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Screening Cation and Anion of Ionic Liquid for Dissolution of Silicon Dioxide using COSMO-RS

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Abstract

Objectives:Silicon dioxide (SiO_2) is one of the common oilfield scales which is hardest scale to dissolve and there is no specific commercial chemical scale removal to dissolve SiO_2. The purpose of this study to screens Ionic Liquids (ILs) that will be used in dissolution of SiO_2due toscale problem in oilfield. **Methods/StatisticalAnalysis:**COSMO-RS since then has become a widely used and fast method for the prediction and screening of ionic liquid properties, is used for sigma profile, sigma potential and solvent capacity for metal dissolution. The best cation and anion have been chosen based on sigma profile, sigma potential and the high solvent capacity from COSMO-RS findings. **Findings:** Ammoniumcation and sulfate anion is the best combination with highest amount of SiO_2 capacity is $7.832x10^{10}$. Ammonium sulfate is the possible ionic liquid to dissolve SiO_2 scale in oilfield.

Keywords: COSMO-RS, SiO2, Sigma Profile, Sigma Potential

1. Introduction

Mineral scale formation in oilfield production systems especially in wellbore has been a problem in the industry for many years. Usually, most of scale found in wellbore is formed by direct precipitation that occurs naturally in reservoir rocks[1]. The typical scale had been found in oilfield such as Calcium Carbonate ($CaCO_3$), Iron Carbonate ($FeCO_3$), calcium sulfate ($CaSO_4$), barium sulfate ($BaSO_4$), strontium sulfate ($SrSO_4$), Silicon Dioxide (SiO_2) and Iron Hydroxides[2-6]. Unlike common oilfield scales, SiO_2 is the hardest scale to dissolve and there is no specific commercial chemical scale removal to dissolve SiO_2 and it's very insoluble in water. This scale problem will affect the diameter of wellbore which ultimately leading in decreasing the production of crude oil mainly.

Chemical scale removal isone of the economical technique especially when scale is hard to accessible[7].Recently, Ionic Liquids (ILs) are widely used in metal extraction[8-10], metal dissolution[11], desulfurization, and scale removal[12] due to their unique chemical and physical properties, such as non-volatile, low melting point, high dissolving ability, high ionic conductivity, high thermal stability, adjustable structure, extensive electrochemical window and others[13-16].

The variety of ILs can be synthesis due to uncountable number of possible cations and anions combination and it is called "designer solvent". In spite of that, it is unfeasible to select potential ILs using experimental method instead[17,18]. This may result in high cost and time consuming since the cost of purchasing pure ILs is quite high. Frequently, there should be a predictive tool or method to screen a potential ILs by predicting the solubility of SiO_2in ILs phases before synthesized its.

The most effective and accurate method for ILs screening is by using the Conductor like Screening Model for Real Solvents (COSMO-RS)[19,20] because there is no experiment data or functional group parameter needed to run this simulation. Hence, COSMO-RS able to calculate charge density, sigma (σ) profile and sigma (σ) potential by only providing the molecular structure of the studied compound. Thus, it is totally practicable for ILs and other mixtures, even the complex and uncommon combinations[21,22].

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In this study, up to 45 combination anions and cations has been screened using COSMO-RS approach to identify potential and effective ILs to dissolve SiO_2 based on capacity. The σ-profile and σ-potential of cations, anions and together with SiO_2 has been analyzed for solubility predictions.

2. COSMO-RS Theory

The COSMO-RS model is a novel method and composed progressive kind of a dielectric modelwhere the compound of interest are placed in a conductor as the reference state[22]. The ability seen in this model is no need the primary experimental data and the detail descriptions of COSMO-RS features given elsewhere[23-25] and COSMO-SAC (segment activity coefficient.The calculation of interaction energy between speciesusing polarization charge densities is the fundamental concept of COSMO-RSmodel, COSMO-RS model have specialty to predict thermodynamic properties based on quantum chemical-COSMO calculation. This calculation start from surface polarization density σ from Density Functional Theory (DFT). Then, targeted compound of cation and anion were optimized using TURBOMOLE program.

The compound of cations and anions surface contain ideal screening charge after optimization and the cosmo. file was imported into the COSMOthermX software package (version C30 1301) using parameter file BP TZVP C30 1301.ctd.[26] to obtain the σ-profile and σ -potential of the cations and anions.

3. Results and Discussion

In this study, the molecular interaction will be focus on sigma profile and sigma potential analysis. Before analysis of the molecular interactions among the cation, anion and solute (SiO_2), the polarity properties are first examined for efficient screening dissolution.

3.1 SiO_2 Polarity Properties

Figure 1 shows the σ-surface and the σ-profile of SiO_2. The σ-surface of SiO_2 is dominated by the red regions of two oxygen lone pair's, strongly positive σ on the hydrogen bond acceptors and the blue region of the silicon atom, which are hydrogen bond donors. These hydrogen bonding areas cause two high peaks in the σ -profile of SiO_2, which are centered at -1.5 e/Å2 and +1.3 e/Å2 respectively, and dominate the σ -profile. The amount of non-polar, green surface area is relatively small.

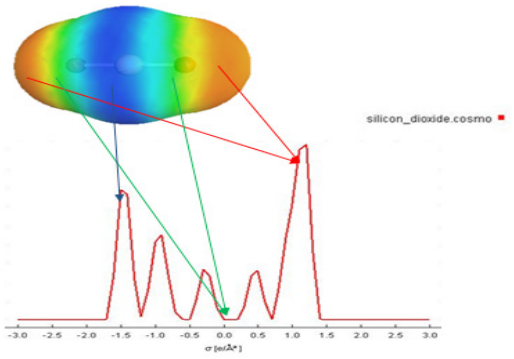

Figure 1. σ -Surface and σ -profiles of SiO_2.

3.1.1 σ-profile Analysis

In the σ-profile, molecules considered as a polar molecule when the screening charge density exceed ±0.0084eÅ−2. Molecules complexity and quality of initial geometry will determine the total calculation time for a single sigma profile. A higher absolute value of σ leads to a stronger compound as a hydrogen bond donors or a hydrogen bond acceptor. The σ-profiles for cation and anion with SiO_2 were plotted shown in Figure 2 , Figure 3 respectively.

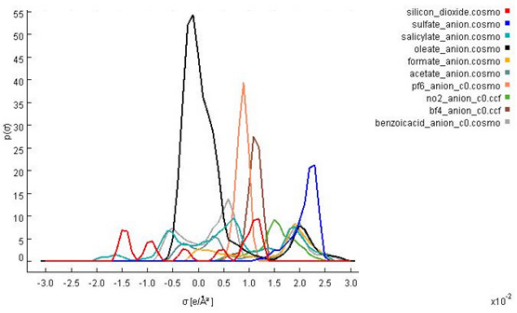

Figure 2. σ -profiles of SiO_2 and anions.

As shown in Figure 2, most of anions σ-profile clearly shows that its charge density results from peaks within non-polar (-0.0084< σ <0.0084) eÅ^{-2}and hydrogen bond acceptor region (σ>0.0084) eÅ^{-2}. This means that some anion in polar region show the ability to form hydrogen bonding among themselves or with other molecules through its oxygen or hydrogen atoms, thus, this kind of anion can act as hydrogen bond acceptor species. Some of the anion has high peak in non-polar region which show its high affinity for non-polar molecules.

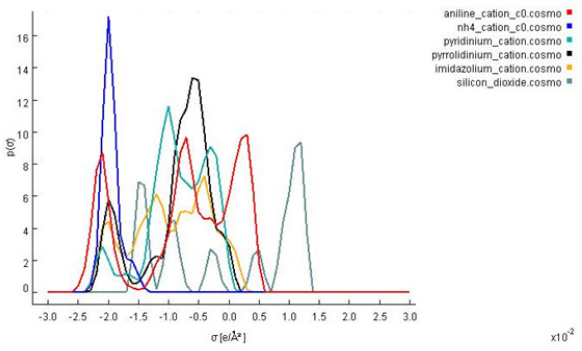

Figure 3. σ -profiles of SiO_2 and cations.

Figure 3 shows clearly shows the peak of cations at the non-polar region and hydrogen bond donors region. This means that most of the cations are weak for hydrogen bond interactions, and can also be classified as a nonpolar compound. This means, most of the cations above has high affinity to non-polar molecules compared to polar molecules.

3.1.2 σ-potential Analysis

In COSMO-RS analysis, the σ-potential indicates the affinity of a component in a mixture towards another. In the σ-potential plot, a higher negative value of μ (σ) indicates an increasing interaction between molecules, whereas a higher positive value signifies an increase in repulsive behavior. For the horizontal axis, increasing negative and positive values for the hydrogen bonding threshold (±0.0084 eÅ^{-2}) indicate the region of a molecule where interactions between hydrogen bond donors and hydrogen bond acceptors occur, respectively. The σ-potential for cations and anions with SiO_2were plotted shown in Figure 4, Figure 5respectively.

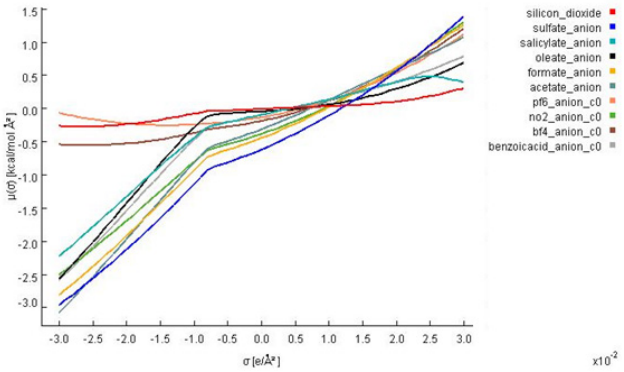

Figure 4. σ -potential of SiO_2 and anions.

Figure 4 shows those σ-potential curves for SiO2 and anions. Most of the anion has curve with high negative value at the hydrogen bond donor's region and has negative value for non-polar region. The result shows that the most of anion show its strong affinity for both hydrogen bond donors and non-polar molecules. High positive value in hydrogen bond acceptor region shows the anion having no affinity for hydrogen bond accepting molecules

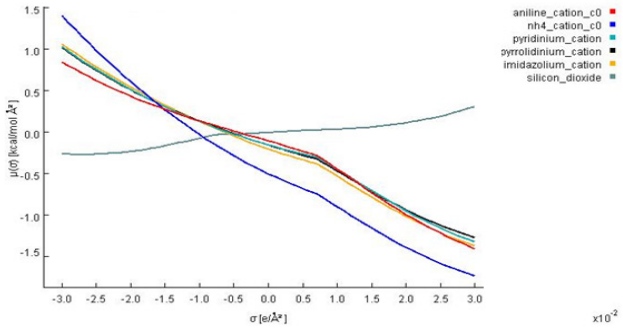

Figure 5. σ -potential of SiO_2 and cations.

Figure 5 shows σ-potential curves for SiO_2 and cations. From the graph, the cation found to has strong potential due to negative value in non-polar region and hydrogen bond acceptor region. The cations show high affinity to non-polar and hydrogen bond acceptors molecules.

From sigma profile, sigma potential of the SiO_2, cationsand anions, its show the characteristic of ionic liquid needed to obtain strong interaction between SiO_2 molecules. It's necessary to select ionic liquid that can act as either hydrogen bond donor or acceptor but lower hydrophobic character. In terms of σ-profile and σ-potential the ionic liquids should have strong peak in Polar Regions (σ< -0.0084 or >0.0084) eÅ^{-2} but low peak in non-polar region (-0.0084 <σ< 0.0084) eÅ^{-2} of the σ -profile. This is an important input in selecting ionic liquids that have high affinity for SiO_2.

3.2 Capacity Prediction based on COSMO-RS

In this study, the capacity of ionic liquid for SiO_2 indicates the maximum amount of SiO_2 that can be dissolved in the ionic liquid. Result for the capacity of the SiO_2 shown in Table 1. Five combination cation and anion with the highest capacity were ranked in order of [NH4:SO_4]> [NH_4:PF6]> [NH_4:BF4]> [Aniline: PF6]>[Imidazolium: PF6].

Table 1. Capacity of the SiO2 in combination of cation and anion

No	Cation	Anion	Solute	Capacity
1	Ammonium	Formate	SiO_2	0.0019
2	Ammonium	Acetate	SiO_2	0.0101
3	Ammonium	Oleate	SiO_2	0.1051
4	Ammonium	Salicylate	SiO_2	0.1337
5	Aniline	Oleate	SiO_2	0.1499
6	Ammonium	Benzoate	SiO_2	0.2349
7	Aniline	Acetate	SiO_2	0.2813
8	Imidazolium	Oleate	SiO_2	0.3394
9	Aniline	Formate	SiO_2	0.3562
10	Aniline	Benzoate	SiO_2	0.4055
11	Aniline	Salicylate	SiO_2	0.4094
12	Pyrrolidinium	Oleate	SiO_2	0.5367
13	Aniline	NO2	SiO_2	0.5471
14	Aniline	Sulfate	SiO_2	0.5594
15	Pyridinium	Oleate	SiO_2	0.7415
16	Imidazolium	Acetate	SiO_2	0.9233
17	Imidazolium	NO_2	SiO_2	0.9504
18	Imidazolium	Salicylate	SiO_2	0.9785
19	Imidazolium	Formate	SiO_2	1.1261
20	Imidazolium	Benzoate	SiO_2	1.1278
21	Pyrrolidinium	Salicylate	SiO_2	1.3921
22	Pyrrolidinium	Benzoate	SiO_2	1.6335
23	Pyrrolidinium	Acetate	SiO_2	2.0089
24	Pyridinium	Salicylate	SiO_2	2.2909
25	Imidazolium	Sulfate	SiO_2	2.4658
26	Pyridinium	Benzoate	SiO_2	2.6918
27	Pyrrolidinium	Formate	SiO_2	2.7413
28	Pyridinium	Acetate	SiO_2	3.2663
29	Pyrrolidinium	NO_2	SiO_2	3.6342
30	Pyridinium	NO_2	SiO_2	4.5308
31	Pyridinium	Formate	SiO_2	4.7148
32	Pyrrolidinium	Sulfate	SiO_2	8.0795
33	Ammonium	NO_2	SiO_2	10.6022
34	Imidazolium	BF_4	SiO_2	11.5217
35	Pyridinium	Sulfate	SiO_2	13.0690
36	Pyridinium	BF_4	SiO_2	15.0093
37	Aniline	BF_4	SiO_2	15.3421
38	Pyrrolidinium	BF_4	SiO_2	15.7528
39	Pyridinium	PF_6	SiO_2	48.9067
40	Pyrrolidinium	PF_6	SiO_2	80.0381
41	Imidazolium	PF_6	SiO_2	130.713
42	Aniline	PF_6	SiO_2	257.295
43	Ammonium	BF_4	SiO_2	1509.819
44	Ammonium	PF_6	SiO_2	5411.564
45	Ammonium	Sulfate	SiO_2	7.832E10

The result in Table 1 shows that the ammonium cation with sulfate anion has higher capacity of SiO_2 and ammonium cation with formate anion has lowest capacity of SiO_2. This finding fulfill the prior work where the ammonium sulfate can dissolve SiO_2[27]. To understand this result, the combination of sigma profile was analyzed in Figure 6 , Figure 7 respectively.

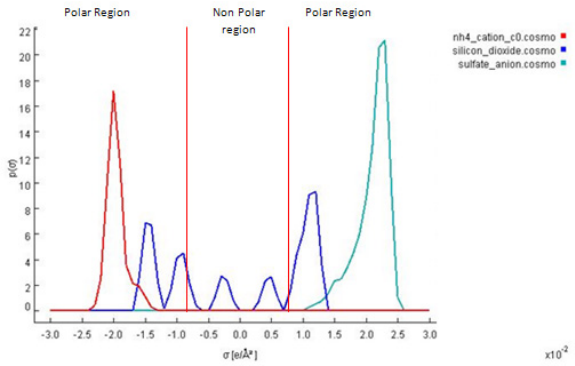

Figure 6. σ –profile for best cation and anion with SiO_2.

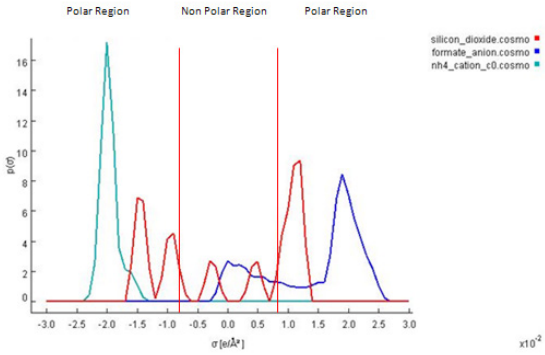

Figure 7. σ –profile for lowest cation and anion with SiO_2.

As shown in Figure 6, high peak of cation and anion located at the polar region. It means the ammonium cation and sulfate anion have ability to form hydrogen bonding with other molecules through its oxygen or hydrogen atoms with oxygen atom in SiO_2molecules. These results indicate that the SiO_2 will dissolve ammonium sulfate ionic liquid. As mention above, polar ionic liquid has strong affinity toward polar molecules which is in polar

regions (σ< -0.0084 or >0.0084). The area of sigma profile in polar region is higher than non-polar region. The polar cation and anion will interact with polar molecules in SiO_2 and give high capacity as shown in Table 1.

Figure 7 shows high peak of cation but lower peak for anion which is located at the polar region. The lower peak of anion in hydrogen bond acceptor region will decrease the affinity SiO_2 polar molecules in hydrogen bonding donor's region. Also, this will give lower capacity of SiO_2 in this combination cation and anion.

4. Conclusion

COSMO-RS is most effective and fastest method for ILs screening and identify potential and effective ILs to dissolve SiO_2. The best characteristic of ionic liquid in terms of σ-profile and σ-potential the ionic liquids should have strong peak in polar region but low peak in non-polar region. In this study, ammoniumcation and sulfate anion is the best combination with highest capacity$7.832x10^{10}$to dissolve $SiO_2$and combination of ammonium cation and formate anion is lowest capacity0.0019 to dissolve SiO_2. Thus, it can be concluded that from COSMO-RS screening, ammonium sulfate is suitable to dissolve SiO_2. The International Conference on Fluids and Chemical Engineering (FluidsChE 2017) is the second in series with complete information on the official website[28] and organized by The Center of Excellence for Advanced Research in Fluid Flow (CARIFF)[29]. The publications on chemical engineering allied fields have been published as a special note in volume 3[30]. Host being University Malaysia Pahang[31] is the parent governing body for this conference.

6. References

1. Elmorsey SA. Challenge and Successful Application for Scale Removal Gemsa Oil Field, Egypt : Field Study. Society of petroleum Engineers. Manama, Bahrain.2013;1–7.
2. Rhudy JS. Removal of Mineral Scale from Reservoir Core by Scale Dissolver. SPE International Symposium on Oilfield Chemistry. New Orleans, Louisiana.1993;1–10. https://doi.org/10.2118/25161-MS
3. Mcclatchie DW, Co BJS, Verity R, Energy FPL. The Removal of Hard Scales from Geothermal Wells : California Case Histories. Society of Petroleum Engineers. Texas. 2000; 1–7.
4. Quiroga MHV, Calmeto JCN, Pinto SL, Assis CAS, Santos I. Hard Scale Mechanical Removal : A Solution for Brazilian Offshore Operations. Society of Petroleum Engineers. 2003; 1–6.
5. Nasr-El-DinH, Al-Humaidan A. Iron Sulfide Scale: Formation Removal and Prevention. Society of Petroleum Engineers.United Kingdom. 2001;1–13.
6. Buell RS (chevron U.S.A. Inc). Water Blasting for Scale Removal in the Rangely Weber Sand Unit. Society of petroleum Engineers Production Operations Symposium, Oklahoma City, 1989; 615–25.
7. Crabtree M, Eslinger D, Fletcher P, Miller M, Johnson A, King G. Fighting Scale Removal and Prevention. Oilfield Review.11(3), 1999;30–45.
8. Saadat F, Bagh G, Mjalli FS, Hashim MA, Hadj-kali MKO, Alnashef IM. Solubility of Sodium Chloride in Ionic Liquids. Industrial and Engineering Chemistry Research. 2013; 52(33):11488–93. https://doi.org/10.1021/ie401282y
9. Valdés Vergara MA, Lijanova IV, Likhanova NV, Olivares Xometl O, Jaramillo Vigueras D, Morales Ramirez AJ. Recycling and recovery of ammonium-based ionic liquids after extraction of metal cations from aqueous solutions. Separation and Purification Technology. 2015;155:110–7. https://doi.org/10.1016/j.seppur.2015.05.031
10. Leyma R, Platzer S, Jirsa F, Kandioller W, Krachler R, Keppler B.K. Novel thiosalicylate-based ionic liquids for heavy metal extractions. Journal of Hazardous Material. 2016;314:164–71. https://doi.org/10.1016/j.jhazmat.2016.04.038 PMid:27131456
11. Parmentier D, Paradis S, Metz SJ, Wiedmer SK, Kroon MC. Continuous process for selective metal extraction with an ionic liquid. Chemical Engineering Research and Design. 2016;109:553–60. https://doi.org/10.1016/j.cherd.2016.02.034
12. Fan Z, Wang T, He Y. Upgrading and viscosity reducing of heavy oils by [BMIM][AlCl4] ionic liquid. Journal of Fuel Chemistry Technology. 2009; 37(6):690–3. https://doi.org/10.1016/S1872-5813(10)60015-1
13. Luo Q, Lin H, Zhang YY, Peng H. Reactions of metal salts with bronsted acidic ionic liquid: Formations of imidazole template metal sulfates or imidazole-metal complexes. InorganicaChimicaActa. 2016; 447:32–7. https://doi.org/10.1016/j.ica.2016.03.023
14. Dashtbozorgi Z, Golmohammadi H, Acree WE. Prediction of gas-to-ionic liquid partition coefficient of organic solutes dissolved in 1-(2-methoxyethyl)-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate using QSPR approaches. Journal of Molecular Liquids. 2015 Jan; 201:21–9. https://doi.org/10.1016/j.molliq.2014.11.025
15. Saien J, Kharazi M. A comparative study on the interface behavior of different counter anion long chain imidazolium ionic liquids. Journal of Molecular Liquids. 2016; 220:136–41. https://doi.org/10.1016/j.molliq.2016.04.028
16. Wellens S, Vander Hoogerstraete T, Möller C, Thijs B, Luyten J, Binnemans K. Dissolution of metal oxides in an acid-saturated ionic liquid solution and investiga-

tion of the back-extraction behaviour to the aqueous phase. Hydrometallurgy. 2014; 144-145:27–33. https://doi.org/10.1016/j.hydromet.2014.01.015
17. Wlazło M,Alevizou EI, Voutsas EC, Domańska U. Prediction of ionic liquids phase equilibrium with the COSMO-RS model. Fluid Phase Equilibria. 2016; 424:16–31. https://doi.org/10.1016/j.fluid.2015.08.032
18. Lotfi M, Mutalib MIA, Wilfred CD, Alitheen NB, Goto M. Analysis of Multiple Solvation Interactions of Methotrexate and Ammonium Based Ionic Liquids Using COSMO-RS. Procedia Engineering. 2016; 148:459–66. https://doi.org/10.1016/j.proeng.2016.06.464
19. Kamgar A, Esmaeilzadeh F. Prediction of H2S solubility in [hmim][Pf6], [hmim][Bf4] and [hmim][Tf2N] using UNIQUAC, NRTL and COSMO-RS. Journal of Molecular Liquids. 2016; 220:631–4. https://doi.org/10.1016/j.molliq.2016.04.110
20. Bavoh CB, Lal B, Nashed O, Khan MS, Lau KK, Bustam MA. COSMO-RS: An ionic liquid prescreening tool for gas hydrate mitigation. Chinese Journal of Chemical Engineering. 2016; 24(11):1619–24. https://doi.org/10.1016/j.cjche.2016.07.014
21. Khan MS, Liew CS, Kurnia KA, Cornelius B, Lal B. Application of COSMO-RS in Investigating Ionic Liquid as Thermodynamic Hydrate Inhibitor for Methane Hydrate. ProcediaEngineering. 2016; 148:862–9. https://doi.org/10.1016/j.proeng.2016.06.452
22. Khan I, Taha M, Pinho SP, Coutinho JAP. Interactions of pyridinium, pyrrolidinium or piperidinium based ionic liquids with water: Measurements and COSMO-RS modelling. Fluid Phase Equilibria. 2016; 414:93–100. https://doi.org/10.1016/j.fluid.2016.01.014
23. Klamt A. COSMO-RS for aqueous solvation and interfaces. Fluid Phase Equilibria. 2016; 407:152–8. https://doi.org/10.1016/j.fluid.2015.05.027
24. Gonfa G, Bustam MA, Sharif AM, Mohamad N, Ullah S. Tuning ionic liquids for natural gas dehydration using COSMO-RS methodology. Journal of National Gas Science and Engineering. 2015; 27:1141–8. https://doi.org/10.1016/j.jngse.2015.09.062
25. Mullins E, Oldland R, Liu YA, Wang S, Sandler SI, Chen C.C, et al. Sigma-profile database for using COSMO-based thermodynamic methods. Industrial and Engineering Chemistry Research. 2006; 45(12):4389–415. https://doi.org/10.1021/ie060370h
26. Ansgar S, Christian H, Reinhart A. Fully optimized contracted Gaussian basis sets of triple zeta valencequality for atoms Li to Kr. Journal of Chemical Physics. 1994; 100(8): 5829. https://doi.org/10.1063/1.467146
27. Mohamed S, Van der Merwe EM, Altermann W, Doucet F.J. Process development for elemental recovery from PGM tailings by thermochemical treatment: Preliminary major element extraction studies using ammonium sulphate as extracting agent. Waste Manag. 2016; 50:334–45. https://doi.org/10.1016/j.wasman.2016.02.021 PMid:26923300
28. FluidChe 2017 Available from: http://fluidsche.ump.edu.my/index.php/en/
29. he Center of Excellence for Advanced Research in Fluid Flow (CARIFF) Available from: http://cariff.ump.edu.my/
30. Natural resources products prospects - International Conference on Fluids and Chemical Engineering FluidsChE 2017 Malaysia,). Indian Journal of science and technology. 2017; S2(1).
31. University Malaysia Pahang. Available from: www.ump.edu.my