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Ionic Liquids as Greener Substitutes for Industrial Scale Inhibition Application-A Perspective

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Abstract

Setting and growth of inorganic scales are major problem in cooling water systems and petroleum-based industries that unfavorably affect the plant transport efficiency, fluid flow rate and lifespan of the metallic equipments. Calcium carbonate, calcium sulfate, calcium phosphate, bicarbonates of sodium, magnesium and calcium with their sulfate, chlorides and nitrates causes inorganic scale problem in cooling water systems. On the other hands, scaling problem in petroleum industries is due to calcium carbonate, barium sulfate, strontium sulfate and iron sulfide etc. Maleic acid-based polymers and organic phosphonates are used as most effective inorganic scale inhibitors in cooling water systems (CWSs; such as boiler industries) and petroleum industries. However, these inorganic scale inhibitors are highly toxic in nature thereby environmentally friendly alternative scale inhibitors are being developed and used. One of such green alternatives is Carboxymethyl Inulin (CMI). Ionic liquids can also be used as environmentally friendly alternative inorganic scale inhibitors. Use of the ionic liquids as inorganic scale inhibitors would be advantageous as due to increasing demands of green scale inhibitors. Present perspective describes the idea about using ionic liquids as green inorganic scale inhibitors in cooling water system and petroleum industries.

INTRODUCTION

Scales are solid deposits that nurture over time and block and hinder the flow of fluids from transport pipelines, pumps and valves etc. formation and growth of scales adversely affect the plant efficiency, production rate and equipment lifespan especially in the cooling water systems and petroleum industries [1,2]. Scaling (formation and growth of scales) offers a foremost confront to the scientists and engineers to insure the optimal fluid flow rate. In the Cooling Water Systems (CWSs), continuous evaporation of pure water results into the increase in the concentration of minerals. If the minerals left unchecked, they get precipitated as scale as their solubility exceeded in such conditions. Scaling is greatly affected by temperature and pH [1,2]. Generally, in CWSs scaling is attributed due to presence of inorganic salts such as calcium carbonate, calcium sulfate, calcium phosphate, bicarbonates of sodium, magnesium and calcium with their sulfate, chlorides and nitrates that are present as impurities in the cooling water and their concentration exceed over time [1,2]. Whereas, scale in petroleum industries is attributed due to numerous salts impurities such as calcium carbonate, barium sulfate, strontium sulfate and iron sulfide etc. and dissolved organic acids (in petroleum fluids) [1,2]. Depending upon their composition scales may be of organic, inorganic or mixed-type. Inorganic and organic scales result major problems in cooling water system and petroleum industries, respectively. It is important to mention that mixed-scales are relatively difficult to treat as compared to the pure inorganic and pure organic scales. Generally, treatment of mixed-scales requires highly severe and expensive remediation treatments using aggressive acidic solutions [1,2]. In petroleum industries presence and accumulation of paraffin was, gas hydrates and asphaltenes cause the development of organic scale [3]. Formation of the calcium carbonate based scale can occurs by the reaction of water with dissolved CO_2 as presented below [3]:

$$CO_{2(dis)} + H_2O_{(liq)} \leftrightarrow H_2CO_{3(dis)} \quad (1)$$

$$H_2CO_{3(dis)} \leftrightarrow H^+_{(dis)} + HCO^-_{3(dis)} \quad (2)$$

$$2HCO^-_{3(dis)} \leftrightarrow CO^{2-}_{3(dis)} + H_2O_{(liq)} + CO_{2(g)} \quad (3)$$

$$Ca^{2+}_{(dis)} + CO^{2-}_{3(dis)} \leftrightarrow CaCO_{3(dep)} \quad (4)$$

Unlike to most of the inorganic salts such as KCl and KI, solubility of the $CaCO_3$ decreases with rise in the temperature.

The problem of scaling can be over coming through mechanical removal, chemical (solution) dissolution and using chemical scale inhibitors. The mechanical removal and solution dissolution are short term practices and valuable merely for mild-scaling situation. Whereas, implementation of Scale Inhibitors (SIs) is one of the most effective, ease and economic methods of scale treatment. SIs inhibitors are the chemical substances that retard or slow down the formation and deposition of scale. In Cooling Water Systems (CWSs), most frequently used sale inhibitors are maleic acid derived polymers and phosphonates.

Table 1 represents the common examples of SIs used in CWSs, petroleum industries and $CaCO_3$ scale inhibitors [4].

Most of the effective scale inhibitors are those that contain Phosphonate, sulphate and carboxylate ions [4]. A combination of two or more such groups in the molecular structure of SIs is enough for effective scale inhibition. The extensive consumption of maleic acid derived polymers and organic phosphonates is attributed due to their high solubility in polar electrolytes, high scale inhibiting ability and excellent thermal and chemical stabilities [4].

AGE OF GREENER SUBSTITUTES: USE OF IONIC LIQUIDS

Although, maleic acid derived polymers and organic phosphonates are most commonly employed as scale inhibitors in the cooling water systems and petroleum industries, however because of the increase demands of sustainable development do not permit the use of these chemicals as they are highly toxic in nature [5,6]. Because of their highly toxicity these chemicals adversely affect the soil and aquatic life of microorganisms. Their discharge in marine can also adversely affect the life and proliferation of marine organisms. It is important to know that organic compounds containing nitrogen and phosphorus are exhibit great toxicity. In view of this, some environmental friendly alternatives scale inhibitors such as Carboxymethyl Inulin (CMI) that does not contains phosphorus and nitrogen are used as "green scale inhibitors" [7]. Another class of environmentally friendly scale inhibitor would the ionic liquids. Ionic liquids or molten salts are the salts of organic cations and inorganic anions that are liquids below 100°C [8]. Even some of the ionic liquids are liquids below Room Temperature (RT) [9,10]. Because of their low volatility, non-toxicity, high thermal and chemical stabilities ionic liquids are established as one of the greenest alternatives to be used for several industrial applications including as corrosion inhibitors [11-17]. Their properties such as corrosion and scale inhibition properties can be suitably tailored by proper selection of cations and anions. Literature survey reveals that plenty of ionic liquids are tested as corrosion inhibitors for different metallic alloys in all electrolytic media however their use as scale inhibitors has not been reported. Because of their high solubility in polar media, high surface activity (ionic nature), strong ability of interact with metallic surface and excellent stability for chemical and thermal treatments, ionic liquids should exhibit strong scale inhibiting ability. Use of ionic liquids that contains phosphoric, sulphonic and carboxylic acid groups or their anions are highly recommended as the organic compounds containing these moieties furnish excellent scale inhibiting tendency. Use of ionic liquids at the place of traditional scale inhibitors will be advantageous for the environmental consideration point of view [18].

REAL WORLD INDUSTRIAL APPLICATIONS OF IONIC LIQUIDS

Ionic liquids are established as green and environmentally friendly chemicals therefore they are currently used as environmentally friendly alternatives in almost all industries (Figure 1). They are widely used as environmental benign solvents for the synthesis of several biologically and industrially useful applications.

In several reactions, ionic liquids act as solvents as well as catalysts. Ionic liquids are also served as reagents for the synthesis of several classes of biologically and industrially useful heterocyclic compounds. Several classes of ionic liquids are effectively used in different areas of science and bio-engineering. Ionic liquids are also evaluated as metallic corrosion inhibitors for different alloys in various electrolytes. Because of their ionic behavior, unlike to traditional organic and polymeric compounds that implantation is limited because of their limited solubility; ionic liquids are extensively employed as corrosion inhibitors. Several classes such as imidazolium, pyridinium, tetra-ammonium and phosphonium based ionic liquids are widely used as inhibitors for mild and carbon steel, aluminum, zinc, copper and magnesium etc. corrosion. Therefore, their use as environmental friendly scale inhibitors is highly recommended.

CHALLENGES

Although, ionic liquids are established as one of the green alternatives for different industrial applications especially in

Table 1: Common scale inhibitors used in the cooling water systems (CWSs), petroleum industries and $CaCO_3$ based scales.

S No.	Name of SIs	Nature of system
1	Maleic acid derived polymers	CWS
2	Phosphonobutane-1,2,4-tricarboxylic acid (PBTC)	CWS
3	Amino-trimethylene phosphonic acid (ATMP)	CWS
4	1-Hydroxyethylidene-1,1-diphosphonic acid (HEDP)	CWS
5	Polyacrylic acid (PAA)	CWS
6	Phosphinopolyacrylates (PPCA)	CWS
7	Polymaleic acids (PMA)	CWS
8	Maleic acid terpolymers (MAT),	CWS
9	Sulfonated phosphonocarboxylic acid (SPOCA)	CWS
10	Sulfonic acid copolymers (SAC)	CWS
11	Polyvinyl sulfonates (PVS)	CWS
12	Diethylenetriamine- penta (methylene phosphonic acid (DTPMP).	Petroleum industry
13	Poly-Phosphono Carboxylic acid (PPCA)	Petroleum industry
14	Polymorphs	$CaCO_3$ inhibitors

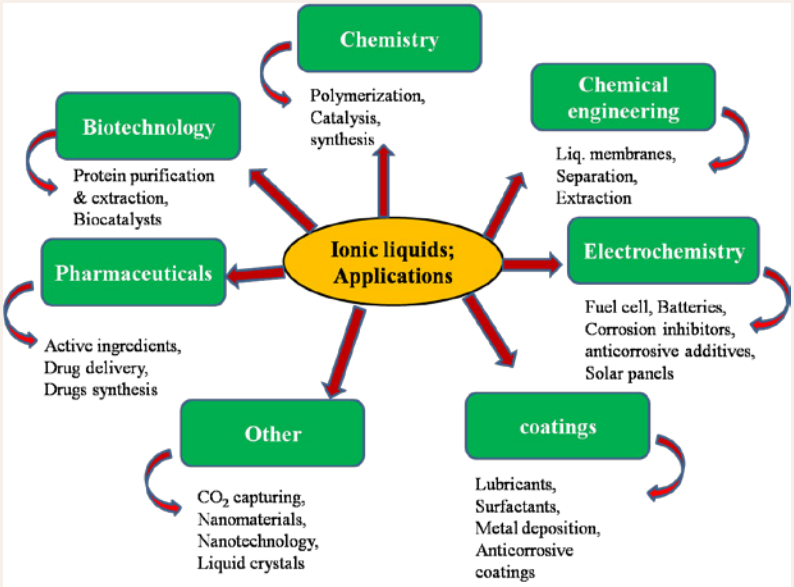

Figure 1 Applications of ionic liquids in various fields of science and technology [19].

the corrosion and scale inhibition systems, however their use experiences several challenge [20,21]. Most of the ionic liquids are highly expensive because of their synthesis using expensive solvents and starting materials [21]. More so, their highly sensitive purification and works-up steps make their synthesis highly expensive. Generally, synthesis of the ionic liquids connected with several step reactions that are coupled with expenditure and liberation of gigantic quantity of toxic solvents that can unfavorably influence the soil and marine life [22,23]. Similar to most of the organic compounds, ionic liquids are non-biodegradable therefore their concentration in soil, water and animal bodies (bioaccumulation) is expected to increase over time [24,25]. Generally, recovery, recycling and reuse of ionic liquids in various industries including in corrosion inhibition is highly restricted that offers a big drawback to use them for different industrial applications. Few classes of ionic liquids especially pyridinium based are highly toxic in nature [26-28].

CONCLUSIONS AND FUTURE TRENDS

On the basis of above discussion, it can be concluded that scaling is major problem in cooling water systems and petroleum-based industries that adversely affect the transport efficiency, plant efficiency and lifespan of the metallic equipments including pipelines, pumps and valves etc. In cooling water system, presence of inorganic salts such as calcium carbonate, calcium sulfate, calcium phosphate, bicarbonates of sodium, magnesium and calcium with their sulfate, chlorides and nitrates causes scaling problem whereas in petroleum industries scaling is attributed due to the presence of calcium carbonate, barium sulfate, strontium sulfate and iron sulfide etc. and dissolved organic acids. Most of the previously used scale inhibitors are maleic acid-based polymers and organic phosphonates in cooling water systems (CWSs) and petroleum industries. Most of the previously used scale inhibitors are toxic in nature therefore development of green scale inhibitors is essential. In this direction, ionic liquids especially those contain phosphoric, carboxylic and sulfonic acid functional groups or their anions would be used as green and environmentally friendly alternatives to the traditional toxic scale inhibitors. Ionic liquids have several advantageous properties such as high solubility, low-flammability and vapor pressure, high thermal and chemical stabilities. Use of the ionic liquids as scale inhibitors would be advantageous for the environmental consideration point of view.

REFERENCES

1. Frenier WW, Ziauddin M. Formation, removal, and inhibition of inorganic scale in the oilfield environment, Society of Petroleum Engineers Richardson, TX, 2008.
2. Liang B, Pan K, Li L, Giannelis EP, Cao B. High performance hydrophilic pervaporation composite membranes for water desalination. Desalination. 2014; 347: 199-206.
3. Kelland MA, Production chemicals for the oil and gas industry, CRC press. 2014.
4. Bezemer C, Bauer KA. Prevention of carbonate scale deposition: A well-packing technique with controlled solubility phosphates. J Pet Technol. 1969; 21: 505-514.
5. Chaussemier M, Pourmohtasham E, Gelus D, Pécoul N, Perrot H, Lédion L, et al. State of art of natural inhibitors of calcium carbonate scaling. A review article. Desalination. 2015; 356: 47-55.
6. Ketrane R, Saidani B, Gil O, Leleyter L, Baraud F. Efficiency of five scale inhibitors on calcium carbonate precipitation from hard water: effect of temperature and concentration. Desalination. 2009; 249: 1397-1404.
7. Kirboga S, Öner M. Investigation of calcium carbonate precipitation in the presence of carboxymethyl inulin. CrystEngComm. 2013; 15: 3678-3686.
8. Wilkes JS. A short history of ionic liquids-from molten salts to neoteric solvents. Green Chemistry.2002; 4: 73-80.
9. Huddleston JG, Willauer HD, Swatloski RP, Visser AE, Rogers RD. Room temperature ionic liquids as novel media for 'clean'liquid–liquid extraction. Chemical Communications. 1998; 16: 1765-1766.
10. Marsh KN, Boxall JA, Lichtenthaler R. Room temperature ionic liquids and their mixtures-a review. Fluid phase equilibria. 2004; 219: 93-98.

11. Amiril S, Rahim E, Syahrullail S. A review on ionic liquids as sustainable lubricants in manufacturing and engineering: Recent research, performance, and applications, Journal of Cleaner Production. 2017; 168: 1571-1589.

12. Verma C, Ebenso EE, Quraishi M. Ionic liquids as green and sustainable corrosion inhibitors for metals and alloys: an overview, J Mol Liq. 2017; 233: 403-414.

13. Huang P, Latham JA, MacFarlane DR, Howlett PC, Forsyth M. A review of ionic liquid surface film formation on Mg and its alloys for improved corrosion performance. Electrochimica Acta. 2013; 110: 501-510.

14. Ye Y, Yang D, Chen H, Guo S, Yang Q, Wang A, et al. high-efficiency corrosion inhibitor of N-doped citric acid-based carbon dots for mild steel in hydrochloric acid environment. J Hazard Mater. 2020; 381: 121019.

15. Ye Y, Zhang D, Zou Y, Zhao H, Chen H. A feasible method to improve the protection ability of metal by functionalized carbon dots as environment-friendly corrosion inhibitor. J Clean Prod. 2020; 264: 121682.

16. Luo J, Cheng X, Zhong C, Chen X, Ye Y, Zhao H, et al. Effect of reaction parameters on the corrosion inhibition behavior of N-doped carbon dots for metal in 1 M HCl solution. J Mol Liq. 2021; 116783.

17. Zeng X, Zheng X, Guo L, Xu Q, Huang H, Tan B. Three imidazole ionic liquids as green and eco-friendly corrosion inhibitors for mild steel in sulfuric acid medium, J Mol Liq. 2021; 324: 115063.

18. Zhao H, Xia S, Ma P. Use of ionic liquids as 'green'solvents for extractions. J Chem Technol Biotechnol. 2005; 80: 1089-1096.

19. Verma C, Alrefaee SH, Quraishi M, Ebenso EE, Hussain CM. Recent developments in sustainable corrosion inhibitors using ionic liquids: A review. J Mol Liq. 2020; 114484.

20. Ueki T, Watanabe M. Macromolecules in ionic liquids: progress, challenges, and opportunities. Macromolecules. 2008; 41: 3739-3749.

21. Baudequin C, Baudoux J, Levillain J, Cahard D, Gaumont AC, Plaquevent JC. Ionic liquids and chirality: opportunities and challenges. Tetrahedron: Asymmetry. 2003; 14: 3081-3093.

22. Thummanagoti S, Yellol GS, Sun CM. Ionic liquid supported multistep divergent synthesis of benzimidazole linked pyrrolo-/pyrido-/isoindolo-benzimidazolones, Tetrahedron letters. 2011; 52: 2818-2822.

23. Ono F, Qiao K, Tomida D, Yokoyama C, Direct preparation of styrene carbonates from styrene using an ionic-liquid-based one-pot multistep synthetic process. Applied Catalysis A: General. 2007; 333: 107-113.

24. Bouquillon S, Courant T, Dean D, Gathergood N, Morrissey S, Pegot B, et al. Biodegradable ionic liquids: selected synthetic applications. Aust J Chem. 2007; 60: 843-847.

25. Stolte S, Abdulkarim S, Arning J, Blomeyer-Nienstedt AK, Bottin-Weber U, Matzke MJ, et al. Primary biodegradation of ionic liquid cations, identification of degradation products of 1-methyl-3-octylimidazolium chloride and electrochemical wastewater treatment of poorly biodegradable compounds. Green Chemistry. 2008; 10: 214-224.

26. Zhao D, Liao Y, Zhang Z, Toxicity of ionic liquids. Clean soil air water. 2007; 35: 42-48.

27. Pham TPT, Cho CW, Yun YS, Environmental fate and toxicity of ionic liquids: A review. Water research. 2010; 44: 352-372.

28. Stolte S, Matzke M, Arning J, Böschen A, Pitner WR, Welz-Biermann U, et al. Effects of different head groups and functionalised side chains on the aquatic toxicity of ionic liquids. Green Chemistry. 2007; 9: 1170-1179.

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