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利用微型可视毛细管反应器测定物质在高温高压水中溶解度

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摘要 目前无机盐和疏水性有机物在超/亚临界水中溶解度的研究虽已取得一定成果, 但由于实验条件苛刻、设备要求高、操作难度大等问题, 溶解度数据仍十分缺乏, 无法满足现代工业应用要求, 大大影响了超/亚临界流体技术在化学合成、萃取分离、环境工程等诸多领域的研究与开发进程, 进一步确定高温高压水中物质的溶解度及其影响因素尚需要开展大量的基础研究工作. 本文综述了无机盐和疏水性有机物在超/亚临界水中溶解度研究进展, 并着重介绍了本课题组利用自行设计研发的耐高温高压微型可视毛细管反应器替代传统不锈钢材质高压反应釜或管式流反应器, 结合显微放大观测技术、高精密冷热台、数字实时录像分析系统和拉曼光谱原位在线检测技术开展无机盐和疏水性有机物在超/亚临界水中溶解度研究工作取得的进展.

关键词
毛细管反应器
超/亚临界流体
溶解度
拉曼光谱

超/亚临界流体技术自20世纪70年代开始崭露头角, 随后便以环保、绿色、高效等优点, 被迅速应用到萃取分离、石油化工、化学反应工程、材料科学、生物技术、环境工程等诸多领域[1~3]. 常用的超/亚临界流体主要有H_2O, CO_2, CH_4等, 其中水是自然界中存在最广泛的溶剂. 研究表明, 通过控制温度和压力可以改变超/亚临界水的极性、密度、扩散系数、表面张力和黏度等性质. 处于高温高压状态的水具有介电常数小、扩散系数高、黏度低、密度低、能完全溶解有机物等特性[4,5]. 优良的溶解特性和反应特性, 使超/亚临界水成为绿色化学领域关注研究的重点之一.

常温常压状态下, 疏水性有机物一般被认为不溶或者微溶于水, 其溶解度数据一直不为人们所重视. 但是在高温高压条件下, 随着介电常数的减小, 超/亚临界水对疏水性有机物的溶解能力显著增强, 甚至可以达到完全互溶的状态. 相比而言, 无机盐在超/亚临界水中的溶解度却非常低, 使得超/亚临界流体技术在实际应用过程中往往会遇到盐沉积引起的反应器内部管路堵塞等问题. 同时, 在高温高压及富氧条件下, 盐类对反应器的腐蚀也较为严重[6]. 因此, 掌握物质在超/亚临界水中的溶解度数据, 构建准确的溶解模型, 对超/亚临界水中化学反应动力学研究, 对超/亚临界流体技术在化学合成、萃取分离、环境工程等领域的应用, 以及高温高压反应器的设计、运行和优化均十分重要[7].

1 无机盐和疏水性有机物在超/亚临界水中溶解度研究进展

超/亚临界水中溶解度的测定从根本上说是高温高压状态下相平衡的研究. 根据相平衡的确定方法, 可以将无机盐和疏水性有机物在超/亚临界水中溶解

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度的测定方法分为2类：静态法和动态法(表S1).

1.1 静态法

静态法是将待测溶质和溶剂放置于固定体积的高压反应釜内，待足够长时间使体系达到平衡. 静态法又可分为静态分析法和静态合成法[8].

静态分析法是将待测溶质和溶剂一起放置在密闭的高压釜中，待体系达到平衡后从高压釜中取样，并在常温常压下利用气相色谱、高效液相色谱等分析技术对取样进行分析，以获得相关溶解度数据. 有学者使用上述实验方法和装置流程分别测定了苯、甲苯[9]、乙醇+水+丙烯、异丙醇+水+丙烯三元体系[10]、苯甲酸和水杨酸[11]、萘普生[12]、灰黄霉素[13]、布地奈德[14]、蒽[15]、硬脂酸、软脂酸[16]、羟苯甲酯、羟苯乙酯、羟苯丁酯[17]等在超/亚临界水中的溶解度.

静态合成法是将预先配置好的已知浓度的物料放入高压釜中，逐渐改变体系的温度或压力，观察高压釜中样品的相态变化，当观察到某一相开始出现或消失，此时的温度、压力及已知的物料浓度即构成一个相边界点，以获得平衡条件下的溶解度数据. 有学者使用上述实验方法和装置流程分别测定了K_2CO_3[18], Na_2SO_4[19], K_2SO_4[20], Li_2SO_4[21], $Ge(OH)_4$和GeO_2[22]，苯、正庚烷、正戊烷、2-甲基戊烷、甲苯[23]，苯酚[24]等在超/亚临界水中的溶解度.

1.2 动态法

动态法是以一定的流速将一定浓度的高温高压溶液连续缓慢地通过高压釜，使水相和固相无机盐/油相疏水性有机物间在高压釜中建立平衡，然后对流出的溶液组分浓度进行分析. 动态法又可分为多相法和单相法.

动态多相法是将预先混合好的溶液连续缓慢地通过高压釜，溶液在高压釜中停留足够长时间以达到相平衡，从取样口收集流出液进行组分分析. 研究人员使用上述实验方法和装置流程分别测定了Na_2SO_4[25~27], Na_2CO_3[27], NaCl[28,29], KCl[28], $MgCl_2$, $CaCl_2$[30], Na_2HPO_4, NaH_2PO_4, $MgSO_4$[31]，甲苯，葵烷[32]，芘，蒽，苊[33]，对苯二甲酸[34]等在超/亚临界水中的溶解度.

动态单相法是将固相无机盐/油相疏水性有机物置于高压釜中，使溶剂相连续缓慢地通过高压釜，与高压釜中溶质溶解饱和后流出，从取样口收集流出液进行组分分析. 研究人员使用上述实验方法和装置流程分别测定了萘[35,36]、苯并[a]芘[35]、苯、甲苯、间二甲苯、对异丙基甲苯、辛烷、三甲基戊烷、四氯乙烯、邻二氯苯、四乙基锡[37]、蒽、苯并[a]蒽、苯并菲、三联苯[36]、喹吖啶酮[38]、木糖、葡萄糖、麦芽糖[39]、无水槲皮素、二水槲皮素[40]、没食子酸、儿茶酸、原儿茶酸[41]等在超/亚临界水中的溶解度.

无机盐和疏水性有机物在超/亚临界水中溶解度的研究虽已取得一定成果，但由于高温高压实验条件苛刻、操作难度大、设备要求高，超/亚临界水中溶解度数据仍十分缺乏，无法满足现代工业应用要求. 并且目前用于无机盐和疏水性有机物在超/亚临界水中溶解度测定的方法均存在一定的不足，传统用于超/亚临界水中溶解度测定的静态分析法取样过程容易破坏相平衡，静态合成法精确确定高压釜中样品的相变化点存在难度，动态法则难以保证取样分析时体系已达到相平衡. 总体来说，进一步确定高温高压水中物质的溶解度及其影响因素尚需要开展大量的基础研究工作，并且仍缺乏一套安全环保、操作便捷，能精确测定高温高压流体溶解度的方法和装置.

2 微型可视毛细管反应器测定高温高压流体溶解度

本课题组利用自行设计研发的耐高温高压微型可视石英毛细管反应器(图1)替代传统不锈钢材质高压反应釜或管式流反应器，结合显微放大观测技术、高精密冷热台、数字实时录像分析系统和拉曼光谱原位在线检测技术开展无机盐和疏水性有机物在超/亚临界水中溶解度研究(图2). 此前，本课题组率先利用此类耐高温高压的微型可视石英毛细管反应器开展了超/亚临界水氧化氯苯[42]、愈创木酚[43]、超/亚临界水中四氯化碳[44]、三氯乙烷[45]水解，超/亚临界水及共溶剂中聚合物(聚碳酸酯[46~49]、聚对苯

图 1 装有石英玻璃丝、水、疏水性有机物的密封毛细管反应器[61] (外径 665 μm，内径 300 μm，长度~1.5 cm)

Figure 1 An image of a sample in a fused silica capillary reactor (FSCR), showing hydrophobic organic compounds, water, vapour, and silica rod in the FSCR[61] (0.3 mm I.D., 0.665 mm O.D., and ~1.5 cm long)

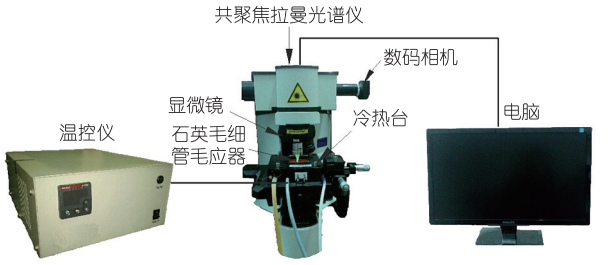

图 2 冷热台-显微放大观测装置图. 包括石英毛细管反应器、冷热台、数码相机、温控仪、显微镜、电脑和共聚焦拉曼光谱仪

Figure 2 Schematic diagram of the experimental apparatus including FSCR, heating-cooling stage, digital camera, temperature controller, microscope, computer, and confocal Raman spectrometer

二甲酸丁二醇酯[50,51]、聚对苯二甲酸乙二醇酯[52,53]、聚对苯二甲酸丙二醇酯[54]、聚酰亚胺[55,56]、聚对萘二甲酸乙二醇酯等)解聚, 亚临界水中聚合物单体(双酚A[57]、对苯二甲酸等)的热稳定性, 煤与塑料共液化[58,59]、煤与聚苯乙烯共液化[60]等研究, 均取得了较为理想的结果.

将制备好的石英毛细管反应器放置于冷热台样品槽中, 通过调节与冷热台相连的温度控制器精确控制体系温度, 并将冷热台置于显微镜下. 利用显微放大观测技术实时观测及记录无机盐和疏水性有机物在亚临界水中的相态变化, 精确捕捉亚临界水体系中无机盐和疏水性有机物随温度升高过程中的晶体析出点和油-水界面消失点, 以及温度降低过程中的晶体消失点和油-水界面重新出现点, 同时结合拉曼光谱原位在线检测溶液体系的混合均匀度, 确保溶液体系已达到相平衡, 通过相界面的变化及拉曼谱带的积分强度测定无机盐和疏水性有机物在超/亚临界水中的溶解度[61~63].

为充分验证实验装置的可行性, 课题组对目前亚临界水中溶解度研究较多的苯溶解度数据进行了测定. Chandler等人[9], Connolly[23], Miller和Hawthorne[35]分别测定了苯在150~275℃, 260~300℃和25~200℃水中的溶解度. 本课题组[62]实验测定了206.7~ 274.8℃苯的溶解度, 实验数据具有良好的重现性, 并且与文献报道值具有较好的吻合性(图3).

在此基础上, 本课题组[61]首次采用显微原位在线放大观测-石英毛细管反应器(FSCR)实验测定装置, 通过氯苯-水体系相界面随温度的变化, 测定了氯苯在亚临界水中的溶解度(图4), 并对实验数据进行了拟合分析, 得到173.3~266.9℃温度范围内氯苯

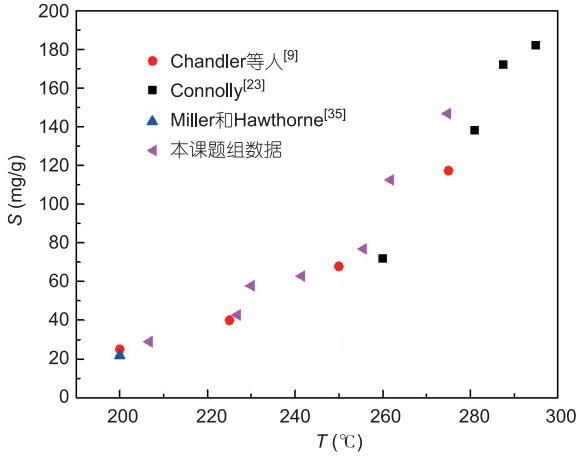

图 3 苯在水中的溶解度数据与文献值的比较[62]

Figure 3 The solubility of benzene from different sources[62]

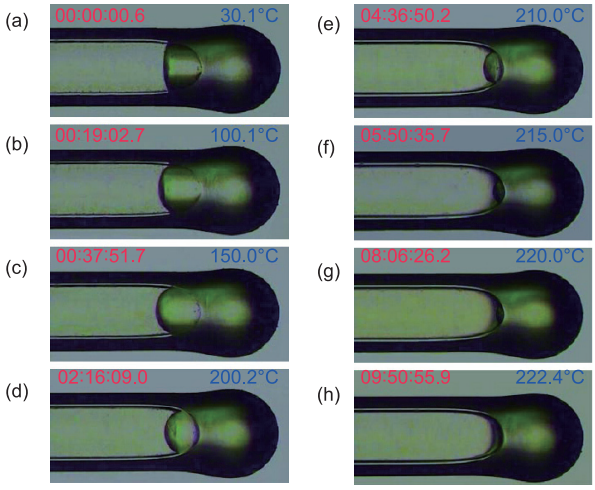

图 4 氯苯在亚临界水中的溶解过程图[61]. 氯苯位于石英毛细管最右端, (a) 从室温 30.1℃开始加热; (b), (c) 氯苯先受热膨胀; (d)~(g) 逐渐溶解; (h) 至 222.4℃氯苯完全溶解

Figure 4 Dissolution of chlorobenzene in water during heating[61]. The C_6H_5Cl is shown at the right end of the FSCR. (a) The images of C_6H_5Cl and H_2O in the capillary under the microscope at 30.1℃. The C_6H_5Cl swelled between 100.0 and 150.0℃ (b), (c), dissolved between 200.2 and 220.0℃ (d)–(g) and dissolved totally at 222.4℃ (h)

在亚临界水中的溶解度数据, 弥补了该温度区间氯苯溶解度数据的空缺.

此后, 本课题组[62]利用此类反应器对2,4-二氯甲苯在亚临界水中的溶解度进行了研究, 初步探讨了疏水性有机物在亚临界水体系中的溶解规律, 并利用石英毛细管显微装置结合拉曼光谱仪对苯-水体系和2,4-二氯甲苯-水体系升温过程及溶解平衡体系的均匀度进行了检验(图5).

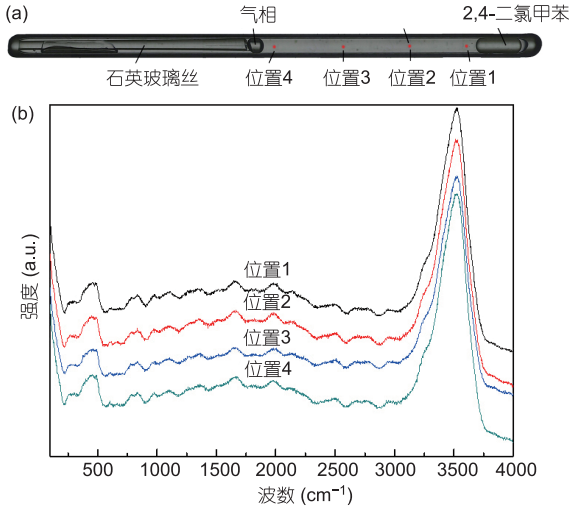

图 5 装有 2,4-二氯甲苯的石英毛细管反应器(a)及其拉曼光谱图(b)[62]. (a) 2,4-二氯甲苯、均匀液相、气相、玻璃丝、拉曼光谱采集位置的样品图, 其中位置 1~4 为拉曼光谱的分析点位; (b) 220.0℃, 20 h体系达到相平衡时在均匀液相采集的拉曼光谱图

Figure 5 Image of 2,4-dichlorotoluene in FSCR (a) and its Raman spectra (b)[62]. (a) Showing 2,4-dichlorotoluene, liquid phase, vapor phase, and silica rod, and four spots for Raman analyses. (b) Raman spectra of liquid phase in the FSCR at 220.0℃, 20 h

此外, 本课题组[63]还利用此类反应器开展了邻氯甲苯、对氯甲苯、2,4-二氯氟苯等疏水性有机物在亚临界水中溶解度、以及氯化钠、氯化钾、硫酸钙、硫酸镁、硫酸铜等无机盐在超/亚临界水中的溶解度和结晶介稳态研究.

3 总结

利用耐高温高压微型可视石英毛细管反应器开展无机盐和疏水性有机物溶解度研究, 该方法将样品容器体积缩小至微升级, 具有低耗、直观、安全等优良性能, 而且不需取样分析, 直接可以进行观测记录, 并可结合拉曼光谱进行原位在线检测分析, 为无机盐和疏水性有机物在高温高压水中溶解性能的研究提供了一种新的方法.

目前, 本课题组正逐步将该类反应器的应用领域由固-液、液-液体系扩展到气(超临界流体)-液体系的溶解度研究, 相继开展了CO_2在乙醇中溶解度及CO_2盐水层中溶解度研究.

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Solubilities of inorganic salts and organic compounds in sub- and supercritical water in fused silica capillary reactor

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Some meaningful achievements have been made on the solubilities of inorganic salts and organic compounds in sub- and supercritical water. But the solubility data remain too scarce to meet the need of modern industry due to the harsh of experimental conditions, equipment requirements and experimental operations, which greatly affects the research and development processes of sub- and supercritical fluid technology in chemical synthesis, extraction and separation, environmental engineering and many other fields. Basic researches still need to be carried out to determine the solubility data and its influence factors of substances in sub- and supercritical water. This paper reviews the research advances of inorganic salts and organic compounds solubility in sub- and supercritical water. The developments of the solubilities of inorganic salts and organic compounds in sub- and supercritical water in fused silica capillary reactor, instead of the traditional stainless steel autoclave or tubular flow reactor, combined with microscopic observation, heating-cooling stage, real-time digital video and *in-situ* Raman designed by author's group are highlighted in this paper.

fused silica capillary reactor, sub- and supercritical water, solubility, Raman spectroscopy

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补充材料

表 S1 无机盐和疏水性有机物在超/亚临界水中溶解度测定方法汇总

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