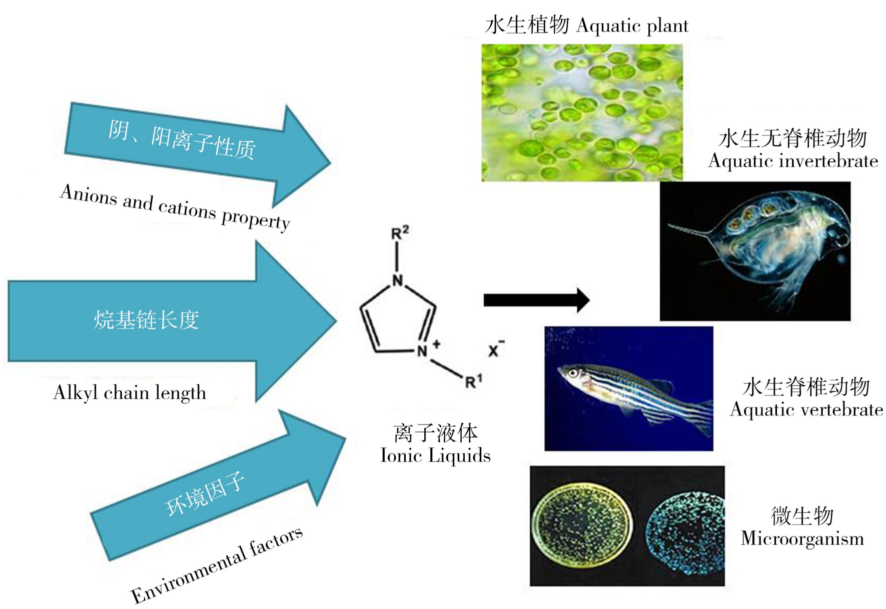

图1 离子液体(ILs)在水中的生态毒性及其影响因子

Fig. 1 Aquatic ecotoxicity of ionic liquids (ILs) and factors affecting the toxicity

$[C_4mim]Cl$ 抑制四尾栅藻(*Scenedesmus quaclricauda*)酶活性,而对其 ROS 和细胞膜损伤影响不大[19]。在 1-烷基-3-甲基咪唑溴盐($[C_nmim]Br$, n=4, 6,8)对四尾栅藻和莱茵衣藻的研究中显示 ILs 毒性比丙酮、苯、甲苯和苯酚更大[20]。海绿藻(*Ocystis submarina*)和硅藻(*Cyclotella meneghiniana*)在暴露 ILs 后恢复能力有显著不同,硅藻比绿藻对 ILs 更为敏感[21]。在一定的浓度范围内(8～32 PSU),ILs 的毒性效应随盐度升高而下降[22]。Pham 等[23]对羊角月牙藻(*Pseudokirchneriella subcapitata*)的研究显示 ILs 在生长率上的毒性影响要比光合作用性能上的影响更明显。ILs 对羊角月牙藻的毒性强弱和烷基链长、暴露时间以及化学结构明显相关,且毒性比传统有机溶剂要强 2～4 个数量级[24]。此外,配制时间久的 1-丁基-3-甲基咪唑四氟硼酸盐($[C_4mim]BF_4$)溶液的半数效应浓度(EC_{50})值明显低于新配制溶液,可能是溶液中$[C_4mim]BF_4$ 形成了氟化物[25],这意味着 ILs 进入水环境中产生的毒性影响可能比在实验室中预期的更大。

1.2　离子液体对水生动物的毒性影响

1.2.1　离子液体对水生无脊椎动物的影响

Pham 等[6]综述了多种 ILs 对大型溞的毒性试验结果,可得毒性最强的是 1-丁基-3-辛基咪唑溴化物($IM_{18}Br$),毒性最低的混合物为$[C_4mim]Cl$。咪唑 ILs 对大型溞有很强毒性,毒性受阳离子侧链长度影响,当侧链长度碳原子数从 4 增加到 12 个会导致 48 h 半数致死浓度(LC_{50}-48 h)降低 470 倍[26]。侧链氧化会降低 ILs 对大型溞的毒性[27-28]。随着 $IM_{18}Br$ 浓度上升,大型溞的 3 个世代和平均后代数目减少,说明 $IM_{18}Br$ 可以对大型溞种群造成有毒影响并间接对淡水食物网造成破坏[29]。不同碳链长度$[C_nmim]Br$ 都严重影响大型溞的摄食行为,对水生生态产生潜在威胁[30]。Costa 等[31]研究发现水螅对 ILs 的耐性比大型溞和月牙藻强。

3 种 ILs $[C_nmim]Cl$(n=4、8、12)暴露对卤虫(Brine Shrimp)个体存活率影响的研究可发现毒性效应随烃基侧链碳链增长而增强[32],这和不同烃链长度 ILs 对日本三角涡虫(*Lugesia japonica* Ichikawa et kawakatsu)的毒性影响结果基本一致[33]。Nędzi 等[34]发现与只暴露于受$[C_4mim]Cl$ 污染水中的藤壶(*Balanus*)相比,当水中有受污染的小球藻时,藤壶的生物浓缩系数会升高 80%,而在高浓度的 ILs 中,油黑壳菜蛤(*Mytilus trossulus*)的解毒作用比藤壶更有效,可能由于其矿物质表面有特有的物理吸附机制。短期暴露于$[C_nmim]Br$ 和$[C_n]_3MePyBr$(1-烷基-3-甲基吡啶溴盐)会减少斑马贻贝(*Dreissena polymorpha*)的摄食率[35],$[C_4mim]Br$ 抑制尖膀胱螺(*Physa acuta*)的生长速率[36]。ILs 在低浓度时可能抑制尖膀胱螺行动,但是一旦浓度高于临界值就会触发其逃跑反应[37]。尖膀胱螺既捕食藻类,也为鱼类和其他脊椎捕食者所摄食,是淡水食物网的重要组成部分。ILs 不仅影响尖膀胱螺的行为,也影响了个体健康和水生食物网内部作用。

1.2.2　离子液体对水生脊椎动物的影响

研究表明 ILs 会对斑马鱼活动产生影响,由于其体积大,耐毒能力变强,所以一些 ILs 对其属于低毒性[38],抑制率随时间延长而增强[10]。$[C_8mim]Cl$ 和 1-辛基-3-甲基咪唑四氟硼酸盐($[C_8mim]BF_4$)处理斑马鱼肝脏,毒性效应随浓度和时间增加而增强,而阴离子对 ILs 的毒性几乎不产生影响[39]。Pretti 等[40]揭示了 ILs 化学结构不同对鱼类造成不同的影响,斑马鱼活动减弱,丧失平衡性,最后甚至死亡,其主要损伤部位是皮肤和腮。$[C_8mim]PF_6$ 会抑制斑马鱼抗氧化酶活性,造成体内 ROS 的积累以及脱氧核糖核酸(DNA)损伤[41]。ROS 含量与 ILs 浓度呈良好的剂量-效应关系,较高浓度的 ILs 会抑制抗氧化酶活性,刺激解毒酶活性以及造成细胞 DNA 损伤[42]。

$[C_8mim]Cl$ 对泥鳅(*Misgurnus anguillicaudatus*)胚胎发育 4 个阶段(囊胚期、原肠胚中期、神经胚期、尾芽期)及仔鱼期的毒性具有明显的剂量-效应关系。在一定剂量内,$[C_8mim]Cl$ 对泥鳅胚胎及仔鱼的发育具有明显的致畸、致死作用[43]。结果与 $IM_{18}Br$ 对黑斑蛙(*Pelophylax nigromaculatus*)早期胚胎时期的毒性影响结果一致[44]。$[C_{16}mim]Cl$ 处理红细胞微核率、血清谷丙转氨酶(GPT)和谷草转氨酶(GOT)活力均明显高于对照组,对泥鳅具有遗传和生理毒性效应[45]。$[C_8mim]Br$ 会诱发金鱼(*Carassius auratus*)皮肤、腮丝以及小肠绒毛的表面损伤[46],产生氧化损伤并引起脂质过氧化作用[47]。$[C_8mim]Br$ 对鲤鱼的免疫系统也有毒性效应,早期暴露于浓度为 363 $\mu mol \cdot L^{-1}$的 ILs 时,鲤鱼的免疫系统被激活,而暴露于 1 090 $\mu mol \cdot L^{-1}$的 ILs 时,会对肝胰脏、肾脏和脾脏造成明显的损伤,抑制其免疫系统[48]。马军国等[49]推断草鱼体内 PXR(细胞色素 CYP3A 的关键转录因子)可能是$[C_8mim]Br$ 作用于 CYP3A 的受体。

表1 不同ILs对水生藻类的毒性

Table 1 The toxicity of different ILs to various aquatic algae

ILs	试验生物 Tested organisms	EC$_{50}$-24 h /(mg·L^{-1})	EC$_{50}$-48 h /(mg·L^{-1})	EC$_{50}$-72 h	EC$_{50}$-96 h	参考文献 References
[C$_4$mim]Cl				6 330.51 μmol·L^{-1}		
[C$_6$mim]Cl				1 026.2 μmol·L^{-1}		
[C$_8$mim]Cl	小球藻 *Chlorella vulgaris*			64.5 μmol·L^{-1}		[21]
[C$_{10}$mim]Cl				15.1 μmol·L^{-1}		
[C$_{12}$mim]Cl				3.68 μmol·L^{-1}		
[C$_4$mim]Br		40.01	24.10	23.66 mg·L^{-1}	22.24 mg·L^{-1}	
[C$_6$mim]Br		17.67	14.70	8.63 mg·L^{-1}	5.88 mg·L^{-1}	
[C$_8$mim]Br		3.06	1.38	0.54 mg·L^{-1}	0.34 mg·L^{-1}	
[C$_{10}$mim]Br		2.29	0.24	0.11 mg·L^{-1}	0.10 mg·L^{-1}	
[C$_{12}$mim]Br	斜生栅藻 *Scenedesmus obliquus*	0.10	0.08	0.08 mg·L^{-1}	0.02 mg·L^{-1}	[12,74]
[C$_6$mim]Cl		1.99	4.84	5.61 mg·L^{-1}	6.27 mg·L^{-1}	
[C$_8$mim]Cl		0.49	0.69	0.97 mg·L^{-1}	1.06 mg·L^{-1}	
[C$_{10}$mim]Cl		0.066	0.031	0.046 mg·L^{-1}	0.062 mg·L^{-1}	
[C$_{12}$mim]Cl		0.005	0.020	0.031 mg·L^{-1}	0.038 mg·L^{-1}	
[C$_{16}$mim]Cl		0.002	0.010	0.015 mg·L^{-1}	0.017 mg·L^{-1}	
[C$_4$mim]Cl		19 548.64		45 mg·L^{-1}		
[C$_6$mim]Cl	眼虫藻 *Euglena gracilis*	965.84		38.5 mg·L^{-1}		[75]
[C$_8$mim]Cl		287.76		0.0011 mg·L^{-1}		
[C$_{12}$mim]Cl		39.35		0.0041 mg·L^{-1}		
[C$_4$mim]BF$_4$	栅藻冬凌草 *Scenedesmus rubescens*	>200	>200	>200 mg·L^{-1}	>200 mg·L^{-1}	[76]
[C$_8$mim]BF$_4$		2.97	0.85	0.31 mg·L^{-1}	0.41 mg·L^{-1}	
[C$_4$mim]Cl					2 884 μmol·L^{-1}	
[C$_4$mim]Br	羊角月牙藻 *Selenastrum capricornutum*				1 047 μmol·L^{-1}	
[C$_4$mim]BF$_4$				63.2 μmol·L^{-1}	2 512 μmol·L^{-1}	[25]
[C$_4$mim]PF$_6$					1 318 μmol·L^{-1}	
[C$_4$mim]OTF					2 188 μmol·L^{-1}	
[C$_4$mim]Br					9 800 μmol·L^{-1}	
[C$_6$mim]Br					3 710 μmol·L^{-1}	
[C$_8$mim]Br	石莼 *Ulva lactuca*				1 420 μmol·L^{-1}	[77]
[C$_{10}$mim]Br					150 μmol·L^{-1}	
[C$_{12}$mim]Br					70 μmol·L^{-1}	
[C$_4$mim]BF$_4$		30.81	28.53	39.92 mg·L^{-1}	45.88 mg·L^{-1}	
[C$_8$mim]BF$_4$	三角褐指藻 *Phaeodactylum tricornutum*	30.17	23.36	28.62 mg·L^{-1}	31.37 mg·L^{-1}	[78]
[C$_{12}$mim]BF$_4$		0.63	0.61	0.68 mg·L^{-1}	0.72 mg·L^{-1}	

注：[C$_n$mim]Cl表示1-烷基-3-甲基咪唑氯盐；[C$_n$mim]Br表示1-烷基-3-甲基咪唑溴盐；[C$_n$mim]BF$_4$表示1-烷基-3-甲基咪唑四氟硼酸盐；[C$_n$mim]PF$_6$表示1-烷基-3-甲基咪唑六氟硼酸盐；[C$_n$mim]OTF表示1-烷基-3-甲基咪唑三氟甲烷磺酸盐。

Note: [C$_n$mim]Cl stands for 1-alkyl-3-methylimidazolium chloride; [C$_n$mim]Br stands for 1-alkyl-3-methylimidazolium bromide; [C$_n$mim]BF$_4$ stands for 1-alkyl-3-methylimidazolium tetrafluoroborate; [C$_n$mim]PF$_6$ stands for 1-alkyl-3-methylimidazolium hexafluorophosphate; [C$_n$mim]OTF stands for 1-alkyl-3-methylimidazolium trifluoromethanesulfonate.

1.3　离子液体对水体微生物的影响

对费氏弧菌(*Vibrio fischeri*)的研究证实了阳离子侧链长度对生物体的影响,侧链长度从[C_2mim]Cl的 2 个碳原子增加到 10 个碳原子导致其 EC_{50}-15 mim 降低了 6 563 倍[50]。Ranke 等[51]考察了不同碳链和阴离子的咪唑 ILs 对费氏弧菌的毒性影响,结果显示化合物与[PF_6]$^-$结合比与其他阴离子结合毒性稍强一些,烷基咪唑 ILs 对费氏弧菌的生物影响比丙酮、乙腈、甲醇和甲基叔丁基醚的影响还大。季铵化合物对费氏弧菌的毒性比吡啶盐和咪唑盐类似物要小[52]。阴离子[$(CF_3SO_2)_2N$]$^-$本身对费氏弧菌没有固有毒性,而所有被测试的化合物与[$(CF_3SO_2)_2N$]$^-$结合后毒性增加[53]。与磷盐类、咪唑类不同,胍盐类 ILs 的毒性不随侧链烷基长度的增加而增强,在烷基侧链上引入含氧基能降低胍盐类和咪唑类 ILs 的毒性[54]。对恶臭假单胞菌的毒性实验可得,当碳链长度在 8 以下时,毒性随之增加,而当碳链长度为 10 时,EC_{50} 值却增加了 1 个数量级。30 种具有不同烷基链长度、阴离子基团和阳离子骨架(甲基咪唑、二甲基咪唑和吡啶)的 ILs 对青海弧菌(*Vibrio qinghaiensis* sp.)的毒性差异很大,毒性取决于烷基链长度,而阴、阳离子骨架对毒性效应无显著影响[55]。

2　离子液体毒性的影响因素(Factors affecting the toxicity of ILs)

2.1　离子液体结构对毒性的影响

2.1.1　阳离子的烷基链长度

一般来说,链长的增加增强了 ILs 的毒性效应[56]。ILs 的毒性和其亲脂性有关。亲脂性越强,ILs 越易与受试生物表面发生相互作用,则毒性越强。Stock 等[57]提出 1-癸基-3-甲基咪唑四氟硼酸盐([C_{10}mim]BF_4)对乙酰胆碱的抑制作用大于 1-丙基-3-甲基咪唑四氟硼酸盐([C_3mim]BF_4),可能由于长链的阳离子更易与该酶上的阴离子位点结合。

表 2　不同 ILs 对水生动物的毒性

Table 2　The toxicity of different ILs to various aquatic animals

ILs	试验生物 Tested organisms	EC_{50}-24 h	EC_{50}-48 h/(mg·L^{-1})	EC_{50}-72 h /(mg·L^{-1})	EC_{50}-96 h /(mg·L^{-1})	参考文献 References
[C_2mim]NO_3	斑马鱼 *Danio rerio*	45 552.2 mg·L^{-1}	4 820.9	4 010.4	3 193.5	[79]
[C_4mim]NO_3		1 752.3 mg·L^{-1}	1 245.8	1 027.4	867.1	
[C_6mim]NO_3		332.9 mg·L^{-1}	237.5	162.9	144.4	
[C_8mim]NO_3		35.6 mg·L^{-1}	33.0	28.8	23.1	
[C_{10}mim]NO_3		9.6 mg·L^{-1}	8.4	6.5	4.5	
[C_{12}mim]NO_3		5.7 mg·L^{-1}	4.8	4.0	3.7	
[C_6mim]Br		390.1 mg·L^{-1}	238.9	190.5	164.4	
[C_6mim]Cl		286.1 mg·L^{-1}	216.6	158.8	128.5	
[C_6mim]BF_4		231.4 mg·L^{-1}	172.0	141.3	120.1	
[C_6mim]PF_6		460.4 mg·L^{-1}	237.4	189.3	146.6	
[C_4mim]Br	大型溞 *Daphnia magna*		8.03			[80]
[C_4mim]Cl			14.8			[75]
[C_4mim]PF_6			19.91			
[C_4mim]BF_4			10.68			
[C_{12}mim]Cl			0.0043			
[C_{16}mim]Cl			0.0034			
[C_{18}mim]Cl			0.0017			
[C_4mim]PF_6	水螅 *Hydra attenuata*		573			[31]
[C_4mpyr]BF_4			245			
[C_4mim]Cl	卤虫 Brine shrimp	171.1 μg·L^{-1}				[32]
[C_8mim]Cl		133.6 μg·L^{-1}				
[C_{12}mim]Cl		17.76 μg·L^{-1}				

注:[$C_n$mim]NO_3 表示 1-烷基-3-甲基咪唑硝酸盐。

Note: [$C_n$mim]NO_3 stands for 1-alkyl-3-methylimidazolium nitrate.

2.1.2 阳离子侧链的功能化程度

在烷基侧链上引进极性功能基团能有效降低毒性[58]。在咪唑烷基链上的 1-位上被氢原子取代可以降低毒性[59]。而将甲基基团或羟乙基基团引入咪唑碳链中能增强它的抗菌活性[60]。此外,细胞毒性很大程度上是由极性功能基团在侧链上的位置决定的[53]。

2.1.3 阳离子性质

Bernot 等[61]总结出 ILs 的毒性与阳离子有关。含芳香烃的咪唑和吡啶类 ILs 比哌啶类似物的总体毒性水平要高[62]。Ismail Hossain 等[63]用数学模型对 ILs 对大型溞的毒性进行研究,定量构效关系(QSAR)表明阳离子组成占 ILs 的毒性的 12% ~ 48%。吡咯类 ILs 对费氏弧菌的毒性小于咪唑类和吡啶类 ILs[64],而咪唑类 ILs 对其毒性又比季鏻盐类 ILs 小[65]。

2.1.4 阴离子性质

阴离子对 ILs 毒性也有一定影响,尤其是较短烷基链的 ILs[66]。一般来说,一些氟化物阴离子如四氟硼酸盐$[BF_4]^-$、六氟磷酸盐$[PF_6]^-$和六氟锑酸盐$[SbF_6]^-$通常会增加 ILs 的毒性。稳定的阴离子如双三氟甲磺酰亚胺盐$[NTF_2]^-$毒性很强,由于它的亲脂性增加了破坏细胞膜磷脂的能力[67]。Garcia 等[68]以发光细菌(*Photobacterium phosphoreum*)为受试对象,发现$[C_4mim]Br$ 与$[C_4mim]Cl$ 对其的毒性小于$[C_4mim]BF_4$ 与$[C_4mim]PF_6$。

2.1.5 阴离子和阳离子的相互影响

分子结构中阴离子和阳离子的相互影响会影响 ILs 的毒性[69]。环境友好的 ILs 可由合适的阴离子和阳离子合成[56]。使用芳香族阳离子和含氟阴离子会增加毒性[70-71]。非质子化的 ILs 对乙酰胆碱酯酶的抑制作用比质子化的 ILs 更强[2]。因此,质子化的 ILs 对环境来说更为安全。

2.2 环境因子的影响

水环境中对 ILs 毒性的影响因子主要是溶解的有机质和盐度。ILs 像表面活性剂一样更倾向于吸附矿物和有机质。因此,污染物在地下水中可以被水介质中固定物吸附,降低地下水污染。相反,若 ILs 聚合在水相中形成胶体,并吸收有机和非有机胶体则会增强地下水污染[73]。盐度增大时,高氯浓度提供了 ILs 中阳离子的离子对环境,与细胞壁结构中的羟基竞争,减少了 ILs 通过细胞壁进入细胞,从而降低了 ILs 对生物的毒性作用[22]。

3 总结与展望(Summary and future research directions)

本文阐述了不同水生生态营养级上的生物,包括水生植物(水藻和浮萍等)、水生动物(水溞、腹足类、斑马鱼和金鱼等)和水体中微生物(费氏弧菌和青海弧菌等)暴露于不同类型不同结构的 ILs 后,对其生物体、组织器官、细胞、超微结构和酶活性等产生的毒性效应,以及毒性效应的影响因素如烷基链长、阴、阳离子和环境因子等。

基于目前 ILs 对水生生态毒性的研究,未来研究可在以下 4 个方面拓展或加强:

(1)ILs 对不同生物级的毒性效应已被广泛研究,应进一步关注其毒性机制的解析。

(2)ILs 降解过程中的中间产物以及最终产物对水生环境的毒性。

(3)运用化学统计学工具及模型如定量-构效模型、线性自由能模型来预测 ILs 毒性。

(4)基于毒理学和降解数据资料,创建绿色结构数据库,以此为生产无毒、可降解性的 ILs 提供关键信息。

参考文献(References):

[1] Erdmenger T, Guerrero-Sanchez C, Vitz J, et al. ChemInform abstract: Recent developments in the utilization of green solvents in polymer chemistry [J]. Chemical Society Reviews, 2010, 41(47): 3317-3333

[2] Paternò A, D' Anna F, Musumarra G, et al. A multivariate insight into ionic liquids toxicities [J]. RSC Advances, 2014, 4(46): 23985-24000

[3] Joshi M D, Anderson J L. ChemInform abstract: Recent advances of ionic liquids in separation science and mass spectrometry [J]. Cheminform, 2012, 43(39): 5470-5484

[4] Liu H, Liu Y, Li J. Ionic liquids in surface electrochemistry [J]. Physical Chemistry Chemical Physics, 2010, 12(8): 1685-1697

[5] Mahmood H, Moniruzzaman M, Yusup S, et al. Particulate composites based on ionic liquid-treated oil palm fiber and thermoplastic starch adhesive [J]. Clean Technologies & Environmental Policy, 2016, 18(7): 2217-2226

[6] Pham T P, Cho C W, Yun Y S. Environmental fate and toxicity of ionic liquids: A review [J]. Water Research, 2010, 44(2): 352

[7] Romero A, Santos A, Tojo J, et al. Toxicity and biodegradability of imidazolium ionic liquids [J]. Journal of Hazardous Materials, 2008, 151(1): 268-273

[8] Tsarpali V, Dailianis S. Toxicity of two imidazolium ionic liquids, [bmim][BF_4] and [omim][BF_4], to standard aquatic test organisms: Role of acetone in the induced toxicity [J]. Ecotoxicology & Environmental Safety, 2015, 117: 62-71

[9] Amde M, Liu J F, Pang L. Environmental application, fate, effects, and concerns of ionic liquids: A review [J]. Environmental Science & Technology, 2015, 49(21): 12611-12627

[10] 牧辉, 彭新晶, 戴宁, 等. 离子液体[C_8mim]PF_6 对水生生物的毒性作用[J]. 中国环境科学, 2009, 29(11): 1196-1201

Mu H, Peng X J, Dai N, et al. Toxicity of [C_8mim]PF_6 to aquatic organisms [J]. China Environmental Science, 2009, 29(11): 1196-1201 (in Chinese)

[11] 段炼, 杜耀, 陆秋琳, 等. 离子液体 1-丁基-3-甲基咪唑氯盐对斜生栅藻的毒性效应[J]. 中国环境科学, 2012, 32(5): 886-891

Duan L, Du Y, Lu Q L, et al. Toxicity of 1-butyl-3-methylimidazolium chloride ionic liquid to *Scenedesmus obliqnus* [J]. Chnia Environmental Science, 2012, 32(5): 886-891 (in Chinese)

[12] Liu H, Zhang X, Chen C, et al. Effects of imidazolium chloride ionic liquids and their toxicity to *Scenedesmus obliquus* [J]. Ecotoxicology & Environmental Safety, 2015, 122: 83-90

[13] Liu H, Zhang X, Dong Y, et al. Enantioselective toxicities of chiral ionic liquids 1-alkyl-3-methyl imidazolium tartrate on *Scenedesmus obliquus* [J]. Aquatic Toxicology, 2015, 169: 179-187

[14] Chen H, Zou Y, Zhang L, et al. Enantioselective toxicities of chiral ionic liquids 1-alkyl-3-methylimidazolium lactate to aquatic algae [J]. Aquatic Toxicology, 2014, 154: 114-120

[15] Deng X Y, Cheng J, Hu X L, et al. Physiological and biochemical responses of a marine diatom *Phaeodactylum tricornutum* exposed to 1-octyl-3-methylimidazolium bromide [J]. Aquatic Biology, 2015, 24(2): 109-115

[16] Zhang B, Li X, Chen D, et al. Effects of 1-octyl-3-methylimidazolium bromide on the antioxidant system of *Lemna minor* [J]. Protoplasma, 2013, 250(1): 103-110

[17] Larson J, Frost P, Lamberti G. Variable toxicity of ionic liquid-forming chemicals to *Lemna minor* and the influence of dissolved organic matter [J]. Environmental Toxicology and Chemistry, 2008, 27(3): 676-681

[18] Jin X, Jin M, Sheng L. Three dimensional quantitative structure-toxicity relationship modeling and prediction of acute toxicity for organic contaminants to algae [J]. Computers in Biology and Medicine, 2014, 51: 205-213

[19] Deng Y, Beadham I, Wu J, et al. Chronic effects of the ionic liquid [C_4mim][Cl] towards the microalga *Scenedesmus quadricauda* [J]. Environmental Pollution, 2015, 204: 248-255

[20] Kulacki K J, Lamberti G A. Toxicity of imidazolium ionic liquids to freshwater algae [J]. Green Chemistry, 2008, 10(1): 104-110

[21] Latala A, Nedzi M, Stepnowski P. Toxicity of imidazolium and pyridinium based ionic liquids towards algae. *Bacillaria paxillifer* (a microphytobenthic diatom) and *Geitlerinema amphibium* (a microphytobenthic blue green alga) [J]. Green Chemistry, 2009, 11(9): 1371-1376

[22] Latala A, Nedzi M, Stepnowski P. Toxicity of imidazolium ionic liquids towards algae. Influence of salinity variations [J]. Green Chemistry, 2010, 12(1): 60-64

[23] Pham T P T, Cho C W, Jeon C O, et al. Identification of metabolites involved in the biodegradation of the ionic liquid 1-butyl-3-methylpyridinium bromide by activated sludge microorganisms [J]. Environmental Science & Technology, 2009, 43(2): 516-521

[24] Cho C W, Pham T P T, Jeon Y C, et al. Toxicity of imidazolium salt with anion bromide to a phytoplankt on *Selenastrum capricornutum*: Effect of alkyl-chain length [J]. Chemosphere, 2007, 69(6): 1003-1007

[25] Pham T P T, Cho C W, Vijayaraghavan K, et al. Effect of imidazolium-based ionic liquids on the photosynthetic activity and growth rate of *Selenastrum capricornutum* [J]. Environmental Toxicology and Chemistry, 2008, 27(7): 1583-1589

[26] Yu M, Wang S H, Luo Y R, et al. Effects of the 1-alkyl-3-methylimidazolium bromide ionic liquids on the antioxidant defense system of *Daphnia magna* [J]. Ecotoxicology and Environmental Safety, 2009, 72(6): 1798-1804

[27] Samorì C, Malferrari D, Valbonesi P, et al. Introduction of oxygenated side chain into imidazolium ionic liquids: Evaluation of the effects at different biological organization levels [J]. Ecotoxicology & Environmental Safety, 2010, 73(6): 1456-1464

[28] Chiara S, Andrea P, Paola G, et al. Acute toxicity of oxygenated and nonoxygenated imidazolium-based ionic liquids to *Daphnia magna* and *Vibrio fischeri* [J]. Environmental Toxicology & Chemistry, 2007, 26(11): 2379-2383

[29] Luo Y R, Li X Y, Chen X X, et al. The developmental toxicity of 1-methyl-3-octylimidazolium bromide on *Daphnia magna* [J]. Environmental Toxicology, 2008, 23(6): 736-744

[30] 李效宇, 罗艳蕊, 李磊, 等. 一种离子液体—溴化1-辛基-3-甲基咪唑对大型溞摄食强度的影响[J]. 环境科学学报, 2008, 28(11): 2331-2335
Li X Y, Luo Y R, Li L, et al. Effects of the ionic liquid 1-methyl-3-octylimidazolium bromide on the feeding intensity of *Daphnia magna* [J]. Acta Scientiae Circumstantiae, 2008, 28(11): 2331-2335 (in Chinese)
[31] Costa S P F, Pinto P C A G, Saraiva M L M F S, et al. The aquatic impact of ionic liquids on freshwater organisms [J]. Chemosphere, 2015, 139: 288
[32] 卢珩俊, 陆胤, 徐冬梅, 等. 咪唑类离子液体系列对卤虫的急性毒性研究[J]. 中国环境科学, 2011, 31(3): 454-460
Lu H J, Lu Y, Xu D M, et al. Research on the acute toxicity of imidazolium ionic liquids on the brine shrimp[J]. China Environmental Science, 2011, 31(3): 454-460 (in Chinese)
[33] 石长应, 王凡, 张合彩, 等. 不同烃链长度咪唑类离子液体对日本三角涡虫的急性毒性[J]. 河南师范大学学报: 自然科学版, 2014(4): 178-182
Shi C Y, Wang F, Zhang H C, et al. The acute toxicity of imidazolium ionic liquids with different hydrocarbon chain length on *Dugesia japonica* [J]. Journal of Henan Normal University: Natural Science, 2014(4): 178-182 (in Chinese)
[34] Nędzi M, Latała A, Nichthauser J, et al. Bioaccumulation of 1-butyl-3-methylimidazolium chloride ionic liquid in a simple marine trophic chain [J]. Oceanological & Hydrobiological Studies, 2013, 42(2): 149-154
[35] Costello D M, Brown L M, Lamberti G A. Acute toxic effects of ionic liquids on zebra mussel (*Dreissena polymorpha*) survival and feeding [J]. Green Chemistry, 2009, 11(4): 548-553
[36] Evans-White M A, Lamberti G A. Direct and indirect effects of a potential aquatic contaminant on grazer-algae interactions [J]. Environmental Toxicology and Chemistry, 2009, 28(2): 418-426
[37] Bernot R J, Kennedy E E, Lamberti G A. Effects of ionic liquids on the survival, movement, and feeding behavior of the freshwater snail, *Physa acuta* [J]. Environmental Toxicology & Chemistry, 2005, 24(7): 1759-1765
[38] Baharuddin S H, Mustahil N A, Abdullah A A, et al. Ecotoxicity study of amino acid ionic liquids towards *Danio rerio* fish: Effect of cations [J]. Procedia Engineering, 2016, 148: 401-408
[39] Liu T, Guo Y, Wang J, et al. Assessing toxic effects of [Omim]Cl and [Omim]BF_4 in zebrafish adults using a biomarker approach [J]. Environmental Science & Pollution Research, 2016, 23(8): 7360-7368
[40] Pretti C, Chiappe C, Pieraccini D, et al. Acute toxicity of ionic liquids to the zebrafish (*Danio rerio*) [J]. Green Chemistry, 2006, 8(3): 238-240
[41] Du Z, Zhu L, Dong M, et al. Effects of the ionic liquid [Omim]PF_6 on antioxidant enzyme systems, ROS and DNA damage in zebrafish (*Danio rerio*) [J]. Aquatic Toxicology, 2012, 124-125(3): 91-93
[42] Zhang C, Shao Y, Zhu L, et al. Acute toxicity, biochemical toxicity and genotoxicity caused by 1-butyl-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium tetrafluoroborate in zebrafish (*Danio rerio*) livers [J]. Environmental Toxicology and Pharmacology, 2017, 51: 131-137
[43] 南平, 王琼琼, 亓蒙, 等. 离子液体[C_8mim]Cl对泥鳅胚胎和仔鱼的毒性[J]. 生态毒理学报, 2014, 9(2): 268-272
Nan P, Wang Q Q, Qi M, et al. Toxicity of [C_8mim]Cl to loach embryonic and larval fish [J]. Asian Journal of Ecotoxicology, 2014, 9(2): 268-272 (in Chinese)
[44] Li X-Y, Zhou J, Yu M, et al. Toxic effects of 1-methyl-3-octylimidazolium bromide on the early embryonic development of the frog *Rana nigromaculata* [J]. Ecotoxicology and Environmental Safety, 2009, 72(2): 552-556
[45] 燕帅国, 南平, 杜启艳, 等. 离子液体[C_{16}mim]Cl对泥鳅的毒性效应[J]. 生态毒理学报, 2013, 8(1): 92-96
Yan S G, Nan P, Du Q Y, et al. Toxicity of [C_{16}mim]Cl to loach (*Misgurnus anguillicaudatus*) [J]. Asian Journal of Ecotoxicology, 2013, 8(1): 92-96 (in Chinese)
[46] Li X Y, Zeng S H, Zhang W H, et al. Acute toxicity and superficial damage to goldfish from the ionic liquid 1-methyl-3-octylimidazolium bromide [J]. Environmental Toxicology, 2013, 28(4): 207-214
[47] 李效宇, 皇培培, 王春雨. 早期胚胎发育期暴露1-辛基-3-甲基咪唑离子液体后对金鱼仔鱼的氧化损伤[J]. 生态毒理学报, 2010, 5(1): 100-104
Li X Y, Huang P P, Wang C Y. Oxidative stress of the ionic liquids 1-octyl-3-methylimidazolium bromide on the goldfish larva *Carassius auratus* hatching from the IL-treated embryos [J]. Asian Journal of Ecotoxicology, 2010, 5(1): 100-104 (in Chinese)
[48] Li X-Y, Miao X-Q, Zhang L-F, et al. Immunotoxicity of 1-methyl-3-octylimidazolium bromide on brocarded carp (*Cyprinus carpio* L.) [J]. Ecotoxicology and Environmental Safety, 2012, 75: 180-186
[49] 马军国, 周春娥, 李效宇. 咪唑类离子液体处理对草鱼CYP3A和PXR基因表达的影响[J]. 水生态学杂志, 2013, 34(6): 70-75

Ma J G, Zhou C E, Li X Y. The effects of imidazolium ionic liquids on CYP3A and PXR gene expression in grass crap [J]. Journsl of Hydroecology, 2013, 34(6): 70-75 (in Chinese)

[50] Luis P, Ortiz I, Aldaco R, et al. A novel group contribution method in the development of a QSAR for predicting the toxicity (*Vibrio fischeri* EC_{50}) of ionic liquids [J]. Ecotoxicology & Environmental Safety, 2007, 67(3): 423-429

[51] Ranke J, Mölter K, Stock F, et al. Biological effects of imidazolium ionic liquids with varying chain lengths in acute *Vibrio fischeri* and WST-1 cell viability assays [J]. Ecotoxicology and Environmental Safety, 2004, 58(3): 396-404

[52] Couling D J, Bernot R J, Docherty K M, et al. Assessing the factors responsible for ionic liquid toxicity to aquatic organisms via quantitative structure-property relationship modeling [J]. Green Chemistry, 2006, 8(1): 82-90

[53] Stolte S, Arning J, Bottin-Weber U, et al. Effects of different head groups and functionalised side chains on the cytotoxicity of ionic liquids [J]. Green Chemistry, 2007, 9(7): 760-767

[54] Ventura S P M, Marques C S, Rosatella A A, et al. Toxicity assessment of various ionic liquid families towards *Vibrio fischeri* marine bacteria [J]. Ecotoxicology and Environmental Safety, 2012, 76: 162-168

[55] 刘保奇, 葛会林, 刘树深. 测定环境污染物对青海弧菌发光强度抑制的微板发光法研究[J]. 生态毒理学报, 2006, 1(2): 186-191

Liu B Q, Ge H L, Liu S S. Microplate luminometry for toxicity bioassay of environmental pollutant on a new type of fresh water luminescent bacterium (*Vibrio-qinghaiensis* sp.-Q67) [J]. Asian Journal of Ecotoxicology, 2006, 1(2): 186-191 (in Chinese)

[56] Fa E S, Siopa F, Figueiredo B F, et al. Sustainable design for environment-friendly mono and dicationic cholinium-based ionic liquids [J]. Ecotoxicology & Environmental Safety, 2014, 108: 302

[57] Stock F, Hoffmann J, Ranke J, et al. Effects of ionic liquids on the acetylcholinesterase—A structure-activity relationship consideration [J]. Green Chemistry, 2004, 6(6): 286-290

[58] Gathergood N, Scammells P J, Garcia M T. Biodegradable ionic liquids Part III. The first readily biodegradable ionic liquids [J]. Green Chemistry, 2006, 8(2): 156-160

[59] Pretti C, Chiappe C, Baldetti I, et al. Acute toxicity of ionic liquids for three freshwater organisms: *Pseudokirchneriella subcapitata*, *Daphnia magna* and *Danio rerio* [J]. Ecotoxicology & Environmental Safety, 2009, 72(4): 1170-1176

[60] Demberelnyamba D, Kim K-S, Choi S, et al. Synthesis and antimicrobial properties of imidazolium and pyrrolidinonium salts [J]. Bioorganic & Medicinal Chemistry, 2004, 12(5): 853-857

[61] Bernot R J, Brueseke M A, Evans-White M A, et al. Acute and chronic toxicity of imidazolium-based ionic liquids on *Daphnia magna* [J]. Environmental Toxicology and Chemistry, 2005, 24(1): 87-92

[62] Quraishi K S, Bustam M A, Krishnan S, et al. Ionic liquids toxicity on fresh water microalgae, *Scenedesmus quadricauda*, *Chlorella vulgaris* & *Botryococcus braunii*; selection criterion for use in a two-phase partitioning bioreactor (TPPBR) [J]. Chemosphere, 2017, 184: 642-651

[63] Ismail Hossain M, Samir B B, El-Harbawi M, et al. Development of a novel mathematical model using a group contribution method for prediction of ionic liquid toxicities [J]. Chemosphere, 2011, 85(6): 990-994

[64] Hernández-fernández F J, Bayo J, Pérez de los R A, et al. Discovering less toxic ionic liquids by using the Microtox® toxicity test [J]. Ecotoxicology & Environmental Safety, 2015, 116: 29-33

[65] Bado-Nilles A, Diallo A O, Marlair G, et al. Coupling of OECD standardized test and immunomarkers to select the most environmentally benign ionic liquids option-towards an innovative "safety by design" approach [J]. Journal of Hazardous Materials, 2015, 283: 202

[66] Amde M, Liu J-F, Pang L. Environmental application, fate, effects, and concerns of ionic liquids: A review [J]. Environmental Science & Technology, 2015, 49(21): 12611-12627

[67] Stefan S, Jürgen A, Ulrike B W, et al. Anion effects on the cytotoxicity of ionic liquids [J]. Green Chemistry, 2006, 8(7): 621-629

[68] Garcia M T, Gathergood N, Scammells P J. Biodegradable ionic liquids: Part II. Effect of the anion and toxicology [J]. Green Chemistry, 2005, 7(1): 9-14

[69] Egorova K S, Ananikov V P. Toxicity of ionic liquids: Eco(cyto)activity as complicated, but unavoidable parameter for task-specific optimization [J]. ChemSusChem, 2014, 7(2): 336-360

[70] Roy K, Das R N, Popelier P L A. Quantitative structure-activity relationship for toxicity of ionic liquids to *Daphnia magna*: Aromaticity vs. lipophilicity [J]. Chemosphere, 2014, 112: 120-127

[71] Costa S P, Pinto P C, Lapa R A, et al. Toxicity assessment of ionic liquids with *Vibrio fischeri*: An alternative fully

automated methodology [J]. Journal of Hazardous Materials, 2015, 284: 136-142

[72] Peric B, Sierra J, Martí E, et al. (Eco)toxicity and biodegradability of selected protic and aprotic ionic liquids [J]. Journal of Hazardous Materials, 2013, 261: 99-105

[73] McCarthy J F, Zachara J M. Subsurface transport of contaminants [J]. Environmental Science & Technology, 1989, 23(5): 496-502

[74] Ma J-M, Cai L-L, Zhang B-J, et al. Acute toxicity and effects of 1-alkyl-3-methylimidazolium bromide ionic liquids on green algae [J]. Ecotoxicology and Environmental Safety, 2010, 73(6): 1465-1469

[75] Wells A S, Coombe V T. On the freshwater ecotoxicity and biodegradation properties of some common ionic liquids [J]. Organic Process Research & Development, 2006, 10(4): 794-798

[76] Tsarpali V, Dailianis S. Toxicity of two imidazolium ionic liquids, [bmim][BF_4] and [omim][BF_4], to standard aquatic test organisms: Role of acetone in the induced toxicity [J]. Ecotoxicology and Environmental Safety, 2015, 117: 62-71

[77] Kumar M, Trivedi N, Reddy C R K, et al. Toxic effects of imidazolium ionic liquids on the green seaweed *Ulva lactuca*: Oxidative stress and DNA damage [J]. Chemical Research in Toxicology, 2011, 24(11): 1882-1890

[78] Deng X-Y, Chen B, Li D, et al. Growth and physiological responses of a marine diatom (*Phaeodactylum tricornutum*) against two imidazolium-based ionic liquids ([C_4mim]BF_4 and [C_8mim]BF_4) [J]. Aquatic Toxicology, 2017, 189: 115-122

[79] Zhang C, Zhu L, Wang J, et al. The acute toxic effects of imidazolium-based ionic liquids with different alkyl-chain lengths and anions on zebrafish (*Danio rerio*) [J]. Ecotoxicology and Environmental Safety, 2017, 140: 235-240

[80] Bernot R J, Brueseke M A, Evanswhite M A, et al. Acute and chronic toxicity of imidazolium-based ionic liquids on *Daphnia magna* [J]. Environmental Toxicology and Chemistry, 2005, 24(1): 87-92

◆