科学通报 2017 年 第 62 卷 第 6 期：546 ~ 562
专辑：胶体与界面化学 评 述
《中国科学》杂志社
SCIENCE CHINA PRESS

基于离子液体的两亲分子自组装

鲁飞，郑利强*

山东大学胶体与界面化学教育部重点实验室，济南 250100
* 联系人，E-mail: lqzheng@sdu.edu.cn

2016-04-13 收稿，2016-05-20 修回，2016-05-23 接受，2016-07-27 网络版发表
国家自然科学基金(21573132)资助

摘要 离子液体是指熔点低于100℃，完全由离子组成的一类有机熔融盐．由于离子液体独特的物理化学性质，离子液体参与的两亲分子自组装受到人们的广泛关注．本文简要综述了基于离子液体的两亲分子自组装的研究进展，主要包括离子液体作为新型溶剂，两亲分子在其中自组装形成的分子聚集体；长链离子液体作为表面活性剂构筑的分子聚集体；以及离子液体作为添加剂调控其他两亲分子聚集体的构筑．研究离子液体参与构筑的两亲分子聚集体，一方面可以将离子液体的特性引入到传统的分子聚集体中，有利于改善分子聚集体的性质，扩大其种类和应用范围，另一方面也可以进一步拓展离子液体自身的应用．

关键词 离子液体，两亲分子，聚集行为，微观结构

离子液体(ionic liquids, ILs)是指在室温下或接近室温时呈液态的一种有机熔融盐[1]．现在，也通常将熔点低于100℃的有机盐统称为离子液体．离子液体是由体积相对较大的阳离子与阴离子构成，不存在中性分子．与传统的离子化合物相比，构成离子液体的阴阳离子通常体积不对称，因此静电作用力无法使离子液体中的阴阳离子呈现密堆积结构，这就使得离子液体的阴阳离子不仅可以自由振动，还可以转动和平动．因此，破坏了离子化合物整个有序的晶体结构，使晶格能显著降低，最终导致熔点下降[2]．图1是离子化合物、离子溶液与离子液体存在形式的区别．

离子液体结构的特殊性使其具有很多独特而优良的物化性质[1]：(1) 几乎无蒸汽压且不具有可燃性，使用和储存均环保安全；(2) 液态温度范围宽；(3) 热稳定性高，通常都高于400℃；(4) 电化学窗口宽，是指离子液体开始发生氧化反应的电位与开始发生还原反应的电位差值，一般可达到3~5 V；(5) 导电性优良，且离子液体黏度越小，密度越大，导电性越好；(6) 可设计性，通过选择不同结构的阴阳离子或调节烷基链长可以调控离子液体的多种物理化学性质．正是由于这些独特的物化性质，离子液体逐渐成为一类新型的介质和材料，被广泛地应用于有机合成、催化、分离萃取、生命科学、电化学、以及胶体与界面化学等众多领域．

两亲分子(amphiphiles)的英文单词来源于希腊语的词根．其中，“αμφιζ”也就是“amphis”意味着两者的、双重的，而“φιλια”也就是“philia”表示亲和的．因此，两亲分子就是同时具有亲水性与疏水性的一类化合物[3]．典型的两亲分子是由亲水的极性头基(hydrophilic head-group)和疏水的非极性尾链(hydrophobic tail-chain)组成的，并且头基与尾链的个数以及两者之间的连接方式可以有多种变化(图2)．两亲分子的头基通常是带有电荷或不带电荷的极性基团，例如杂环、磷酸根、磺酸根、铵根、氨基酸、多肽、糖等；疏水尾链通常是饱和或不饱和的碳氢长

引用格式：鲁飞，郑利强．基于离子液体的两亲分子自组装．科学通报, 2017, 62: 546–562
Lu F, Zheng L Q. Amphiphile self-assembly based on ionic liquids (in Chinese). Chin Sci Bull, 2017, 62: 546–562, doi: 10.1360/N972016-00418

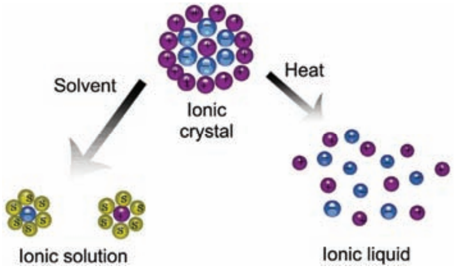

图 1 (网络版彩色)离子化合物、离子溶液与离子液体的存在形式示意图

Figure 1 (Color online) Schematic illustration of ionic compound, ionic solution and ionic liquid

链，可以是直链型也可以是支状型. 表面活性剂分子是最典型的两亲分子. 由于表面活性剂分子的两亲性，其溶于水后，在浓度较低的情况下，会在气液界面发生单分子排列，亲水基团朝向水，而疏水基团伸向空气，从而降低了溶液的表面张力. 当表面活性剂的浓度增大到一定程度后，气液界面上不能容纳更多的表面活性剂分子，体相中的表面活性剂分子就会在多种非共价弱相互作用(如氢键、静电力、疏水作用、范德华力、π-π堆积作用等)驱动下，以极性基朝向极性溶剂、非极性基远离极性溶剂的方式自发聚集形成多种具有特殊性能的有序结构[4]. 目前发现的聚集结构有胶束(球状、蠕虫状、棒状及碟状)、囊泡(单层或多层)、纳米管、纳米纤维、溶致液晶(层状、六角、立方)、微乳液等. 两亲分子的自组装体是化学、生物学、物理学、材料学等多学科的交叉领域，在生命、能源、信息等现代高新技术中发挥着越来越重要的作用.

正如前面所述，离子液体具有多种独特的物理化学性质，两亲分子的自组装体也是当今多学科交叉的研究热点. 因此，越来越多的科学家着眼于如何将离子液体的优势与两亲分子自组装体有机结合起来，研究离子液体参与的两亲分子自组装过程. 将离子液体的特性引入到传统的两亲分子组装体中，有助于改善传统组装体的性质，也拓展了离子液体自身的应用和发展. 下面就离子液体参与的两亲分子自组装作简要概述.

1 离子液体作为溶剂参与的两亲分子自组装

1.1 胶束

作为溶剂参与胶束形成的离子液体可以分为2类[5]，即质子性离子液体(protic ionic liquids, PILs)和非质子性离子液体(aprotic ionic liquids, APILs). 质子性离子液体与水类似，可以接受和给出质子，同时能形成三维氢键网络结构. 硝酸乙基胺(ethylammonium nitrate, EAN)、硝酸丙基胺(propylammonium nitrate, PAN)都是常见的质子性离子液体. 而非质子性离子液体通常不具备形成氢键的能力，主要是多种咪唑类离子液体，如1-丁基-3-甲基咪唑四氟硼酸盐(1-butyl-3-methylimidazolium tetrafluoroborate, [bmim][BF_4])、1-丁基-3-甲基咪唑六氟磷酸盐(1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF_6])、1-丁基-3-甲基咪唑双三氟甲磺酰亚胺(1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [bmim][Tf_2N])等.

早在20世纪80年代，Evans 等人[6,7]就研究了阳离子表面活性剂烷基三甲基溴化铵(alkyl trimethylammonium bromide, C_nTAB)和烷基溴化吡啶(alkyl pyridinium bromide, C_nPyBr)在 EAN 中的胶束化行为. 研究发现，EAN不仅可以作为溶剂还可以作为助表面活性剂参与胶束的形成. Varela课题组[8]研究了一系列阳离子表面活性剂烷基三甲基氯化铵(alkyl trimethylammonium chloride, [C_nTA]Cl, n=12, 14)、烷基三甲基溴化铵([C_nTA]Br, n=10, 12, 14, 16)和

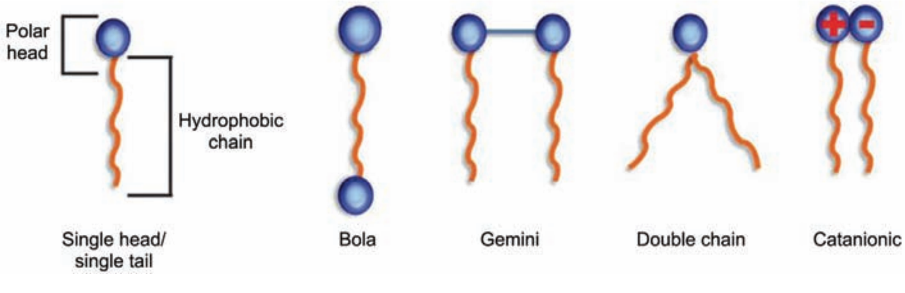

图 2 (网络版彩色)两亲分子的类型[3]

Figure 2 (Color online) Amphiphile classification[3]

十二烷基吡啶氯(dodecylpyridinium chloride, [C$_{12}$Py]Cl)在EAN和PAN中的胶束化行为. 从表1中可以看出, 随着烷基链长的增加几种表面活性剂在EAN和PAN中的临界胶束浓度(critical micelle concentration, CMC)都会降低. 并且, 它们的CMC值还与溶剂有直接关系, 按照PAN>EAN>水顺序依次降低. Warr课题组[9,10]系统研究了一系列非离子表面活性剂长链烷基聚氧乙烯醚(alkyl poly(oxyethyleneglycol)ether, C$_n$E$_m$)在EAN和PAN中的胶束化行为. 结果表明, C$_n$E$_m$在PAN中形成胶束的能力要比在EAN中的弱. 虽然质子性离子液体与水类似, 但其溶剂化作用明显小于水, 并且这种溶剂化作用随着离子液体烷基链的增长而减弱. 因此, 多种表面活性剂在质子性离子液体中成胶束的能力比在水中的弱, 在质子性离子液体中的CMC值更高.

近几年, 一些非质子性离子液体作为溶剂的研究也越来越深入. Anderson等人[11]研究了阴离子表面活性剂十二烷基硫酸钠(sodium dodecylsulfate, SDS)与非离子表面活性剂聚氧乙烯月桂醚(polyoxyethylene lauryl ether, Brij35)在咪唑类离子液体[bmim][PF$_6$]和[bmim]Cl中的聚集行为. 证明了胶束形成的主要驱动力是表面活性剂分子碳氢链和离子液体之间的疏溶剂作用, 并且这种疏溶剂作用小于水中的疏水作用. Fletcher和Pandey[12]系统研究了不同类型的阴离子型表面活性剂SDS、阳离子型表面活性剂[C$_{16}$TA]Br以及非离子型表面活性剂Brij35, TritonX-100, Tween 20在1-乙基-3-甲基咪唑二(三氟甲基)硫酰胺(1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [emim][Tf$_2$N])中的聚集行为. 研究发现, 阴离子表面活性剂不溶于[emim][Tf$_2$N], 阳离子表面活性剂虽然可以溶解但不能形成聚集体, 只有非离子表面活性剂在[emim][Tf$_2$N]中可以形成聚集体.

De Lauth-Viguerie课题组[13]分别研究了长链烷基聚氧乙烯醚类表面活性剂(alkyl poly(oxyethyleneglycol) ether, C$_n$E$_m$)在[bmim][BF$_4$], [bmim][PF$_6$]和[bmim][Tf$_2$N]中的胶束化行为. 研究表明, C$_n$E$_m$形成胶束的尺寸与离子液体的结构有直接关系. Inoue课题组[14]系统研究了一系列聚氧乙烯类非离子表面活性剂C$_n$E$_m$在[bmim][PF$_6$]中的聚集行为. 与[bmim][BF$_4$]和水相比, C$_n$E$_m$与[bmim][PF$_6$]之间的疏溶剂作用力更弱, 使得表面活性剂分子在气液界面的吸附量更低, CMC值更大, 胶束聚集数更小. Lodge课题组[15]首次报道了两嵌段共聚物聚(1,2-丁二烯)-聚氧乙烯(poly(1,2-butadiene)-poly(oxyethylene), PB- PEO)在[bmim][PF$_6$]中的聚集行为. 发现, 通过改变两嵌段的组成比例, 可以实现从球形胶束到蠕虫状胶束再到单层囊泡的转变. 另外, PB-PEO在[bmim][PF$_6$]中形成的聚集体具有很高的热稳定性, 在100℃时聚集体仍能保持形貌不变.

本课题组关于表面活性剂在非质子性离子液体中的聚集行为方面也作了大量工作. 本课题组[16]在研究非离子表面活性剂Tween 20在[bmim][BF$_4$]和[bmim][PF$_6$]中的聚集行为时发现, Tween 20在两种离子液体中都先形成纳米微球, 再进一步聚集形成胶束. 本课题组[17]在研究另一种阳离子型氟表面活性剂(perfluoro *n*-butylsulfonyl fluoride, FC-4)在[bmim][BF$_4$], [bmim][PF$_6$]及[bmim][Tf$_2$N]中的胶束化行为时也发现了类似的现象, FC-4在[bmim][BF$_4$]中形成的聚集体是传统的胶束, 而在[bmim][PF$_6$]中

表1 几种阳离子表面活性剂在EAN, PAN和水中的CMC值(25℃)[8]

Table 1 CMCs of the analyzed compounds in EAN, PAN and water at 25℃[8]

表面活性剂	CMC$_{\text{EAN}}$(mol kg^{-1})	CMC$_{\text{PAN}}$(mol kg^{-1})	CMC$_{\text{water}}$(mol kg^{-1})
[C$_{10}$TA]Br	0.174±0.040	–	0.602
[C$_{12}$TA]Br	0.100±0.010	0.26±0.10	0.0133
[C$_{14}$TA]Br	0.0249±0.037	0.161±0.0050	0.00341
[C$_{16}$TA]Br	–	0.113±0.0012	0.001
[C$_{10}$TA]Cl	0.105±0.032	–	0.00226
[C$_{12}$TA]Cl	0.0330±0.0060	–	0.00447
[C$_{14}$TA]Cl	0.100±0.010	0.293±0.061	0.0112
[C$_{16}$TA]Cl	0.01270±0.000050	0.100±0.024	0.00097

FC-4分子形成的是离散纳米球，在[bmim][Tf_2N]中先形成预胶束，随着浓度的进一步增大再形成胶束．本课题组[18]也系统研究了一系列两亲嵌段聚合物聚氧乙烯-聚氧丙烯-聚氧乙烯共聚物(PEO_m-PPO_n-PEO_m, L61, L64, F68)在[bmim][BF_4]和[bmim][PF_6]中的胶束化行为，发现嵌段聚合物的CMC值随着PEO链长的增加逐渐增大，说明PEO_m-PPO_n-PEO_m在两种离子液体中形成胶束的主要驱动力是疏溶剂作用力．此外，非离子表面活性剂Triton X-100也可以在[bmim][BF_4]和[bmim][PF_6]中形成胶束[19]．冷冻蚀刻透射电子显微镜镜(FF-TEM)结果表明，Triton X-100在[bmim][BF_4]中形成的是不规则的球形聚集体，并且聚集体尺寸要大于水中的胶束(图3). ^{1}H NMR与二维同核NOE实验(2D ROESY)证明Triton X-100中氧乙烯基团上电负性的氧原子与离子液体阳离子之间的静电相互作用是胶束形成的主要驱动力，这与Triton X-100与水分子之间形成的氢键作用类似．Sarkar课题组[20]还研究了TritonX-100在[bmim][PF_6]与EAN混合溶剂中的聚集行为．将EAN加入TX-100的[bmim][PF_6]溶液后，EAN可以插入TX-100/[bmim][PF_6]胶束中，进一步改变胶束的微环境；反之则不会影响胶束的结构．

质子性离子液体与非质子性离子液体均可以作为溶剂支持表面活性剂分子在其中形成胶束．与水相比，两类离子液体的溶剂化作用都有一定程度的减小．因此，表面活性剂分子在离子液体中形成胶束的能力要弱于水中．同时，离子液体的溶剂化作用与离子液体烷基链长、反离子有直接关系，从而显著影响了表面活性剂分子在离子液体中的聚集行为．

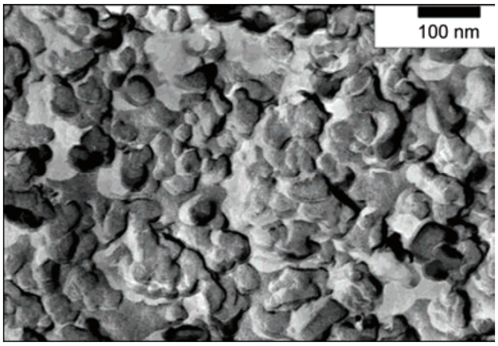

图 3 Triton X-100 在[bmim][BF_4]中浓度为 1.5 CMC时的FF-TEM图[19]

Figure 3 FF-TEM image of Triton X-100/[bmim][BF_4] solution at 1.5 CMC[19]

1.2 液晶

以离子液体EAN为溶剂形成的液晶体系最早是由Evans课题组报道的[21]．在此基础上，Araos和Warr[22]系统研究了非离子表面活性剂C_nE_m在EAN中形成的液晶．随后，Hao课题组[23]具体研究了$C_{12}E_6$在EAN中形成的液晶，并将其应用于增溶多壁碳纳米管．Drummond课题组[24]报道了油酸单甘油酯(monoolein, myverol 18-99K)和植烷三醇(phytantriol)在 EAN 等形成的液晶. Wagner课题组[25]采用流变、电导率、小角中子散射(SANS)等多种方法研究了阳离子表面活性剂[C_{16}TA]Br在EAN中相行为，发现当[C_{16}TA]Br浓度在45%~62%(质量分数)时，随着温度的变化，可以发生溶液和六角液晶相的可逆相转变．Chen课题组先后报道了非离子表面活性剂P123[26]，Brij97[27]和阳离子型季铵盐类Gemini表面活性剂(C_sH_{2s}-α,ω-(Me_2N^+-$C_mH_{2m+1}Br^-$)$_2$, s=2, m=10, 12, 14)在EAN[25,28]，PAN和硝酸丁基铵(BAN)[29]中形成的液晶体系．此外, Wagner课题组[30]还比较了植物甾醇类非离子表面活性剂(phytosterol ethoxylate, BPS-10)在非质子性离子液体[bmim][BF_4]和质子性离子液体EAN中的形成的液晶相态的差异．研究发现, EAN形成的三维空间网络结构更容易促进液晶的形成．Wagner课题组[31]还研究了嵌段共聚物P123在非质子性离子液体[bmim][PF_6]中形成的液晶相，证明了PEO基团是液晶形成的关键．与水作为溶剂形成的溶致液晶体系相比，离子液体作为溶剂形成的液晶具有优良的高温稳定性，这为溶致液晶在高温条件下的应用提供了可能，具有一定的实际意义．

与离子液体参与构筑的两组分液晶体系不同，离子液体参与构筑的三组分液晶体系主要以非质子性离子液体[bmim][BF_4]和[bmim][PF_6]为主．Li课题组研究了水/Brij97/[bmim][BF_4]([bmim][PF_6])三元液晶体系[32]与水/$C_{18}E_{20}$/[bmim][BF_4]三元液晶体系[33]．在此基础上，Chen课题组[34]构筑了水/Brij30/[bmim][BF_4]([bmim][PF_6])三元液晶体系，并系统研究了温度和浓度对液晶相态的影响．

1.3 囊泡

关于两亲分子在离子液体介质中形成囊泡体系的报道较为有限．Kimizuka[35,36]在2001年首次报道了糖脂和二烷基二甲基铵在离子液体中形成的囊泡相，研究表明两亲分子的羟基与离子液体阴离子之间形

成的氢键作用是囊泡形成的主要驱动力. Hao等人[37]发现了一种氟表面活性剂($Zn(OOCCH_2C_6F_{13})_2$)在[bmim][BF_4]中可以形成囊泡, 而这种阴离子表面活性剂与阳离子表面活性剂十四烷基二甲基氧化铵(tetradecyldimethylamine oxide, C_{14}DMAO)形成的复配体系在[bmim][PF_6]中也可以形成囊泡. Gayet等人[38]研究发现一种磷脂酰胆碱类两亲分子(1,2-dipalmitoyl-*sn*-glycero-3-phosphatidylcholine, DPPC)在咪唑类离子液体([bmim][BF_4], [bmim][PF_6], [emim][Tf_2N])和吡啶类离子液体(*N*-benzylpyridinium bis(trifluoromethylsulfonyl)imide, [bnpy][Tf_2N])中均可以自发形成囊泡. 最近, Wagner课题组[39]发现阳离子型表面活性剂双十六烷基二甲基溴化铵(didodecyldimethylammonium bromide, DDAB)在EAN中可以形成囊泡. 当DDAB浓度为2%~68%(质量分数)时, 体系可以形成双相, 其中上相为~30 μm 的巨型囊泡与海绵相(L_3)的共存相, 而下相是~2.5 μm的囊泡相(图4).

2 离子液体作为表面活性剂参与的两亲分子自组装

当离子液体的烷基链达到一定长度时, 离子液体自身即可符合表面活性剂的双亲结构特点, 从而形成一类新型表面活性剂, 通常称之为“表面活性离子液体”. 基于其两亲性结构, 表面活性离子液体也可以形成各式各样的具有独特结构、形貌和性质的分子组装体.

2.1 胶束

2.1.1 阳离子型表面活性离子液体

不同链长、反离子的咪唑类离子液体是研究最为广泛的一类表面活性离子液体. 早在2004年, Bowers等人[40]就研究了[bmim]Cl, [bmim][BF_4]和1-辛基-3-甲基咪唑碘(1-octyl-3-methylimidazolium iodide, [C_8mim]I)在水溶液中的聚集行为. 随后, El Seoud等人[41]系统研究了不同链长的1-烷基-3-甲基咪唑氯化物(1-alkyl-3-methylimidazolium chloride, [$C_n$mim]Cl)在水溶液中的胶束化行为, 发现胶束形成的主要驱动力是氯离子与咪唑质子氢之间的氢键作用. 在此基础上, Inoue等人[42], Jungnickel等人[43], Lopes等人[44]又分别采用不同手段佐证[$C_n$mim]Cl(n=2~18)在水溶液中的聚集行为. Singh和Kumar[45]采用^{1}H NMR法分析了4种不同头基、反离子和烷基链长的离子液体[bmim]-Cl, [C_8mim]Cl, [bmim][BF_4]和1-丁基-3-甲基吡啶氯([bmPy]Cl)形成的胶束的微观结构, 阐明了离子液体的结构变化以及与水之间的相互作用对胶束过程的影响. 此外, Wang等人[46], Vanyúr等人[47]和Goodchild等人[48]系统研究了不同烷基链长的1-烷基-3-甲基咪唑溴化物([$C_n$mim]Br)在水溶液中的聚集行为. 研究证明, 只有烷基链长$n \geq 6$时, [$C_n$mim]Br才能形成一定结构的聚集体. 本课题组[49]系统研究了不同烷基链长的[$C_n$mim]Br(n=10, 12, 14, 16)和不同反离子的1-十二烷基-3-甲基咪唑四氟硼酸盐(1-dodecyl-3-methylimidazolium tetrafluoroborate, [C_{12}mim][BF_4])在水溶液中的聚集行为. 研究表明, [$C_n$mim]Br在水溶液中的表面活性优于相同烷基链长的季铵盐型阳离子表面活性剂. 而且, 由于[BF_4]$^-$的水合作用小于Br^-, [BF_4]$^-$能更有效地屏蔽咪唑极性头基之间的静电斥力, 因此[C_{12}mim][BF_4]降低表面张力的能力优于[C_{12}mim]Br.

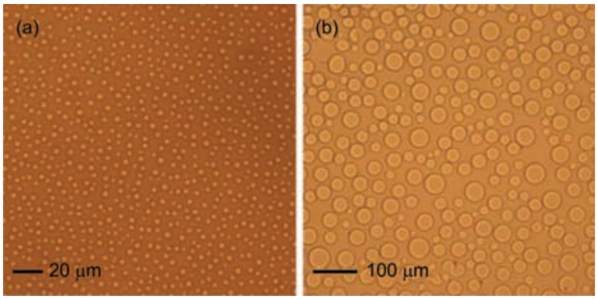

图 4 (网络版彩色)30%DDAB/EAN溶液下相(a)和上相(b)的亮场电子显微镜照片[39]

Figure 4 (Color online) Micrographs recorded at 25°C for the lower phase (a) and the upper phase (b) of 30wt% DDAB/EAN solution[39]

除了咪唑类表面活性离子液体, 人们还研究了其他不同头基的阳离子型表面活性离子液体. Baker等人[50]首次研究了*N*-烷基-*N*-甲基吡咯烷溴化物(*N*-alkyl-*N*-methylpyrrolidinium bromide, [C_nMPyrr]Br)在水溶液中的聚集行为. 在此基础上, Tariq等人[51]研究了不对称型*N*,*N*-二烷基吡咯烷溴化物(*N*,*N*-dialkylpyrrolidinium bromide, [C_1C_{12}Pyrr]Br, [C_4C_{12}Pyrr]Br, [C_4C_8Pyrr]Br)在水溶液中的胶束化行为. 本课题组[52]也研究了一系列不同烷基链长的[C_nMPyrr]Br(n=12, 14, 16)在水溶液中的胶束化行为并计算了热力学参数. 除了吡咯头基的表面活性离子液体, Sastry等人和Blesic等人[53,54]还研究了不同烷基链长的吡啶氯化物[C_nPy]Cl(n=4, 10, 12, 14, 16, 18)以及*N*-十二烷基-*N*-甲基哌啶溴化物(*N*-dodecyl-*N*-methylpiperidinium bromide, [C_{12}MPip]Br)在水溶液中的聚集行为，并与不同头基结构的离子液体[C_{12}MPyrr]Br和[C_{12}mim]Br进行了对比，结果发现阳离子的结构和电荷密度，阴离子的种类以及烷基链的长度都对胶束形成有显著影响.

此外，一些具有特殊结构的表面活性离子液体也得到了广泛系统的研究. Ao等人[55]设计合成了咪唑头基的Gemini型表面活性离子液体([C_n-4-$C_n$im]Br_2, n=10, 12, 14). 研究发现，[C_n-4-$C_n$im]Br_2与相同碳链长度的单链咪唑型表面活性离子液体相比，表现出更优异的表面活性. 本课题组[56]也系统比较了吡咯头基的Gemini型表面活性离子液体([$C_n$py-4-$C_n$py]Br_2, n=10, 12, 14)在水中的胶束化行为. 本课题组[57]还研究了*N*,*N*-双癸烷吡咯溴化物(didecylpyrrolidium bromide, DC_{10}PB)在水中的聚集行为. 偏光显微镜(POM)、低温透射电子显微镜(cryo-TEM)以及小角X射线散射(SAXS)结果表明，随着浓度的逐渐增大，DC_{10}PB可以从胶束相变为囊泡相，最终变为层状液晶相. 最近，一类新型硅基表面活性离子液体硅氧烷羧酸铵(siloxane ammonium carboxylate [Si(n)N(2)-CA(1), (n=3, 4)])被设计合成出来[58](图5). 硅氧烷基团的引入可以有效降低离子液体的熔点，并能显著提高其表面活性，可以使水的表面张力降低至~20 mN/m.

表面活性离子液体作为一类新型表面活性剂，其在水中形成胶束的驱动力主要是疏水作用、静电相互作用、氢键作用等. 因此，表面活性离子液体的头基、烷基链长以及反离子的结构都会对其胶束化行为产生影响，头基之间相互作用越强，CMC值越低；烷基链越长，CMC值越低；增加反离子的碱性也可以降低CMC值.

2.1.2 阴离子型表面活性离子液体

2011年，Eastoe课题组[59,60]采用表面张力和SANS法研究了阴离子为十二烷基硫酸、2-乙基己基琥珀酸酯磺酸等的表面活性离子液体在水溶液中的聚集行为，并将这类离子液体命名为“阴离子型表面活性离子液体(anionic surfactant ionic liquids, SAILs)”，其结构式如图6所示. 这种阴离子型表面活性离子液体表现出优异的表面活性，可以有效降低水的表面张力，其中[bmim][TC]可以使水的表面张力降至~25 mN/m.

在此基础上，Yu课题组[61]比较了不同反离子的1-丁基-3-甲基咪唑十二烷基硫酸盐(1-butyl-3-methylimidazolium dodecyl sulfate, [bmim][DS])和*N*-丁基-*N*-甲基吡咯烷十二烷基硫酸盐(*N*-butyl-*N*-methylpyrrolidinium dodecyl sulfate, [C_4MPyrr][DS])在水溶

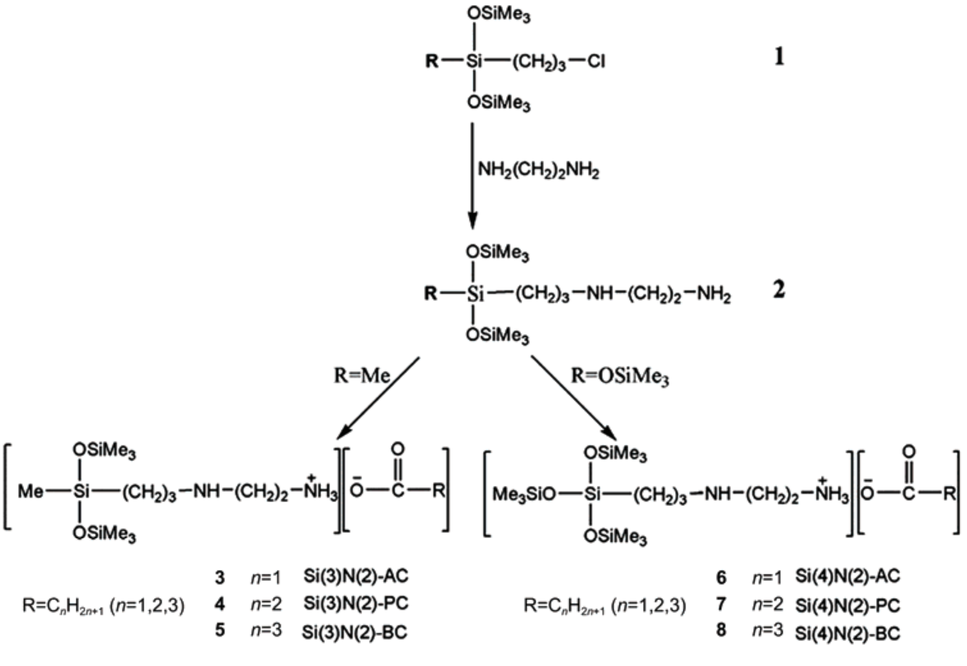

图 5 硅基表面活性离子液体[Si(n)N(2)-CA(1), (n=3, 4)]的合成路线[58]

Figure 5 Synthesis routes of siloxane ammonium carboxylate [Si(n)N(2)-CA(1), (n=3, 4)][58]

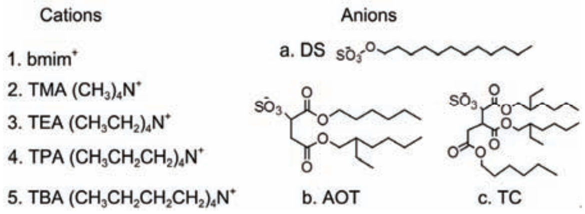

图 6　阴离子型表面活性离子液体的结构式[59,60]

Figure 6　Structures of anionic surfactant ionic liquids[59,60]

液中的聚集行为. 此后，Yu课题组[62]又系统研究了一系列1-烷基-3-甲基咪唑烷基硫酸盐(1-alkyl-3-methylimidazolim alkyl sulfates, [C$_n$mim][C$_m$SO4], n=6, 8, 10; m=12, n=4; m=10, 14)在水中的聚集行为，发现阳离子或阴离子烷基链的增长均可提高[C$_n$mim][C$_m$SO4]的表面活性. 此外，Yu课题组[63]还比较了不同头基的阴离子表面活性离子液体1-丁基-3-甲基咪唑2−乙基己基琥珀酸酯磺酸盐（1-butyl-3-methylimidazolium bis(2-ethylhexyl)sulfosuccinate, C$_4$mim-AOT)与1-丁基-3-甲基咪唑2−乙基己基琥珀酸酯磷酸盐（1-butyl-3-methylimidazolium bis(2-ethylhexyl) phosphate, C$_4$mim-DEHP）水中的胶束化行为. 最近，Yin等人[64]通过电导分析法、荧光分析法、DLS、^{1}H NMR、TEM等方法发现C$_4$mim-AOT在水中可以形成两种聚集体，即~10 nm的胶束和~100 nm的囊泡.

Pereiro等人[65]研究了一类水溶性较好的新型氟表面活性离子液体在水溶液中的聚集行为，发现随着浓度的增大，氟表面活性离子液体形成的球形胶束逐渐融合，并进一步形成层状聚集体.

2.1.3　功能化表面活性离子液体

利用离子液体的“可设计性”，人们又开始在表面活性离子液体的分子上引入功能性基团，合成了一些功能性表面活性离子液体并研究了他们在水溶液中的聚集行为. Liu等人[66]合成了一种两性表面活性离子液体1-羧甲基-3-十二烷基咪唑盐(1-carboxymethyl-3-dodecylimidazolium salt, CMDim)，并研究了其在水溶液中聚集行为. 研究发现，由于羧基的引入，pH对胶束过程可以起到调控作用. 在此基础上，Yu课题组[67]研究了不同烷基链长的COOH 功能化的表面活性离子液体1-羧甲基-3-烷基咪唑溴(1-carboxymethyl-3-dodecylimidazolium bromide, [C$_n$, N′-CO$_2$H-Im]Br, n= 10, 12, 14)在水溶液中的聚集行为. 表面张力结果表明，相比于传统的咪唑类离子液体，羧基的引入促进了胶束的形成并且提高了离子液体的表面活性. 本课题组[68]研究了头基带有苯环结构的1-(2,4,6-三甲基苯基)-3-烷基咪唑溴化物(1-(2,4,6-trimethylphenyl)-3-alkylimidazolium bromide, [C$_n$pim]Br, n=10, 12, 14)在水中的聚集行为. 苯环结构的引入使得[C$_n$pim]Br具有更优异的表面活性以及稳定的荧光性质. 此外，本课题组[69]设计合成了反离子为β-萘磺酸根的咪唑类表面活性离子液体1-十二烷基-3-甲基咪唑β-萘磺酸盐(1-dodecyl-3-methylimidazoliumb-naph-thalene sulfonate, [C$_{12}$mim][Nsa]). 研究表明，随着浓度的逐渐增大，[C$_{12}$mim][Nsa]可以自发地由胶束相到L$_\alpha$相再到层状液晶相. 结合SAXS和^{1}H NMR分析，β-萘磺酸根在静电引力、疏水作用力以及π-π堆积作用的协同影响下吸附在咪唑头基附近，有效地屏蔽了咪唑头基之间的静电斥力，诱导[C$_{12}$mim][Nsa]发生相转变. 随后，Yu课题组[70]又设计合成了具有光响应性的1-烷基-3-甲基咪唑反式肉桂酸盐(1-alkyl-3-methylimidazolium *trans*-cinnamate, [C$_n$mim][CA], n=4, 6, 8, 10, 12). 研究发现，只有n=8, 10, 12时[C$_n$mim][CA]的聚集行为才会受到紫外光的影响. 紫外光照使得反式肉桂酸盐变为顺式，降低了[C$_n$mim][CA]的表面活性，引起CMC、聚集体的离子化程度以及吉布斯自由能的增大.

向烷基链中引入功能性基团是表面活性离子液体功能化的另一种途径. Firestone课题组[71]合成了尾链带有噻吩基团的咪唑类表面活性离子液体，并研究了其在水中的聚集行为. 由于噻吩基团的引入，这类离子液体具有了电化学活性，并可以通过聚合反应制备水溶性的阳离子聚合物. Sirieix-Plénet课题组[72]设计合成了尾链链端为二茂铁基团的1-(11-二茂铁基十一烷基)-3-甲基咪唑溴化物([Fc11mim]Br)，并分别研究了[Fc11mim]Br在氧化态和还原态时在水中的聚集行为，如图7所示. 本课题组[73]研究了疏水尾链为咔唑基团的咪唑型表面活性离子液体1-[n-(N-咔唑)烷基]-3-甲基咪唑溴化物(1-[n-(N-carbazole) alkyl]-3-methylimidazolium bromide, [CzC$_n$mim]Br)在水中的胶束化行为. 咔唑基团的引入使[CzC$_n$mim]Br在水中更容易形成胶束，并具有稳定且高强度的荧光性质. 最近，Fan和Zhao[74]合成了尾链含有吡咯基团的咪唑类表面活性离子液体(Py(CH$_2$)$_{12}$mim$^+$Br$^-$)，通过介电弛豫光谱系统研究了其在水中的聚集行为. 吡咯基团的引入加强了Py(CH$_2$)$_{12}$mim$^+$Br$^-$分子间的疏水作用力和π-π堆积作用，促进了胶束的形成.

本课题组[75]还合成了长链手性离子液体S-3-

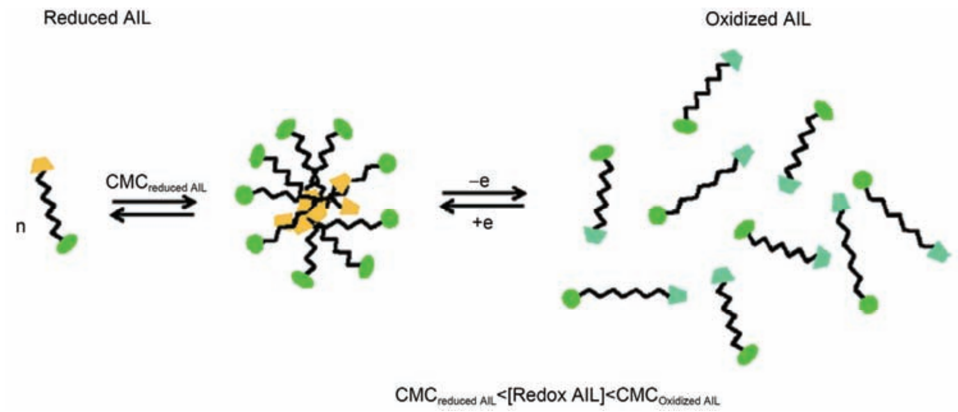

图 7 (网络版彩色) [Fc11mim]Br还原态和氧化态在水中的聚集形态示意图[72]
Figure 7 (Color online) Schematic illustration of the proposed aggregation structures of [Fc11mim]Br in the reduced and oxidized forms[72]

十六烷基-1-(1-羟基异丙基)咪唑溴 (*S*-3-hexadecyL^{-1}-(1-hydroxy-propan-2-yl)-imidazolium bromide, [C_{16}hpim]-Br), 并研究了其在水中的胶束化行为. 随后, 又设计合成了一种带有Y型疏水碳链的咪唑类手性离子液体*S*-(+)-1-(2,3-二辛酰氧-丙烷基)-3-甲基咪唑氯化物((*S*)-(+)-1-(2,3-bis(octanoyloxy)-propyl)-3-methylimidazolium chloride, [Bopmim]Cl), 如图8所示[76].

2.2 液晶

表面活性离子液体参与构筑的溶致液晶可以追溯到1991年, Bleasdale等人[77]报道了烷基吡啶氯化物[C_{16}Py]Cl在水、甘油、甲酰胺等溶剂中形成的液晶. 随后, Firestone课题组[78,79]发现咪唑类表面活性离子液体[C_{10}mim]Br和[C_{10}mim][NO_3] 在水中可以形成液晶. 咪唑环、反离子和水之间形成的氢键网络结构是液晶形成的关键. 随着水含量的增加, [C_{10}mim]Br和[C_{10}mim][NO_3]都依次出现了从层状相到六角孔状层状相, 再到不规则六角相的相转变过程. 此外, Inoue等人[80]详细研究了[C_{12}mim]Br在水中形成的液晶相, 并绘制了该体系的T-X相图(图9). 本课题组[81]利用示差扫描量热法(DSC)和POM绘制了Gemini型表面活性离子液体[C_{12}im-4-C_{12}im]Br_2/H_2O体系的T-X相图, 发现其可形成六角液晶相和层状液晶相.

最近, Yu课题组在功能化表面活性离子液体构筑的液晶体系方面作了一系列工作. 首先, Yu课题组[82]研究了阴离子功能化的表面活性离子液体1-十二烷基-3-甲基咪唑水杨酸盐(1-dodecyl-3-methylimidazolium salicylate, C_{12}mimSal)与1-十二烷基-3-甲基咪唑3-羟基-2-萘甲酸盐(1-dodecyl-3-methylimidazolium 3-hydroxy-2-naphthoate, C_{12}mimHNC)的相行为. POM和SAXS数据表明, C_{12}mimSal可以形成六角液晶相和立方液晶相, 而C_{12}mimHNC只能形成层状液晶相. 密度泛函计算证明C_{12}mimSal的阴阳离子之间存在更强的静电作用、疏水作用以及π-π堆积作用. 此外, Yu课题组[83]还研究了含有光响应性反离子的1-十二烷基-3-甲基咪唑肉桂酸盐(1-dodecyl-3-methylimidazolium cinnamate, [$C_n$mim][CA])与1-十二烷基-3-甲基咪唑对羟基肉桂酸盐(1-dodecyl-3-methylimidazolium

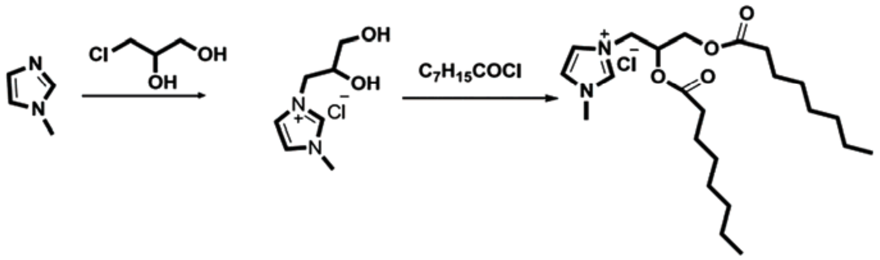

图 8 (*S*)-(+)-1-(2,3-bis(octanoyloxy)-propyl)-3-methylimidazolium chloride的合成示意图[76]
Figure 8 Synthesis scheme of (*S*)-(+)-1-(2,3-bis(octanoyloxy)-propyl)-3-methylimidazolium chloride[76]

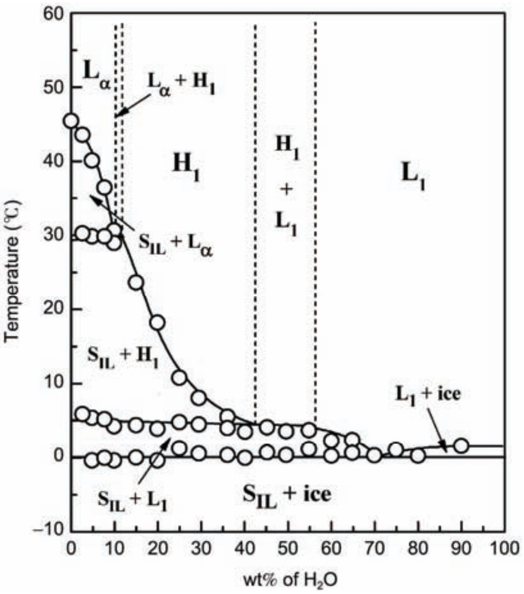

图 9 $\mathrm{[C_{12}mim]Br}$/水二元体系的T-X相图[80]
Figure 9 T-X phase diagram of $\mathrm{[C_{12}mim]Br/H_2O}$ mixture[80]

cinnamate, $\mathrm{[C_{\mathit{n}}mim][PCA]}$)形成的液晶相，发现紫外光引起的反离子的顺反异构化可以影响液晶相的晶格参数.

表面活性离子液体参与构筑的三元液晶体系同样受到广泛研究. Chen课题组[84,85]研究了$\mathrm{[C_8mim]Cl}$/癸醇/水以及$\mathrm{[C_{16}mim]Cl}$/癸醇/水三元体系的相行为，发现了六角状液晶和层状液晶. 咪唑阳离子、氯离子、癸醇以及水之间的氢键作用以及离子液体烷基链与癸醇烷基链之间的疏水作用力是液晶形成的主要驱动力. 本课题组[86,87]也研究了$\mathrm{[C_{\mathit{n}}mim]Br}$/对二甲苯/水三元体系的相行为，发现$\mathrm{[C_{12}mim]Br}$可以形成六角相、立方相、层状相三种液晶相态，而$\mathrm{[C_{14}mim]Br}$与$\mathrm{[C_{16}mim]Br}$只能形成六角状液晶和层状液晶. 此外，本课题组[88]也研究了*N*-烷基-*N*-甲基吡咯溴(*N*-alkyl-*N*-methylpyrrolidinium bromide, C$_n$MPB, n=12, 14, 16)/癸醇/水三元体系形成的液晶相. 相关研究为进一步丰富离子液体构建的溶致液晶体系提供了理论依据.

3 表面活性离子液体在室温离子液体中的聚集行为

近几年，表面活性离子液体在室温离子液体中的聚集行为也引起越来越多的关注. 这种纯粹由离子液体构建的分子组装体体系可以更加完整地体现离子液体的各种独特性能. Kunz课题组[89]研究了$\mathrm{[C_{16}mim]Cl}$和$\mathrm{[C_{16}mim][BF_4]}$在EAN中的聚集行为，发现形成的聚集体具有优良的热稳定性，在高于200℃时仍能稳定存在. 本课题组[90,91]分别研究了$\mathrm{[C_{\mathit{n}}mim]Br}$($n$=10, 12, 14, 16)在$\mathrm{[bmim][BF_4]}$和EAN中的胶束化行为，FF-TEM结果表明$\mathrm{[C_{\mathit{n}}mim]Br}$在$\mathrm{[bmim][BF_4]}$形成的胶束尺寸更大. 随后，本课题组[92]又研究了一系列*N*-芳基咪唑类表面活性离子液体$\mathrm{[C_{\mathit{n}}pim]Br}$在$\mathrm{[bmim][BF_4]}$中的聚集行为，发现头基中芳香基团的引入可以促进$\mathrm{[C_{\mathit{n}}pim]Br}$在$\mathrm{[bmim][BF_4]}$中形成胶束. 在此基础上，本课题组[93]系统比较了不同结构类型的咪唑类表面活性离子液体在EAN中的胶束化行为(图10). 研究发现，烷基链长、反离子的碱性以及阳离子的结构变化对咪唑类表面活性离子液体在EAN中的表面活性和聚集行为均有显著影响. 此外，本课题组[94]也研究了吡咯类表面活性离子液体C$_n$MPB(n=12, 14, 16)在EAN中的聚集行为，发现C$_n$MPB在EAN中的表面活性要弱于其在水中. 本课题组[95]还比较了膦型表面活性离子液体C$_n$TPB(n=12, 14)在质子型离子液体EAN与非质子型离子液体$\mathrm{[bmim][BF_4]}$中的胶束化行为，发现C$_n$TPB与EAN之间存在更强的疏溶剂作用.

迄今为止，表面活性离子液体在室温离子液体中聚集行为的相关研究还很有限，所涉及的离子液体结构也仅限于常见的*N*-烷基咪唑型、*N*-烷基-*N*-甲基吡咯烷型等. 这类纯粹由离子液体构建的两亲分子自组装体系，能更好地体现离子液体独特的优良性质，探索不同结构的表面活性离子液体在室温离子液体中的聚集行为，有助于拓宽离子液体参与的两亲分子组装体的种类和应用范围.

表面活性离子液体在室温离子液体中构筑的液晶体系也有系统的报道. Chen课题组[96]研究了$\mathrm{[C_{16}mim]Cl}$/EAN构筑的六角液晶、层状液晶、反连续立方相液晶以及高温层状液晶. 由于离子液体几乎不挥发、高的热稳定等特点，液晶相的温度考察范围超过100℃. 随后，本课题组[97]分别研究了$\mathrm{[C_{16}MPyrr]Br}$在EAN和水中构筑的液晶相. 研究发现$\mathrm{[C_{16}MPyrr]Br}$在EAN和水中都可以形成六角相和立方相液晶. DSC结果表明，$\mathrm{[C_{16}MPyrr]Br}$在EAN中构建的液晶相表现出更好的高温稳定性. 本课题组[98]还研究了$\mathrm{[C_{14}mim]Cl}$/EAN二元液晶体系，并成功将多壁碳纳米管分散到形成的六角液晶相中，且没有破坏六

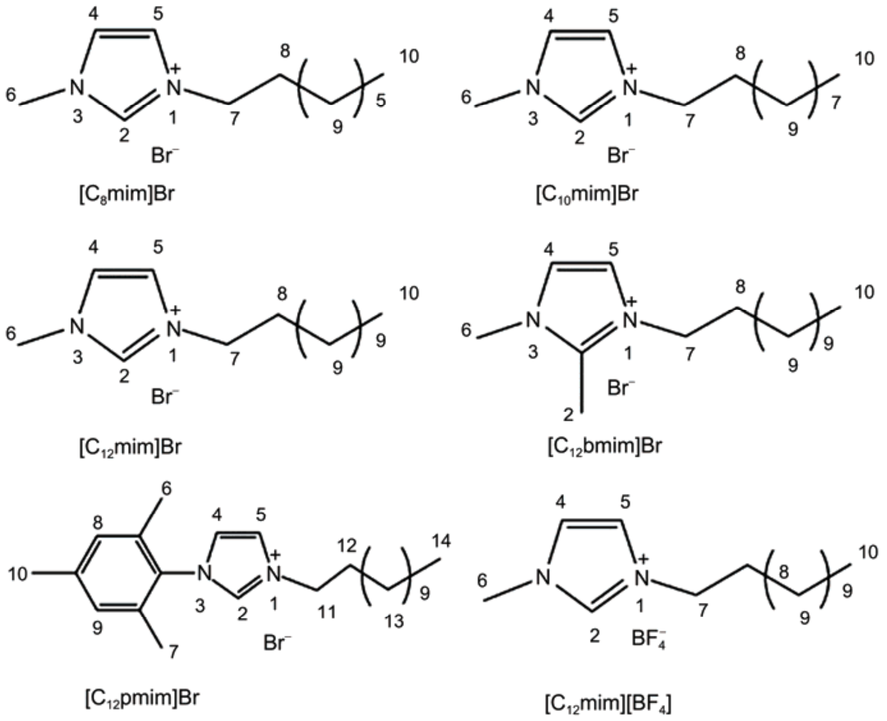

图 10 咪唑类表面活性离子液体的结构式[93]

Figure 10 Chemical structures of the surface active imidazolium ILs used in this study[93]

角相液晶的结构.

最近，一些具有特殊结构的表面活性离子液体也成功构筑了液晶体系．Yu课题组[99]研究了1-丁基-3-甲基咪唑十二烷基硫酸酯([C_4mim][$C_{12}H_{25}SO_4$])在H_2O/EAN混合溶剂中的聚集行为，发现这一简单的咪唑类表面活性离子液体不仅能够在富水环境下形成种类丰富的溶致液晶(包括六角相、层状相及反双连续立方相)，更能作为一种有效的小分子凝胶因子在富EAN环境下较大的浓度范围内形成超分子凝胶．此外，Yu课题组[100]还研究了阴离子功能化的表面活性离子液体1-十二烷基-3-甲基咪唑间羟基苯甲酸盐与对羟基苯甲酸盐(*m*-C_{12}mimHB，*p*-C_{12}mimHB)在水和EAN中形成的液晶相，并将多壁碳纳米管分散在六角液晶相中，进一步提高了六角液晶相的黏度.

4 离子液体作为添加剂调控传统两亲分子组装体

近几年，离子液体作为添加剂调控传统两亲分子组装体也受到了越来越多的关注．由于离子液体的独特性质，离子液体在调控两亲分子组装体的结构和性质方面也起到了独特的作用.

2004年, Reddy课题组[101]率先研究了一系列不同链长和反离子的咪唑类离子液体，[$C_n$mim]Cl(*n*=4，6，8)，[C_1mim]I和[C_8mim][BF_4] 对阴离子表面活性剂SDS水溶液中聚集行为的影响，发现加入离子液体的烷基链长越长对SDS聚集行为的影响越明显．随后，Pandey课题组[102~105]分别研究了离子液体[bmim]-[PF_6]和[bmim][BF_4]对阴离子表面活性剂SDS，十二烷基苯磺酸钠(sodium dodecylbenzenesulfonate, SDBS)和两性表面活性剂3-磺丙基十二烷基二甲基甜菜碱(*N*-dodecyl-*N*,*N*-dimethyl-3-ammonio-1-propanesulfonate，SB-12)水溶液胶束化行为的影响．当[bmim][BF_4]加入到SDS胶束溶液中时，低浓度时起到了电解质和共表面活性剂的作用，从而促进了SDS胶束的形成；而当浓度高于30%时则起到了共溶剂的作用，不利于SDS胶束的形成[102]．将[bmim]-[PF_6]加入到SDS胶束溶液中时，随着[bmim][PF_6]浓度的增加SDS的CMC值逐渐降低，直至[bmim][PF_6]浓度达到~0.1%后，SDS的CMC值则不再变化[103]．[bmim][BF_4]在SB-12的胶束水溶液中则主要起到了电解质和共表面活性剂的作用，从而促进了SB-12胶束的形成[104].

Sarkar课题组[106]研究了一系列阴离子型离子液体1-烷基-3-甲基咪唑烷基硫酸盐(1-alkyl-3-methylimidazolium alkylsulfate, $[C_2mim][C_nSO_4]$(n=2, 4, 6))对两性表面活性剂3-磺丙基十六烷基二甲基甜菜碱(*N*-cetyl-*N*,*N*-dimethyl-3-ammonio-1-propanesulfonate, SB-16)胶束水溶液的影响. 研究发现, $[C_2mim][C_nSO_4]$的加入可以降低SB-16的CMC值和胶束尺寸, 且随着阴离子烷基链长的增加影响程度越来越明显. Sarkar课题组[107]还对比研究了2种质子型离子液体, 己酸二甲基乙醇基铵(dimethylethanol ammonium hexanoate, DAH)和甲酸二甲基乙醇基铵(dimethylethanol ammonium formate, DAF)对阳离子表面活性剂$[C_{16}TA]Br$胶束化行为的影响. 相比于DAF, DAH的加入使$[C_{16}TA]Br$胶束聚集数和尺寸增加的更加显著, 这是由于DAH烷基链较长, 起到了共表面活性剂的作用, 从而参与了胶束的形成.

最近, Pal和Pillania[108]研究了三取代离子液体1-丁基-2,3-二甲基咪唑氯(1-butyl-2,3-dimethylimidazolium chloride, [bdmim][Cl])对SDS胶束化行为的影响, 发现[bdmim][Cl]的加入阻碍了SDS胶束的形成, 使得SDS的CMC值增大, 胶束聚集数减小. 在此基础上, Pal和Pillania[109]又研究了[bdmim][Br]对十四烷基三甲基溴化铵(TTAB)聚集行为的影响. 与SDS不同, [bdmim][Br]的加入促进了TTAB的胶束化行为. 本课题组[110]系统研究了酸碱功能化的咪唑类离子液体1-羧甲基-3-甲基咪唑氯([MimCM]Cl)和1-氨乙基-3-甲基咪唑氯([MimAE]Cl)对SDS胶束水溶液的影响(图11), 作为对比, 同时研究了1-乙基-3-甲基咪唑氯([Emim]Cl)和1-羟乙基-3-甲基咪唑氯([MimHE]Cl)的影响. 相比于[Emim]Cl, 氨基的引入可以进一步促进SDS胶束的形成, 羧基的引入则起到相反作用, 而羟基的引入影响不大. Lu等人[111]利用哌嗪类离子液体1-乙基哌嗪四氟硼酸盐(1-ethylpiperazinium tetrafluoroborate, $[C_2pi][BF_4]$)或1-苯基哌嗪四氟硼酸盐(1-phenylpiperazinium tetrafluoroborate, $[Phpi][BF_4]$)与SDS构筑了双水相体系. 研究表明, $[C_2pi][BF_4]$与$[Phpi][BF_4]$的阳离子头基与SDS之间的静电作用力以及阳离子-π相互作用是双水相形成的主要驱动力. Mahajan课题组[112]研究了$C_n$mimCl(n=8,10,12)与SDBS构筑的混合胶束体系, 并通过改变二者的比例得到了囊泡胶束共存相.

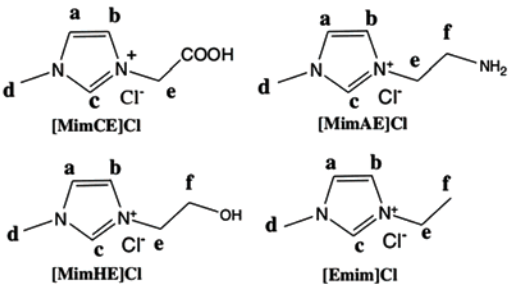

图 11 酸碱功能化离子液体的结构式[110]

Figure 11 Chemical structures of the acid/basic functional ILs[110]

离子液体对非离子表面活性剂水溶液中的聚集行为同样具有显著的影响. Pandey课题组[113,114]研究了$[bmim][PF_6]$, $[bmim][BF_4]$对非离子表面活性剂Triton X-100胶束体系的影响. 研究发现, $[bmim][PF_6]$对Triton X-100在水溶液中的胶束化行为没有影响, 而$[bmim][BF_4]$的加入则使Triton X-100的CMC值增大且胶束的尺寸降低. Guo课题组[115]研究了[bmim]Br对非离子表面活性剂Pluronic P104聚集行为的影响. 随后, Guo课题组[116]又将$[bmim][BF_4]$加入到Tween 80和Brij30复配形成的蠕虫状胶束体系中, 发现

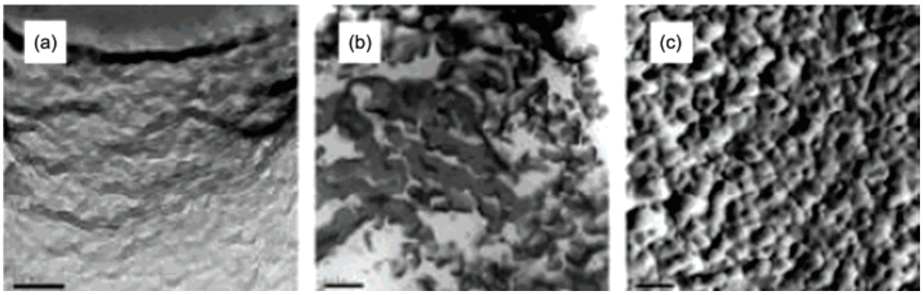

图 12 $[bmim][BF_4]$浓度为 0(a), 0.04 (b)和 0.22 mol L^{-1}(c)时Tween80(30%)+Brij 30 胶束体系的 FF-TEM图[116]. X_{Brij30}=0.54; 标尺为 0.2 μm

Figure 12 Freeze-fractured images of micelles (0.30 (mass fraction) Tween80+Brij 30 surfactant systems with X_{Brij30}=0.54) at different $[bmim][BF_4]$ concentrations. (a) 0, (b) 0.04, and (c) 0.22 mol L^{-1}[116]. The scale bar is 0.2 μm

$[bmim][BF_4]$可以诱导蠕虫状胶束转变成球形胶束.图12是加入不同浓度$[bmim][BF_4]$时体系的FF-TEM照片. 本课题组[117]也利用等温滴定量热法系统研究了$C_n$mimBr(n=8,10,12,14,16)以及C_nMPB(n=12, 14, 16)对$PEO_nPPO_mPEO_n$聚集行为的影响. 研究发现, 离子液体与聚合物之间的相互作用与离子液体和聚合物的烷基链长有关, 与离子液体的头基无关.

离子液体对表面活性离子液体水溶液中的聚集行为也可产生影响. 本课题组[118]研究了含有芳香反离子的短链离子液体1-丁基-3-甲基咪唑苯磺酸盐(1-butyl-3-methylimidazolium benzenesulfonate, bmimBsa)和1-丁基-3-甲基咪唑萘磺酸盐(1-butyl-3-methylimidazolium 2-naphthalenesulfonate, bmimNsa)对C_{12}mimBr聚集行为的影响, 并以1-丁基-3-甲基咪唑甲磺酸盐(1-butyl-3-methylimidazolium methylsulfonate, bmimMsa)作为对比. 研究发现, 离子液体对C_{12}mimBr聚集行为的影响符合bmimNsa>bmimBsa>bmimMsa的顺序. 在疏水作用、静电作用以及π-π堆积作用的协同调控下, bmimNsa可以诱导C_{12}mimBr由胶束相变为囊泡相. 随后, 本课题组[119]又研究了反离子为苯甲酸盐的离子液体[bmim][PhCOO]对烷基三苯基膦型表面活性离子液体C_{12}TPB胶束化行为的影响. 由于[PhCOO]阴离子与C_{12}TPB头基之间的静电作用和π-π堆积作用, [bmim][PhCOO]能有效地屏蔽C_{12}TPB头基之间的静电斥力, 使C_{12}TPB分子排列更加紧密, 从而显著提高C_{12}TPB水溶液的表面活性.

5 结束语

离子液体参与的两亲分子自组装已成为近十年来的一大研究热点. 离子液体可以作为溶剂、表面活性剂、添加剂3种不同方式参与到两亲分子的自组装过程中. 不论离子液体起到什么样的角色, 利用离子液体构筑新型两亲分子组装体, 一方面可以将离子液体的优良特性引入传统的两亲分子组装体中, 另一方面也可以进一步拓展离子液体的应用.

此外, 基于离子液体的“可设计性”, 可以通过向离子液体阴阳离子中引入功能基团的方式实现离子液体的功能化. 若将离子液体的“可设计性”与两亲分子组装体有效结合起来, 建立离子液体的结构与其构筑的两亲分子组装体性质之间的关系, 将有望实现两亲分子组装体的可控自组装, 并实现两亲分子组装体的功能化, 这也必将成为离子液体参与的两亲分子自组装的研究热点和发展方向.

参考文献

1 Rogers R D, Seddon K R. Ionic liquids—Solvents of the future? Science, 2003, 302: 792–793

2 Tian P, Kang Y H, Song X M. Green Solvent: Phase Equilibrium and Microstructure of Ionic Liquids (in Chinese). Beijing: Science Press, 2009 [田鹏, 康艳红, 宋溪明. 绿色溶剂: 离子液体的相平衡和微观结构. 北京: 科学出版社, 2009]

3 Sorrenti A, Illa O, Ortuño R. Amphiphiles in aqueous solution: Well beyond a soap bubble. Chem Soc Rev, 2013, 42: 8200–8219

4 Zhao G X, Zhu B Y. Principles of Surfactant Action (in Chinese). Beijing: China Light Industry Press, 2003 [赵国玺, 朱步瑶. 表面活性剂作用原理. 北京: 中国轻工业出版社, 2003]

5 Greaves T L, Drummond C J. Ionic liquids as amphiphile self-assembly media. Chem Soc Rev, 2008, 37: 1709–1726

6 Evans D F, Yamauchi A, Roman R, et al. Micelle formation in ethylammonium nitrate, a low-melting fused salt. J Colloid Interface Sci, 1982, 88: 89–96

7 Evans D F, Yamauchi A, Wei G J, et al. Micelle size in ethylammonium nitrate as determined by classical and quasi-elastic light scattering. J Phys Chem, 1983, 87: 3537–3541

8 Fernandez-Castro B, Mendez-Morales T, Carrete J, et al. Surfactant self-assembly nanostructures in protic ionic liquids. J Phys Chem B, 2011, 115: 8145–8154

9 Araos M U, Warr G G. Structure of nonionic surfactant micelles in the ionic liquid ethylammonium nitrate. Langmuir, 2008, 24: 9354–9360

10 Atkin R, Bobillier S M, Warr G G. Propylammonium nitrate as a solvent for amphiphile self-assembly into micelles, lyotropic liquid crystals, and microemulsions. J Phys Chem B, 2009, 114: 1350–1360

11 Anderson J L, Pino V, Hagberg E C, et al. Surfactant solvation effects and micelle formation in ionic liquids. Chem Commun, 2003, 19: 2444–2445

12 Fletcher A, Pandey S. Surfactant aggregation within room-temperature ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide. Langmuir, 2004, 20: 33–36

13 Patrascu C, Gauffre F, Nallet F, et al. Micelles in ionic liquids: Aggregation behavior of alkyl poly(ethyleneglycol)-ethers in 1-butyl-3-methyl-imidazolium type ionic liquids. ChemPhysChem, 2006, 7: 99–101
14 Misono T, Sakai H, Sakai K, et al. Surface adsorption and aggregate formation of nonionic surfactants in a room temperature ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate (BmimPF$_6$). J Colloid Interface Sci, 2011, 358: 527–533
15 He Y, Li Z, Simone P, et al. Self-assembly of block copolymer micelles in an ionic liquid. J Am Chem Soc, 2006, 128: 2745–2750
16 Wu J, Li N, Zheng L, et al. Aggregation behavior of polyoxyethylene (20) sorbitan monolaurate (Tween 20) in imidazolium based ionic liquids. Langmuir, 2008, 24: 9314–9322
17 Li N, Zhang S, Zheng L, et al. Aggregation behavior of a fluorinated surfactant in 1-butyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl)imide ionic liquid. Langmuir, 2009, 25: 10473–10482
18 Zhang S, Li N, Zheng L, et al. Aggregation behavior of pluronic triblock copolymer in 1-butyl-3-methylimidazolium type ionic liquids. J Phys Chem B, 2008, 112: 10228–10233
19 Gao Y, Li N, Li X, et al. Microstructures of micellar aggregation formed within 1-butyl-2-methylimidazolium type ionic liquids. J Phys Chem B, 2009, 113: 123–130
20 Rao V G, Mandal S, Ghosh S, et al. Aggregation behavior of triton X-100 with a mixture of two room-temperature ionic liquids: Can we identify the mutual penetration of ionic liquids in ionic liquid containing micellar aggregates? J Phys Chem B, 2012, 116: 13868–13877
21 Evans D, Kaler E, Benton W. Liquid crystals in a fused salt: β,γ-Distearoylphosphatidylcholine in *N*-ethylammonium nitrate. J Phys Chem, 1983, 87: 533–535
22 Araos M, Warr G. Self-assembly of nonionic surfactants into lyotropic liquid crystals in ethylammonium nitrate, a room-temperature ionic liquid. J Phys Chem B, 2005, 109: 14275–14277
23 Jiang W, Yu B, Liu W, et al. Carbon nanotubes incorporated within lyotropic hexagonal liquid crystal formed in room-temperature ionic liquids. Langmuir, 2007, 23: 8549–8553
24 Greaves T L, Weerawardena A, Fong C, et al. Formation of amphiphile self-assembly phases in protic ionic liquids. J Phys Chem B, 2007, 111: 4082–4088
25 Lopez-Barron C R, Wagner N J. Structural transitions of ctab micelles in a protic ionic liquid. Langmuir, 2012, 28: 12722–12730
26 Zhang G, Chen X, Zhao Y, et al. Lyotropic liquid-crystalline phases formed by pluronic P123 in ethylammonium nitrate. J Phys Chem B, 2008, 112: 6578–6584
27 Ma F, Chen X, Zhao Y, et al. A nonaqueous lyotropic liquid crystal fabricated by a polyoxyethylene amphiphile in protic ionic liquid. Langmuir, 2010, 26: 7802–7807
28 Wang X, Chen X, Zhao Y, et al. Nonaqueous lyotropic liquid-crystalline phases formed by Gemini surfactants in a protic ionic liquid. Langmuir, 2012, 28: 2476–2484
29 Li Q, Wang X, Yue X, et al. Phase transition of a quaternary ammonium gemini surfactant induced by minor structural changes of protic ionic liquids. Langmuir, 2014, 30: 1522–1530
30 Yue X, Chen X, Li Q. Comparison of aggregation behaviors of a phytosterol ethoxylate surfactant in protic and aprotic ionic liquids. J Phys Chem B, 2012, 116: 9439–9444
31 Wang L, Chen X, Chai Y, et al. Lyotropic liquid crystalline phases formed in an ionic liquid. Chem Commun, 2004, 24: 2840–2841
32 Wang Z, Liu F, Gao Y, et al. Hexagonal liquid crystalline phases formed in ternary systems of Brij 97-water-ionic liquids. Langmuir, 2005, 21: 4931–4937
33 Wang Z, Zhou W, Li G. Ternary cubic phases containing ionic liquid. J Colloid Interface Sci, 2008, 318: 405–410
34 Zhuang W, Chen X, Cai J, et al. Characterization of lamellar phases fabricated from Brij-30/water/1-butyl-3-methylimidazolium salts ternary systems by small-angle X-ray scattering. Colloids Surf A, 2008, 318: 175–183
35 Kimizuka N, Nakashima T. Spontaneous self-assembly of glycolipid bilayer membranes in sugar-philic ionic liquids and formation of ionogels. Langmuir, 2001, 17: 6759–6761
36 Kimizuka N. Self-assembly in mesoscopic dimension and artificial supramolecular membranes. Curr Opin Chem Biol, 2003, 7: 702–709
37 Hao J, Song A, Wang J, et al. Self-assembled structure in room-temperature ionic liquids. Chem Eur J, 2005, 11: 3936–3940
38 Gayet F, Marty J D, Brulet A, et al. Vesicles in ionic liquids. Langmuir, 2011, 27: 9706–9710
39 Lopez-Barron C R, Li D, DeRita L, et al. Spontaneous thermoreversible formation of cationic vesicles in a protic ionic liquid. J Am Chem Soc, 2012, 134: 20728–20732
40 Bowers J, Butts C P, Martin P J, et al. Aggregation behavior of aqueous solutions of ionic liquids. Langmuir, 2004, 20: 2191–2198
41 El Seoud O A, Pires P A R, Abdel-Moghny T, et al. Synthesis and micellar properties of surface-active ionic liquids: 1-Alkyl-3-methylimidazolium chlorides. J Colloid Interface Sci, 2007, 313: 296–304

42 Inoue T, Ebina H, Dong B, et al. Electrical conductivity study on micelle formation of long-chain imidazolium ionic liquids in aqueous solution. J Colloid Interface Sci, 2007, 314: 236–241

43 Jungnickel C, Luczak J, Ranke J, et al. Micelle formation of imidazolium ionic liquids in aqueous solution. Colloids Surf A, 2008, 316: 278–284

44 Blesic M, Marques M H, Plechkova N V, et al. Self-aggregation of ionic liquids: Micelle formation in aqueous solution. Green Chem, 2007, 9: 481–490

45 Singh T, Kumar A. Aggregation behavior of ionic liquids in aqueous solutions: Effect of alkyl chain length, cations, and anions. J Phys Chem B, 2008, 111: 7843–7851

46 Wang J, Wang H, Zhang S, et al. Conductivities, volumes, fluorescence, and aggregation behavior of ionic liquids [C_4mim][BF_4] and [$C_n$mim]Br (n=4, 6, 8, 10, 12) in aqueous solutions. J Phys Chem B, 2007, 111: 6181–6188

47 Vanyúr R, Biczók L, Miskolczy Z. Micelle formation of 1-alkyl-3-methylimidazolium bromide ionic liquids in aqueous solution. Colloids Surf A, 2007, 299: 256–261

48 Goodchild I, Collier L, Millar S L, et al. Structural studies of the phase, aggregation and surface behaviour of 1-alkyl-3-methylimidazolium halide+water mixtures. J Colloid Interface Sci, 2007, 307: 455–468

49 Dong B, Li N, Zheng L, et al. Surface adsorption and micelle formation of surface active ionic liquids in aqueous solution. Langmuir, 2007, 23: 4178–4182

50 Baker G A, Pandey S, Pandey S, et al. A new class of cationic surfactants inspired by *N*-alkyl-*N*-methyl pyrrolidinium ionic liquids. Analyst, 2004, 129: 890–892

51 Tariq M, Podgorsek A, Ferguson J L, et al. Characteristics of aggregation in aqueous solutions of dialkylpyrrolidinium bromides. J Colloid Interface Sci, 2011, 360: 606–616

52 Zhao M, Zheng L. Micelle formation by *N*-alkyl-*N*-methylpyrrolidinium bromide in aqueous solution. Phys Chem Chem Phys, 2011, 13: 1332–1337

53 Sastry N V, Vaghela N M, Macwan P M, et al. Aggregation behavior of pyridinium based ionic liquids in water-surface tension, ^{1}H NMR chemical shifts, SANS and SAXS measurements. J Colloid Interface Sci, 2012, 371: 52–61

54 Blesic M, Lopes A, Melo E, et al. On the self-aggregation and fluorescence quenching aptitude of surfactant ionic liquids. J Phys Chem B, 2008, 112: 8645–8650

55 Ao M, Xu G, Zhu Y, et al. Synthesis and properties of ionic liquid-type gemini imidazolium surfactants. J Colloid Interface Sci, 2008, 326: 490–495

56 Zhang S, Yan H, Zhao M, et al. Aggregation behavior of gemini pyrrolidine-based ionic liquids 1,1′-(butane-1,4-diyl)bis(1-alkylpyrrolidinium) bromide ([$C_n$py-4-$C_n$py][Br_2]) in aqueous solution. J Colloid Interface Sci, 2012, 372: 52–57

57 Gu Y, Shi L, Gao H, et al. Phase behavior of didecylpyrrolidium bromide in aqueous solution. Colloids Surf A, 2013, 420: 82–88

58 Wang G, Li P, Du Z, et al. Surface activity and aggregation behavior of siloxane-based ionic liquids in aqueous solution. Langmuir, 2015, 31: 8235–8242

59 Brown P, Butts C, Dyer R, et al. Anionic surfactants and surfactant ionic liquids with quaternary ammonium counterions. Langmuir, 2011, 27: 4563–4571

60 Brown P, Butts C P, Eastoe J, et al. Anionic surfactant ionic liquids with 1-butyl-3-methyl-imidazolium cations: Characterization and application. Langmuir, 2012, 28: 2502–2509

61 Jiao J, Dong B, Zhang H, et al. Aggregation behaviors of dodecyl sulfate-based anionic surface active ionic liquids in water. J Phys Chem B, 2012, 116: 958–965

62 Jiao J, Han B, Lin M, et al. Salt-free catanionic surface active ionic liquids 1-alkyl-3-methylimidazolium alkylsulfate: Aggregation behavior in aqueous solution. J Colloid Interface Sci, 2013, 412: 24–30

63 Cheng N, Ma X, Sheng X, et al. Aggregation behavior of anionic surface active ionic liquids with double hydrocarbon chains in aqueous solution: Experimental and theoretical investigations. Colloids Surf A, 2014, 453: 53–61

64 Yin T, Wu J, Wang S, et al. Structural rearrangement in the aqueous solution of surface active ionic liquid 1-butyl-3-methylimidazolium bis(2-ethylhexyl) sulfosuccinate. Soft Matter, 2015, 11: 4717–4722

65 Pereiro A B, Araujo J M, Teixeira F S, et al. Aggregation behavior and total miscibility of fluorinated ionic liquids in water. Langmuir, 2015, 31: 1283–1295

66 Liu X, Dong L, Fang Y. A novel zwitterionic imidazolium-based ionic liquid surfactant: 1-Carboxymethyl-3-dodecylimidazolium inner salt. J Surfactants Deterg, 2011, 14: 497–504

67 Wang X, Yu L, Jiao J, et al. Aggregation behavior of COOH-functionalized imidazolium-based surface active ionic liquids in aqueous solution. J Mol Liq, 2012, 173: 103–107

68 Shi L, Li N, Yan H, et al. Aggregation behavior of long-chain *N*-aryl imidazolium bromide in aqueous solution. Langmuir, 2011, 27: 1618–1625

69 Shi L, Wei Y, Sun N, et al. First observation of rich lamellar structures formed by a single-tailed amphiphilic ionic liquid in aqueous solutions. Chem Commun, 2013, 49: 11388–11390

70 Yang J, Wang H, Wang J, et al. Light-modulated aggregation behavior of some unsubstituted cinnamate-based ionic liquids in aqueous solutions. RSC Adv, 2015, 5: 96305–96312

71 Burns C T, Lee S, Seifert S, et al. Thiophene-based ionic liquids: Synthesis, physical properties, self-assembly, and oxidative polymerization. Polym Adv Technol, 2008, 19: 1369–1382

72 Chamiot B, Rizzi C, Gaillon L, et al. Redox-switched amphiphilic ionic liquid behavior in aqueous solution. Langmuir, 2009, 25: 1311–1315

73 Dong B, Gao Y, Su Y, et al. Self-aggregation behavior of fluorescent carbazole-tailed imidazolium ionic liquids in aqueous solutions. J Phys Chem B, 2010, 114: 340–348

74 Fan X, Zhao K. Aggregation behavior and electrical properties of amphiphilic pyrrole-tailed ionic liquids in water, from the viewpoint of dielectric relaxation spectroscopy. Soft Matter, 2014, 10: 3259–3270

75 Li X, Gao Y, Liu J, et al. Aggregation behavior of a chiral long-chain ionic liquid in aqueous solution. J Colloid Interface Sci, 2010, 343: 94–101

76 Gao H, Shi L, Zhang S, et al. Aggregation behavior of imidazolium-based chiral surfactant in aqueous solution. Colloid Polym Sci, 2012, 291: 1077–1084

77 Bleasdale T, Tiddy G, Wyn-Jones E. Cubic phase formation in polar nonaqueous solvents. J Phys Chem, 1991, 95: 5385–5386

78 Firestone M A, Dzielawa J A, Zapol P, et al. Lyotropic liquid-crystalline gel formation in a room-temperature ionic liquid. Langmuir, 2002, 18: 7258–7260

79 Firestone M A, Rickert P G, Seifert S, et al. Anion effects on ionogel formation in N, N'-dialkylimidazolium-based ionic liquids. Inorg Chim Acta, 2004, 357: 3991–3998

80 Inoue T, Dong B, Zheng L. Phase behavior of binary mixture of 1-dodecyl-3-methylimidazolium bromide and water revealed by differential scanning calorimetry and polarized optical microscopy. J Colloid Interface Sci, 2007, 307: 578–581

81 Zhang S, Yuan J, Ma H, et al. Aqueous phase behavior of ionic liquid-related gemini surfactant revealed by differential scanning calorimetry and polarized optical microscopy. Colloid Polym Sci, 2010, 289: 213–218

82 Xu W, Wang T, Cheng N, et al. Experimental and DFT studies on the aggregation behavior of imidazolium-based surface-active ionic liquids with aromatic counterions in aqueous solution. Langmuir, 2015, 31: 1272–1282

83 Bi Y, Wei H, Hu Q, et al. Wormlike micelles with photoresponsive viscoelastic behavior formed by surface active ionic liquid/azobenzene derivative mixed solution. Langmuir, 2015, 31: 3789–3798

84 Zhang G, Chen X, Xie Y, et al. Lyotropic liquid crystalline phases in a ternary system of 1-hexadecyl-3-methylimidazolium chloride/1-decanol/water. J Colloid Interface Sci, 2007, 315: 601–606

85 Zhang G, Chen X, Zhao Y, et al. Effects of alcohols and counterions on the phase behavior of 1-octyl-3-methylimidazolium chloride aqueous solution. J Phys Chem B, 2007, 111: 11708–11713

86 Zhang J, Dong B, Zheng L, et al. Lyotropic liquid crystalline phases formed in ternary mixtures of 1-cetyl-3-methylimidazolium bromide/p-xylene/water: A SAXS, POM, and rheology study. J Colloid Interface Sci, 2008, 321: 159–165

87 Li X, Zhang J, Dong B, et al. Characterization of lyotropic liquid crystals formed in the mixtures of 1-alkyl-3-methylimidazolium bromide/*p*-xylene/water. Colloids Surf A, 2009, 335: 80–87

88 Shi L, Zhao M, Zheng L. Lyotropic liquid crystalline phases formed in ternary mixtures of *N*-alkyl-*N*-methylpyrrolidinium bromide/1-decanol/water. RSC Adv, 2012, 2: 11922–11929

89 Thomaier S, Kunz W. Aggregates in mixtures of ionic liquids. J Mol Liq, 2007, 130: 104–107

90 Li N, Zhang S, Zheng L, et al. Aggregation behavior of long-chain ionic liquids in an ionic liquid. Phys Chem Chem Phys, 2008, 10: 4375–4377

91 Wu J, Zhang J, Zheng L, et al. Characterization of lyotropic liquid crystalline phases formed in imidazolium based ionic liquids. Colloids Surf A, 2009, 336: 18–22

92 Shi L, Li N, Zheng L. Aggregation behavior of long-chain *N*-aryl imidazolium bromide in a room temperature ionic liquid. J Phys Chem C, 2011, 115: 18295–18301

93 Shi L, Zheng L. Aggregation behavior of surface active imidazolium ionic liquids in ethylammonium nitrate: Effect of alkyl chain length, cations, and counterions. J Phys Chem B, 2012, 116: 2162–2172

94 Shi L, Zhao M, Zheng L. Micelle formation by *N*-alkyl-*N*-methylpyrrolidinium bromide in ethylammonium nitrate. Colloids Surf A, 2011, 392: 305–312

95 Lu F, Shi L, Gu Y, et al. Aggregation behavior of alkyl triphenyl phosphonium bromides in aprotic and protic ionic liquids. Colloid Polym Sci, 2013, 291: 2375–2384

96 Zhao Y, Chen X, Wang X. Liquid crystalline phases self-organized from a surfactant-like ionic liquid C_{16}mimCl in ethylammonium nitrate. J Phys Chem B, 2009, 113: 2024–2030

97 Zhao M, Gao Y, Zheng L. Liquid crystalline phases of the amphiphilic ionic liquid *N*-hexadecyl-*N*-methylpyrrolidinium bromide formed in the ionic liquid ethylammonium nitrate and in water. J Phys Chem B, 2010, 114: 11382–11389

98 Zhao M, Gao Y, Zheng L. Lyotropic liquid crystalline phases formed in binary mixture of 1-tetradecyl-3-methylimidazolium chloride/ethylammonium nitrate and its application in the dispersion of multi-walled carbon nanotubes. Colloids Surf A, 2010, 369: 95–100

99 Cheng N, Hu Q, Bi Y, et al. Gels and lyotropic liquid crystals: Using an imidazolium-based catanionic surfactant in binary solvents. Langmuir, 2014, 30: 9076–9084

100 Xu W, Yin Q, Gao Y, et al. Solvent and substituent effects on the aggregation behavior of surface-active ionic liquids with aromatic counterions and the dispersion of carbon nanotubes in their hexagonal liquid crystalline phase. Langmuir, 2015, 31: 12644–12652

101 Beyaz A, Oh W S, Reddy V P. Ionic liquids as modulators of the critical micelle concentration of sodium dodecyl sulfate. Colloids Surf B, 2004, 35: 119–124

102 Behera K, Pandey S. Concentration-dependent dual behavior of hydrophilic ionic liquid in changing properties of aqueous sodium dodecyl sulfate. J Phys Chem B, 2007, 111: 13307–13315

103 Behera K, Pandey S. Modulating properties of aqueous sodium dodecyl sulfate by adding hydrophobic ionic liquid. J Colloid Interface Sci, 2007, 316: 803–814

104 Behera K, Pandey S. Ionic liquid induced changes in the properties of aqueous zwitterionic surfactant solution. Langmuir, 2008, 24: 6462–6469

105 Rai R, Baker G A, Behera K, et al. Ionic liquid-induced unprecedented size enhancement of aggregates within aqueous sodium dodecylbenzene sulfonate. Langmuir, 2010, 26: 17821–17826

106 Rao V G, Ghatak C, Ghosh S, et al. The chameleon-like nature of zwitterionic micelles: The effect of ionic liquid addition on the properties of aqueous sulfobetaine micelles. Chem Phys Chem, 2012, 13: 1893–1901

107 Rao V G, Ghatak C, Ghosh S, et al. Ionic liquid-induced changes in properties of aqueous cetyltrimethylammonium bromide: A comparative study of two protic ionic liquids with different anions. J Phys Chem B, 2011, 115: 3828–3837

108 Pal A, Pillania A. Effect of trisubstituted imidazolium based ionic liquid 1-butyl-2,3-dimethylimidazolium chloride on the aggregation behaviour of sodium dodecylsulphate in aqueous media. Colloids Surf A, 2014, 452: 18–24

109 Pal A, Pillania A. The effect of hydrophilic ionic liquid 1-butyl-2,3-dimethylimidazolium bromide on the aggregation behavior of tetradecyltrimethylammonium bromide in aqueous media. J Mol Liq, 2015, 209: 6–13

110 Shi L, Jing X, Gao H, et al. Ionic liquid-induced changes in the properties of aqueous sodium dodecyl sulfate solution: Effect of acidic/basic functional groups. Colloid Polym Sci, 2013, 291: 1601–1612

111 Lu X, Cao Q, Yu J, et al. Formation of novel aqueous two-phase systems with piperazinium-based ionic liquids and anionic surfactants: Phase behavior and microstructure. J Phys Chem B, 2015, 119: 11798–11806

112 Chabba S, Kumar S, Aswal V K, et al. Interfacial and aggregation behavior of aqueous mixtures of imidazolium based surface active ionic liquids and anionic surfactant sodium dodecylbenzenesulfonate. Colloids Surf A, 2015, 472: 9–20

113 Behera K, Dahiya P, Pandey S. Effect of added ionic liquid on aqueous Triton X-100 micelles. J Colloid Interface Sci, 2007, 307: 235–245

114 Behera K, Pandey M D, Porel M, et al. Unique role of hydrophilic ionic liquid in modifying properties of aqueous Triton X-100. J Chem Phys, 2007, 127: 184501

115 Zheng L, Guo C, Wang J, et al. Effect of ionic liquids on the aggregation behavior of PEO-PPO-PEO block copolymers in aqueous solution. J Phys Chem B, 2007, 111: 1327–1333

116 Guo P, Guo R. Ionic liquid induced transition from wormlike to rod or spherical micelles in mixed nonionic surfactant systems. J Chem Eng Data, 2010, 55: 3590–3597

117 Liu J, Zhao M, Zhang Q, et al. Interaction between two homologues of cationic surface active ionic liquids and the PEO-PPO-PEO triblock copolymers in aqueous solutions. Colloid Polym Sci, 2011, 289: 1711–1718

118 Gu Y, Shi L, Cheng X, et al. Aggregation behavior of 1-dodecyl-3-methylimidazolium bromide in aqueous solution: Effect of ionic liquids with aromatic anions. Langmuir, 2013, 29: 6213–6220

119 Lu F, Shi L, Yan H, et al. Aggregation behavior of dodecyltriphenylphosphonium bromide in aqueous solution: Effect of aromatic ionic liquids. Colloids Surf A, 2014, 457: 203–211

Summary for “基于离子液体的两亲分子自组装”

Amphiphile self-assembly based on ionic liquids

LU Fei & ZHENG LiQiang*

Key Laboratory of Colloid and Interface Chemistry, Shandong University, Ministry of Education, Jinan 250100, China
* Corresponding author, E-mail: lqzheng@sdu.edu.cn

Ionic liquids (ILs), as a class of compounds composed of ions with melting points at or near room temperature, have unusual physicochemical properties including low volatility, high temperature stability, high ionic conductivity and easy recyclability. Thus ILs have been applied widely in the range of organic synthesis, catalysis, chromatography, analytical chemistry, biochemistry and so on. Perhaps the most unique capability of ILs is to support the self-assembly of amphiphiles. Due to the extraordinary properties of ILs, the self-assembled aggregates based on ILs have attracted a lot of attentions during the last decades. ILs are now not only considered as important alternative solvents, but also as materials with unique and tuneable properties which can be easily adjusted by suitable selection of cations and anions for a specific function. Based on the unique designability of ILs, it will be expected to achieve the controllability of the nanostructures and properties of IL-based self-assembled aggregates by tailoring the structures of ILs.

Here, the research progress of amphiphile self-assembly based on ILs was reviewed. Firstly, the room-temperature ILs can be considered as solvents to participate in the self-assembly process and classified as protic ionic liquids (PILs) and aprotic ionic liquids (AILs), respectively. Up to now, a number of AILs based on imidazolium cations and many alkylammonium PILs, such as ethylammonium nitrate (EAN), have been used as self-assembly media to support amphiphile to form various aggregates including micelles, vesicles, microemulsions and liquid crystals. Different from AILs, the PILs can build up hydrogen-bonding networks which are similar to water molecules due to their protic nature and general properties. The different solvent properties of PILs and AILs have significant influence on the aggregation behavior of amphiphilic molecules. Secondly, the long chain analogues of common ionic liquids, named as surfactive ionic liquids (SAILs), could possess inherent surface active properties and self-assemble to form different aggregates with specific structures, shapes and properties in aqueous solutions like traditional amphiphilic molecules. Various long-chain SILs with different cationic headgroups based on imidazolium, pyrrolidinium, piperidinium etc. have been synthesized and investigated. Except for cationic SAILs, the aggregation behaviors of a series of anionic SAILs based on organic surfactant anions and imidazolium cations have also been studied to expand the application of SAILs in the filed of colloid and interface chemistry. SILs, as a novel kind of surfactants, can self-assembly into different kinds of aggregates driven by intermolecular interactions including hydrophobic interaction, electrostatic interaction, hydrogen bonding and so on. Thus, the type of cations, the alkyl chain length, and the nature of the counterions have key effect on the aggregation behavior of SAILs. Thirdly, the physicochemical properties of the given surfactant solutions can also be modified by the addition of external ionic liquids. Due to the tailoring properties of ILs, “task-specific” ILs (TSILs) have emerged by introducing functional groups as a part of substituent to impart a particular capability to ILs and further modulate the aggregation behavior of surfactant solutions. This is also a practical way for us to determine the role of one specific intermolecular interaction on the self-assembly process.

The present work summarized the amphiphile self-assembly based on ILs, including room-temperature ILs as solvents, long-chain ILs as amphiphiles and ILs as external additives. Our aim is to establish the dependence of aggregation behavior of amphiphiles on the unique structures of ILs. This review is helpful to achieve the controllability and functionalization of traditional self-assembled aggregates by the incorporation of functional ILs.

ionic liquids, amphiphiles, aggregation behavior, microstructure

doi: 10.1360/N972016-00418