Investigation of Potential Azeotrope Breakers Using DFT and COSMO Approach

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ABSTRACT: Different combinations of cations (imidazolium, pyridinium, pyrrolidinium, phosphonium, and ammonium) and anions (basic anions, sulfate, phosphate, and borate) were studied based on the COSMO volume and quantum chemical parameters such as highest occupied molecular orbital/lowest unoccupied molecular orbital (HOMO/LUMO) energies, HOMO–LUMO energy gap, global hardness and softness, electronegativity, electrophilicity index, and chemical potential using the density functional theory (DFT) method. Further, the sigma profile and sigma potential for the selected cations and anions were generated using a COSMO-RS model. The activity coefficient at infinite dilution was also studied for the butanol–water system to find a greater degree of nonideality. A feasible entrainer for the azeotrope breaker for a butanol–water system is proposed.

1. INTRODUCTION

Butanol is a widely used organic solvent in the chemical process industries because of its extensive use in the production of active pharmaceutical ingredients, polymers, and herbicide esters, paint thinner, and coating applications such as hydraulic brake fluids. In recent decades, butanol has been found to be more important in the area of fuel additive application because it increases the octane level of the fuel and decreases the harmful exhaust emission from the vehicles. The presence of water in butanol may lead to the formation of a minimum-boiling azeotrope. Thus, the separation of butanol–water mixture is the most challenging problem in process industries. Various techniques have been studied for the separation of OH–H2O to achieve an effective low-cost method. In chemical process industries, distillation is a widely used technique for the separation of binary and multicomponent mixtures based on the difference in their boiling points.1 Simple distillation is the one that involves the separation of components into distillate and residue, where the distillate consists of more volatile components and the residue is with less volatile components. Simple distillation is applicable only for components having a relative volatility $\alpha$ above 1.0 greater the degree of separability in case of $\alpha$ value less than 1.0 the system becomes invalid because of the equilibrium condition of vapor and liquid or the coexistence of both the phases. Hence, there is a need for azetroptic distillation to find a solution for the above problem. In such a case, a third component (entrainer) may be added to the binary mixture, which will form a new low-boiling azetrope with one of the original constituents, which in turn alters the relative volatility ($\alpha$) of the binary mixture.2 Azeotropes can be either homogeneous or heterogeneous. Homogeneous azetroptic distillation is a technique where the entrainer is added to form a tertiary phase and the entrainer is completely miscible with the original components. Heterogeneous azetroptic distillation is a technique where the entrainer forms a hetero azetrope with one of the original azetrope component. It can be further classified as a minimum-boiling azetrope and maximum-boiling azetrope. The selection of an appropriate entrainer for the azetroptic distillation is based on the fact that the added entrainer should enrich phase splitting, which should result in the formation of a minimum-boiling azetrope. Considering the suitability, toxicity, and recyclability of the entrainer, ionic liquid (ILs) are the alternative for regular solvents.2,3 Ionic liquids (ILs) are considered as unique chemicals in the areas of chemical research and process industries because of their physical and chemical properties. ILs have a wide range of applications such as in making electrolytes of batteries, lubricants, plastics, polymers, reaction catalysts, solvents, and mainly entrainers in azetroptic distillations. The main advantage of ILs is their ability of tuning the physical and chemical properties by changing the combinations of anions and cations.3 This helps to obtain different ILs for multiple applications and makes them task-specific. The ionic liquids are also known as liquid salts. ILs are a nonaqueous polar alternative for the phase transfer process, and they are hydrophobic in nature. ILs can control reaction kinetics, and they have high thermal stability, thermal conductivity,

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etc. In the field of chemical research, ILs are considered as environmentally friendly and they are regarded as "green solvents". This makes ILs a promising alternative for organic solvents.\(^5,6\) A variety of ionic liquids can be synthesized due to uncountable number of possible cation and anion combinations and they are also called "designer solvent". The most effective and accurate method for IL screening is the use of a conductor-like screening model for real solvent (COSMO-RS) because there are no experimental data and parameters needed to run this simulation. The recoverability of ionic liquids is more feasible when compared with normal solvents.\(^7\) In the present work, the investigation of a suitable ionic liquid combination was performed for the separation of a close-boiling azeotropic mixture. Based on the quantum chemical parameters, the sigma profile and sigma potential were predicted and validated using the activity coefficient by the COSMO-RS model with help of COSMOthemX'18 pack.

2. THEORY OF COSMO-RS MODEL

The conductor-like screening model for realistic solvents (COSMO-RS) is the most progressive kind of dielectric model, where the molecules are placed in a conductor as the reference state. The advantage of this model is the prior prediction of thermodynamic properties of fluids and liquid mixtures based on quantum chemical calculations.\(^8\) The procedure involved in the COSMO-RS calculation is divided into two steps. The first step comprises the quantum chemical calculations, which are performed only once for each component involved in the system and stored as COSMO files in the database.\(^2\) Using the COSMO file, thermodynamic properties such as chemical potential, activity coefficient, etc. are predicted, which is considered as the second step. In the COSMO-RS model, the molecular interaction energies such as electrostatic misfit ($E_{misfit}$), hydrogen bond interaction ($E_{hb}$), and van der Waals interaction ($E_{vdW}$)\(^9\) energies are described as a function of polarization charge densities $\sigma$ and $\sigma'$.\(^9\) This descriptor can be calculated using any quantum chemical program in the form of.cosmo file output. In the.cosmo file, the surface of the species is divided into segments with a certain surface charge density. By applying a local averaging algorithm on the surface charge densities over effective contact segments, a probability function ($\sigma$-profile) can be plotted.\(^8\) The $\sigma$-profile and $\sigma$-potential aid to understand the behavior of the compounds and their mixtures in terms of charge interactions. From the chemical potential, the activity coefficient at infinite dilution can be calculated for the selection of solvents directly.\(^10\)

3. COMPUTATIONAL DETAILS

Before the COSMO-RS computation, the individual cation and anion are drawn in visualization software MOLDEN. Geometry optimization is performed for the structure prepared in MOLDEN, using Gaussian03 software utilizing the Hartree–Fock level (HF)
Table 1. List of Cations and Anions Used in This Work

| No. | Name of the compound          | Acronym | Structure | Sigma surface [μm²] | Cosmo volume [μm³] |
|-----|-------------------------------|---------|-----------|---------------------|--------------------|
| 1   | 1-Benzyl-3-Methylimidazolium  | [CMI]   | ![Image](image1.png) | ![Image](image2.png) | 1275.42            |
| 2   | 1-Pentyl-3-Methylimidazolium  | [CMI]   | ![Image](image3.png) | ![Image](image4.png) | 1410.31            |
| 3   | 1-Octyl-3-Methylimidazolium   | [CMI]   | ![Image](image5.png) | ![Image](image6.png) | 1545.98            |
| 4   | 1-Propyl-3-Methylimidazolium  | [CMI]   | ![Image](image7.png) | ![Image](image8.png) | 1541.89            |
| 5   | 1-Octyl-3-Methylimidazolium   | [CMI]   | ![Image](image9.png) | ![Image](image10.png) | 1425.15            |
| 6   | 1-Methyl-Pyridinium           | [CMPY]  | ![Image](image11.png) | ![Image](image12.png) | 831.31             |
| 7   | 1-Ethyl-Pyridinium            | [CMPY]  | ![Image](image13.png) | ![Image](image14.png) | 984.12             |
| 8   | 1-Butyl-Pyridinium            | [CMPY]  | ![Image](image15.png) | ![Image](image16.png) | 1233.09            |
| 9   | 1-Pentyl-Pyridinium           | [CMPY]  | ![Image](image17.png) | ![Image](image18.png) | 1390.07            |
| 10  | 1-Hexyl-Pyridinium            | [CMPY]  | ![Image](image19.png) | ![Image](image20.png) | 1528.50            |
| 11  | 1-Butyl-Pyridinium            | [CMPY]  | ![Image](image21.png) | ![Image](image22.png) | 1585.50            |
| 12  | 1-Methyl-1-Methyl-Pyridinium  | [CMPYR] | ![Image](image23.png) | ![Image](image24.png) | 960.85             |
| 13  | 1-Ethyl-1-Methyl-Pyridinium   | [CMPYR] | ![Image](image25.png) | ![Image](image26.png) | 1081.13            |
| 14  | 1-Butyl-1-Methyl-Pyridinium   | [CMPYR] | ![Image](image27.png) | ![Image](image28.png) | 1542.06            |
| 15  | 1-Hexyl-1-Methyl-Pyridinium   | [CMPYR] | ![Image](image29.png) | ![Image](image30.png) | 1559.28            |
| 16  | 1-Octyl-1-Methyl-Pyridinium   | [CMPYR] | ![Image](image31.png) | ![Image](image32.png) | 1939.12            |
| 17  | Tetra-Bu2Ph-Picophenium       | [IBPF]  | ![Image](image33.png) | ![Image](image34.png) | 2510.44            |
| S.no. | Name of the compound | Acronym | Structure | Sigma surface | Contour volume (Å³) |
|-------|----------------------|---------|-----------|---------------|-------------------|
| 18    | Tetra-Methyl-Phosphonium | [TMP]   | ![Structure](image1) | ![Sigma Surface](image2) | 837.61            |
| 19    | Tetra-Dimethyl-Phosphonium | [TDMP]  | ![Structure](image3) | ![Sigma Surface](image4) | 1323.27          |
| 20    | Tetra-Pentyl-Phosphonium  | [TPP]   | ![Structure](image5) | ![Sigma Surface](image6) | 5055.96          |
| 21    | Tetra-Hexyl-Phosphonium   | [THP]   | ![Structure](image7) | ![Sigma Surface](image8) | 3615.26          |
| 22    | Tetra-Decyl-Phosphonium   | [TDSP]  | ![Structure](image9) | ![Sigma Surface](image10) | 4728.78          |
| 23    | Tetra-Butyl-Phosphonium   | [TBP]   | ![Structure](image11) | ![Sigma Surface](image12) | 4651.19          |
| 24    | Tetra-Octyl-Phosphonium   | [TOP]   | ![Structure](image13) | ![Sigma Surface](image14) | 577.76           |
| 25    | Tetra-Decyl-Phosphonium   | [TDOPP] | ![Structure](image15) | ![Sigma Surface](image16) | 1390.55          |
| 26    | Tetra-Octyl-Phosphonium   | [TOOP]  | ![Structure](image17) | ![Sigma Surface](image18) | 2418.18          |
| 27    | Tetra-Butyl-Phosphonium   | [TBOP]  | ![Structure](image19) | ![Sigma Surface](image20) | 2038.30          |
| 28    | Tetra-Hexyl-Phosphonium   | [THOP]  | ![Structure](image21) | ![Sigma Surface](image22) | 3482.43          |

| S.no. | Name | Acronym | Molecular structure | Sigma structure | Contour volume (Å³) |
|-------|------|---------|---------------------|-----------------|-------------------|
| 1     | Acetate | [CH₃COOH] | ![Molecular Structure](image23) | ![Sigma Structure](image24) | 475.62            |
| 2     | Nitrate | [NO₃⁻]   | ![Molecular Structure](image25) | ![Sigma Structure](image26) | 504.75            |
| 3     | Thiocyanate | [SCN⁻]  | ![Molecular Structure](image27) | ![Sigma Structure](image28) | 458.55            |
| Rank | Name          | Acronym | Molecular Structure | Sigma Structure | Volume (Å³) |
|------|---------------|---------|---------------------|-----------------|-------------|
| 4    | Formate      | [HCO₂]⁻  | ![Molecular Structure](image1) | ![Sigma Structure](image2) | 463.22      |
| 5    | Oxamate      | [C₆H₅NO₃]⁻ | ![Molecular Structure](image3) | ![Sigma Structure](image4) | 248.51      |
| 6    | Salicylate   | [C₆H₆O₃]⁻ | ![Molecular Structure](image5) | ![Sigma Structure](image6) | 300.69      |
| 7    | Benzoate     | [C₆H₅O₂]⁻ | ![Molecular Structure](image7) | ![Sigma Structure](image8) | 95.74       |
| 8    | Methyl Sulfate| [C₆H₅SO₃]⁻ | ![Molecular Structure](image9) | ![Sigma Structure](image10) | 628.36      |
| 9    | Ethyl Sulfate| [C₆H₅SO₄]⁻ | ![Molecular Structure](image11) | ![Sigma Structure](image12) | 704.77      |
| 10   | Styryl Sulfate| [C₆H₅SO₃]⁻ | ![Molecular Structure](image13) | ![Sigma Structure](image14) | 1067.81     |
| 11   | Pentyl Sulfate| [C₆H₅SO₃]⁻ | ![Molecular Structure](image15) | ![Sigma Structure](image16) | 760.86      |
| 12   | Hexyl Sulfate| [C₆H₅SO₃]⁻ | ![Molecular Structure](image17) | ![Sigma Structure](image18) | 1200.92     |
| 13   | Heptyl Sulfate| [C₆H₅SO₃]⁻ | ![Molecular Structure](image19) | ![Sigma Structure](image20) | 1476.76     |
| 14   | Octyl Sulfate| [C₆H₅SO₃]⁻ | ![Molecular Structure](image21) | ![Sigma Structure](image22) | 1615.96     |
| 15   | 2-Methoxy-ethyl Sulfate| [C₆H₅O₂S]⁻ | ![Molecular Structure](image23) | ![Sigma Structure](image24) | 1004.82     |
| 16   | 1-Ethoxy-ethyl Sulfate| [C₆H₅O₂S]⁻ | ![Molecular Structure](image25) | ![Sigma Structure](image26) | 1741.54     |
with a triple-zeta valence polarized (TZVP) basis set in COSMOthermX’18, which offers accurate values for the orbital energy. From the final optimized structures, COSMO files are produced that contain the basic information for calculation such as surface segments and charge distribution. From the geometry optimization, the total energy values in addition to highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy values are retrieved and used for the determination of LUMO−HOMO energy gap, chemical potential (μ), electronegativity (χ), global hardness (η), global softness (s), and electrophilicity index (ω), since the range-separated functionals are a way to accurately calculate HOMO/LUMO energies for all of the studied combinations of ILs. Further, for the generation of sigma profiles and sigma potentials of 28 cations and 24 anions (Table 1), suitable ionic liquids are predicted as the azeotropic breaker for the butanol−water system. Thereafter, sigma profiles, sigma potentials, and activity coefficients at infinite dilution for the selected ionic liquids are generated.

4. GLOBAL SCALAR PROPERTIES

Density functional theory (DFT) has been found to be successful in providing theoretical insights into the chemical reactivity and selectivity in terms of seven basic parameters, that is, LUMO and HOMO energies, LUMO−HOMO energy gap, chemical potential (μ), electronegativity (χ), global hardness (η), global softness (s), and electrophilicity index (ω) in the quantum chemistry method.

4.1. HOMO/LUMO Energies.

The interaction of molecular orbitals deals with the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital)
energies. The HOMO energy value is related to the ionization potential (IP), whereas the LUMO energy value is related to the electron affinity (EA) through eqs 1 and eqs 1. Increasing values of the HOMO energy show the tendency of a molecule to donate electrons to apt electron acceptors, while the lower LUMO energy shows the electrophilic nature of a molecule.12

\[ \text{EA} = -\text{LUMO} \]  
\[ \text{IP} = -\text{HOMO} \]

4.2. HOMO−LUMO Energy Gap. The difference between HOMO and LUMO energy values gives the HOMO−LUMO energy gap as mentioned in eq 3.

Table 2. Ranking of Different Cation Groups Based upon the Scalar Properties

| most favorable | HOMO energy (lowest to highest) | HOMO−LUMO energy gap (lowest to highest) | global softness (highest to lowest) | electrophilicity index (highest to lowest) |
|----------------|---------------------------------|------------------------------------------|-----------------------------------|------------------------------------------|
| Imidazolium Group | [C5MIM] [C8MIM] [C8MIM] [C4MIM] | [C5MIM] [C8MIM] [C8MIM] [C4MIM] | [C5MIM] [C8MIM] [C8MIM] [C4MIM] |
| Pyridinium Group | [C5MPY] [C4MPY] [C4MPY] [C8MPY] | [C5MPY] [C4MPY] [C4MPY] [C8MPY] | [C5MPY] [C4MPY] [C4MPY] [C8MPY] |
| Pyrrolidinium Group | [C5MPYR] [C4MPYR] [C4MPYR] [C1MPYR] | [C5MPYR] [C4MPYR] [C4MPYR] [C1MPYR] | [C5MPYR] [C4MPYR] [C4MPYR] [C1MPYR] |
| Phosphonium Group | [TMP] [THP] [THP] [THP] | [TMP] [THP] [THP] [THP] | [TMP] [THP] [THP] [THP] |
| Ammonium Group | [M4AMM] [B4AMM] [B4AMM] [M4AMM] | [M4AMM] [B4AMM] [B4AMM] [M4AMM] | [M4AMM] [B4AMM] [B4AMM] [M4AMM] |

Figure 4. Global hardness vs global softness of anions.
Electronegativity (\(\chi\)) is also called as absolute electronegativity,4 which can be determined by the average values of the HOMO and LUMO energies obtained from optimized structures of cations and anions explain the electron donor and electron acceptor properties.12 Therefore, a high HOMO energy and low LUMO energy contribute toward making a molecule more stable.14 Global softness is the reciprocal of global hardness as described below in eq 7.

\[
\eta = \frac{\mu^2}{2\eta}
\]

Electronegativity implies the capability of a molecule to attract electrons, which can be determined by the average values of the HOMO/LUMO energy\(^1\) as per eq 5.

\[
\chi = \frac{-(\text{HOMO} - \text{LUMO})}{2} = \left[ \frac{\text{IP} + \text{EA}}{2} \right]
\]

### 4.3. Electrophilicity Index (\(\omega\)) and Electronegativity (\(\chi\)).

The electrophilicity index is a measure of energy drop due to the electron stream between the acceptor and donor.13 The mathematical expression is described as follows

\[
\omega = \frac{\mu^2}{2\eta}
\]

Electronegativity implies the capability of a molecule to attract electrons, which can be determined by the average values of the HOMO/LUMO energy\(^1\) as per eq 5.

\[
\chi = \frac{-(\text{HOMO} - \text{LUMO})}{2} = \left[ \frac{\text{IP} + \text{EA}}{2} \right]
\]

### 4.4. Chemical Potential (\(\mu\)).

Chemical potential is a form of energy that can be released or absorbed during the molecular interaction or phase transition with respect to the number of electrons in the molecule. It is simply the negative of Mulliken electronegativity (\(\chi\)), also called as absolute electronegativity,\(^3\) as mentioned in eq 6.

\[
\mu = \frac{\text{HOMO} - \text{LUMO}}{2} = -\left[ \frac{\text{IP} + \text{EA}}{2} \right]
\]

### 4.5. Global Hardness (\(\eta\)) and Softness (\(s\)).

Global hardness is related to the stability of the interacting molecules, and global softness measures the extent of charge transfer within the molecule. Molecules with a small HOMO–LUMO energy gap become soft, which requires a small amount of energy to bring them to the excitation state. In terms of reactivity, the molecules with a high softness value are more reactive and less stable than hard molecules.14 Global softness is the reciprocal of global hardness as described below in eq 7.

\[
s = \frac{1}{\eta} = \frac{2}{\text{(HOMO} - \text{LUMO})} = \frac{2}{(I-A)}
\]

### 5. RESULTS AND DISCUSSION

#### 5.1. HOMO/LUMO Energy Values.

The HOMO/LUMO energy values obtained from optimized structures of cations and anions explain the electron donor and electron acceptor properties, which are represented in Figures 1 and 2. From Koopman’s theory, HOMO energy is associated with the amount of energy required to remove an electron from a molecule (ionization potential) and LUMO energy is allied with the amount of energy released when a proton is added to a system (electron affinity). Low HOMO energy designates a high ionization potential and better electron donor properties, whereas high LUMO energy indicates high electron affinity and better electron acceptor properties.\(^1\) Therefore, a high HOMO energy and low LUMO energy contribute toward making a molecule more stable. Figures 1 and 2 show that all cations have the highest negative HOMO energy values than anions, which in turn indicates better electron donor properties. Consequently, anions are better electron acceptors.

In Figure 1, it can be seen that cations of the imidazolium group, 1-pentyl-3-methylimidazolium \([\text{C}_5\text{MIM}]\) (−0.52063 hartree), have better electron donor properties due to its highly negative HOMO energy values followed by 1-hexyl-3-methylimidazolium \([\text{C}_6\text{MIM}]\) (−0.51968 hartree) and 1-heptyl-3-methylimidazolium \([\text{C}_7\text{MIM}]\) (−0.51952 hartree), whose HOMO energy values are almost similar to each other. In the case of the pyridinium cation group, 1-butylpyridinium...
[C₆MPY] (−0.54657 hartree) has high tendency to donate electrons followed by 1-pentylpyridinium [C₅MPY] (−0.54574 hartree) and 1-hexylpyridinium [C₆MPY] (−0.54343 hartree). Among the pyrrolidinium cation groups, 1-octyl-1-methylpyrrolidinium [C₈MPYR] has better electron donor properties with the HOMO energy value of −0.52079 hartree. In the phosphonium group, tetramethyl phosphonium [TMP] has the highest negative HOMO energy value (−0.53431 hartree) compared with other cations of this group. In the ammonium cation group, tetramethyl ammonium [M₄AMM] (−0.47373 hartree) has high ability to donate electrons followed by tetrapentyl ammonium [P₄AMM] with the HOMO energy value of −0.43851 hartree.

For anions in Figure 2, the trend followed based on the highest to lowest LUMO energy values (unstable to stable) is acetate > dicyanamide > nitrate > benzoate > salicylate > perchlorate > thiocyanate (0.41183, 0.39551, 0.33041, 0.23163, 0.22207, 0.11047, and −0.39746 hartrees, respectively). Therefore, in general anions, acetate has better electron acceptor properties. In the sulfate anion group, methyl sulfate [CH₃O₄S] has high ability to donate electrons (−0.39737 hartree) followed by ethyl sulfate [C₂H₅SO₄] (−0.35159 hartree), whereas in the phosphate anion group, dimethyl phosphate [(CH₃)₂PO₄] has a high LUMO energy value (0.38414 hartree) compared with diethyl phosphate (0.36375 hartree) and dibutyl phosphate (0.32892 hartree). Further analyses reveal that the chemical stability increases with an increase in the substituent alkyl chain length and branching. Based on the borate anion group, tetrachloroborate [BCL₄] has a high LUMO energy value (0.26005 hartree) with electron acceptor property. Therefore, a suitable ionic liquid can be chosen by merging the HOMO of selected anions and LUMO of selected cations of different groups so that the ionic liquid has high reactivity and less stability toward the butanol−water system.

5.2. HOMO/LUMO Energy Gap. The gap between the HOMO and LUMO energy says high chemical polarizability characteristics properties of the cations and anions. The cations with a less energy gap are more reactive, less stable, and have a tendency to attract other ions based upon the HOMO/LUMO energy gap. The order of effective cations and anions is shown in Tables 2 and 3, respectively.

5.3. Global Hardness (η) and Global Softness (s). Global hardness and global softness are another important quantum parameters that are described on the basis of the HOMO−LUMO energy gap. Hardness is an indicator of molecule’s ability to be polarized, whereas softness is an indicator of its ability to accept electrons. In general, a molecule having a maximum softness
with minimum hardness leads to the extended molecular interaction through a H-bond network in the water−butanol system.4 Global hardness and softness for selected cations and anions are determined, as shown in Figures 3 and 4 and reported in Tables 2 and 3.

Based on the cations provided in Table 2, it was found that 1-octyl-3-methylimidazolium [C8MIM] was the most reactive cation with a softness value of 8.8570 hartree followed by 1-butyl-3-methylimidazolium [C4MIM] (6.5113 hartree) of the imidazolium group. In the case of the pyridinium group, 1-methyl-pyridinium [C1MPY] has the highest global softness value (5.9737 hartree), which was expectedly seen to have the lowest global hardness value (0.1674 hartree) followed by 1-ethyl-pyridinium [C2MPY] (5.5971 hartree). From the pyrrolidinium group, the 1-butyl-1-methyl-pyrrolidinium [C4MPYR] cation was highly polarizable with a softness value of 8.5657 hartree, which shows that it is a more reactive cation than other molecules in the group. Based on the phosphonium group, tetrahexyl phosphonium [THP] shows a high softness value (9.7618 hartree), which indicates that it is a less stable and high reactive cation. In the case of ammonium group, tetrabutyl ammonium [B4AMM] has high tendency to react among others in the group with a softness value of 9.3344 hartree.

Based on the anions provided in Table 3, it can be seen that the order followed in the general anion group from the highest to lowest softness value is as follows: perchlorate > thiocyanate > salicylate > benzoate > nitrate > acetate, dicyanamide (6.5751, 6.3105, 6.2703, 5.3507, 3.7439, 3.6726, and 3.5606 hartrees, respectively). In the case of sulfate group, butyl sulfate [C4H9SO4] shows the highest global softness (4.5801 hartree) value, which...
indicates its high polarizability and more reactivity than other molecules in this group. In the phosphate group, dimethyl phosphate \((\text{CH}_3)_2\text{PO}_4\) shows high polarizability with a softness value of 3.7639 hartree, higher than those of other two phosphate anions. In the borate group, it is observed that bismalonatoborate has high softness with low hardness values, which implies its high reactivity. From the prediction of selected cations and anions based on the global softness and global hardness values, their combinations of ionic liquids have high reactivity and less stability toward the butanol−water system.

5.4. Electrophilicity Index and Electronegativity. Other scalar parameters such as the electrophilicity index and electronegativity are used to understand the nucleophilic and electrophilic nature of cations and anions. The cations with high electrophilicity can accept the maximum number of electrons, whereas anions with high nucleophilic properties can donate electrons. In general, a high electrophilicity index is indicative of better electron acceptor properties and a low electrophilicity index is indicative of better electron donor properties.\(^4,12,15\) The plots of electrophilicity index vs electronegativity for cations and anions are shown in Figures 5 and 6 and reported in Tables 2 and 3. All cations have a high electrophilicity and electrophilicity index as compared to anions, which implies better electron acceptor properties. Based on the imidazolium group, 1-butyl-3-methylimidazolium \([\text{C}_4\text{MIM}]\) has high electrophilicity index (0.3072 hartree) value implies that it has high ability to accept electrons than other cations in this group. From the pyrrolidinium cation group, it is observed that 1-methyl-1-methyl-pyrrolidinium \([\text{C}_1\text{MPYR}]\) shows high electrophilicity index values (0.3028 hartree) among other ions in the group, which implies that it can act as an acceptor. In the phosphonium cation group, tetramethyl phosphonium \([\text{TMP}]\) has better electron acceptor properties with the electrophilicity index value of 0.3365 hartree. From the ammonium cation group, tetramethyl ammonium \([\text{M}_4\text{AMM}]\) shows better acceptor properties because of its high electrophilicity index (0.2663 hartree) and electronegativity (0.3023 hartree) values.

The lower electrophilicity index and electronegativity values of an anion indicate that it has better nucleophilic and electron donor properties. In general anions, benzoate \([\text{C}_7\text{H}_5\text{O}_2]\) has better nucleophilic properties compared with other anions in the group. In the case of sulfate anion group, octyl sulfate shows low electrophilicity value (0.0013 hartree), which indicates its donor properties. From the phosphate group, it can be seen that dibutyl phosphate \([(\text{CH}_3)_2\text{PO}_4]\) is a better nucleophile than other two anions with the electrophilicity index value of 0.0059 hartree. Based on the borate anion group, trifluorochloroborate \([\text{BCLF}_3]\) is a better electron donor due to its low electrophilicity and electronegativity values. From the observations, it is found that combinations of selected cations and anions are highly reactive and less stable toward the butanol−water system.

5.5. Sigma (\(\sigma\)) Profile. The sigma (\(\sigma\)) profile can be used to predict the strength of interaction of different molecules in

![Sigma profile for general anions](image1)

![Sigma profile for sulfate based anions](image2)

![Sigma profile for phosphate based anions](image3)

![Sigma profile for borate based anions](image4)
which molecules are considered as a polar molecule. Two vertical dashed lines in which the $\sigma$-profile is divided into three regions with screening charge density exceed $\pm 0.0084 \text{ e/Å}^2$. A negative sigma value $\sigma < 0.0084 \text{ e/Å}^2$ shows the ability of a molecule to donate electrons, and a positive sigma value $\sigma > 0.0084 \text{ e/Å}^2$ shows the ability of a molecule to accept electrons for hydrogen bonding. Between two dashed lines, molecules are nonpolar and do not form hydrogen bonds with other molecules.16

The sigma profiles for cations are shown in Figure 7a–e. In the case of cations from Figure 7a, it is observed that $[\text{C}_3\text{MIM}]$ shows a broad peak on the negative side of the sigma profile with a screening charge density $\sigma$ of $-0.01 \text{ e/Å}^2$, confirming its ability to form hydrogen bonds with other polar molecules. From Figure 7b, it can be seen that $[\text{C}_2\text{MPY}]$ acts as a hydrogen bond donor even though the sigma profiles of $[\text{C}_3\text{MPY}]$, $[\text{C}_2\text{MPY}]$, and $[\text{C}_1\text{MPY}]$ show similar prominent peaks on the negative side with $\sigma$ of $-0.01 \text{ e/Å}^2$ due to its lowest peak in the nonpolar region. In Figure 7c, none of the cations of the pyrrolidinium group show peaks in the negative area, which implies their inability to act as a hydrogen bond donor. In Figure 7d, $[\text{TMP}]$ shows a small peak in the negative area of the sigma profile, indicating the possibility of interaction with other polar molecules. From Figure 7e, $[\text{M}_4\text{AMM}]$ shows a small peak in the negative sigma profile region, implying its ability to act as a hydrogen bond donor.

The sigma profiles for anions are shown in Figure 8a–d. In Figure 7a, perchlorate has a broad peak that lies on the positive side of the sigma profile with a screening charge density...
(σ) of 0.01 e/Å², denoting its ability to act as a hydrogen bond acceptor followed by nitrate, thiocyanate, and acetate. From Figure 8b, methyl sulfate has high tendency to form hydrogen bonds with other polar molecules and acts as a hydrogen bond acceptor with a screening charge density of 0.02 e/Å² owing to its lowest peak in the nonpolar region and highest peak in the polar region followed by 2-methoxy ethyl sulfate. Similarly dimethyl phosphate from Figure 8c and trifluorochloroborate from Figure 8d show the highest peak on the positive side of sigma profile with a σ of 0.01 e/Å², implying its ability to act as a hydrogen bond acceptor.

5.6. Sigma (σ) Potential. In the COSMO-RS approach, the sigma potential is used to quantify the affinity of a solvent to a molecular surface of polarity “σ”². As can be seen in Figures 9 and 10, the σ values fall in the range of −0.03 to +0.03 e/Å². A negative value of σ indicates the ability of molecules to donate a hydrogen bond (hydrogen bond donor), whereas a positive value denotes the ability of molecules to accept a hydrogen bond (hydrogen bond acceptor). If the sigma potential of molecules is parabolic in nature, that is, lies on the positive or the negative side, it means that they are not capable to donate or accept a hydrogen bond. In the σ-potential plot, the molecules having higher negative values of μ(σ) show an increase in interaction with other molecules, but the vice versa for the molecules having a higher positive value.17 The sigma potentials for cations are shown in Figure 9a−e. As can be seen in these figures, cations such as [C₄MIM], [C₆MPY], [C₃MPYR], [TMP], and [M₄AMM] have the curves with higher negative values at the hydrogen bond acceptor region and lower negative values for the nonpolar region. The results show that cations have a strong affinity for hydrogen bond acceptor and nonpolar molecules. High positive values for cations in the hydrogen bond donor region show that the cations have no affinity for hydrogen bond donor molecules.

The sigma potentials for anions are shown in Figure 10a−d, and it can be observed that anions such as acetate, methyl sulfate, dimethyl phosphate, and trifluorochloroborate have the curves with higher negative values at the hydrogen bond donor region and a negative value in the nonpolar region. It is clearly understood that they have strong affinity for hydrogen bond donor and nonpolar molecules and have no affinity for hydrogen bond acceptor molecules.

Figure 10. Sigma potentials for (a) general anions, (b) sulfate anions, (c) phosphate anions, and (d) borate anions.

Table 4. List of Suitable Ionic Liquids for the Water−Butanol System Based on the Selected Cations and Anions from Global Scalar Parameters

| Imidazolium-based ILs | Pyridinium-based ILs | Pyrrolidinium-based ILs | Phosphonium-based ILs | Ammonium-based ILs |
|------------------------|----------------------|-------------------------|-----------------------|--------------------|
| [C₈MIM][ClO₄]− | [C₄MPY][ClO₄]− | [C₄MPY][ClO₄]− | [C₄MPY][ClO₄]− | [B₄AMM][ClO₄]− |
| [C₆MIM][ClO₄]− | [C₄MPY][ClO₄]− | [C₄MPY][ClO₄]− | [C₄MPY][ClO₄]− | [B₄AMM][ClO₄]− |
| [C₄MPY][ClO₄]− | [C₆H₄SO₄]− | [C₆H₄SO₄]− | [C₆H₄SO₄]− | [B₄AMM][ClO₄]− |
| [C₄MPY][ClO₄]− | [C₆H₄SO₄]− | [C₆H₄SO₄]− | [C₆H₄SO₄]− | [B₄AMM][ClO₄]− |
| [C₄MPY][ClO₄]− | [C₆H₄SO₄]− | [C₆H₄SO₄]− | [C₆H₄SO₄]− | [B₄AMM][ClO₄]− |
| [C₄MPY][ClO₄]− | [C₆H₄SO₄]− | [C₆H₄SO₄]− | [C₆H₄SO₄]− | [B₄AMM][ClO₄]− |
| [C₄MPY][ClO₄]− | [C₆H₄SO₄]− | [C₆H₄SO₄]− | [C₆H₄SO₄]− | [B₄AMM][ClO₄]− |
| [C₄MPY][ClO₄]− | [C₆H₄SO₄]− | [C₆H₄SO₄]− | [C₆H₄SO₄]− | [B₄AMM][ClO₄]− |
| [C₄MPY][ClO₄]− | [C₆H₄SO₄]− | [C₆H₄SO₄]− | [C₆H₄SO₄]− | [B₄AMM][ClO₄]− |
| [C₄MPY][ClO₄]− | [C₆H₄SO₄]− | [C₆H₄SO₄]− | [C₆H₄SO₄]− | [B₄AMM][ClO₄]− |
| [C₄MPY][ClO₄]− | [C₆H₄SO₄]− | [C₆H₄SO₄]− | [C₆H₄SO₄]− | [B₄AMM][ClO₄]− |
| [C₄MPY][ClO₄]− | [C₆H₄SO₄]− | [C₆H₄SO₄]− | [C₆H₄SO₄]− | [B₄AMM][ClO₄]− |
| [C₄MPY][ClO₄]− | [C₆H₄SO₄]− | [C₆H₄SO₄]− | [C₆H₄SO₄]− | [B₄AMM][ClO₄]− |
| [C₄MPY][ClO₄]− | [C₆H₄SO₄]− | [C₆H₄SO₄]− | [C₆H₄SO₄]− | [B₄AMM][ClO₄]− |

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5.7. Activity Coefficient ($\gamma^{\infty}$). The degree of nonideality of a compound in solution is quantified by the activity coefficient at infinite dilution ($\gamma^{\infty}$). It describes the behavior of a dissolved compound, i.e., the solute, which is completely surrounded by solvent molecules.$^{18,19}$ The generated COSMO file is used to predict the activity coefficient at infinite dilution of the system with selected ionic liquids as listed in Table 4. The suitability prediction by varying the ionic liquid with the respective cation groups and butanol–water concentrations is shown in Figure 11a–d, and the values for the same are given as the Supporting Information.

From Figure 11a, $\mathrm{C}_{n}\mathrm{MIM}\left[(\mathrm{CH}_3)_2\mathrm{PO}_4\right]$ and $\mathrm{C}_{n}\mathrm{MIM}\cdot\mathrm{C}_{n}\mathrm{H}_2\mathrm{SO}_4$ show that the activity coefficient at infinite dilution is less than 1 (i.e., $\gamma < 1$), which means that these combinations of ILs could be used as a potential entrainer for the butanol–water separation process. From Figure 11b, it is observed that the concentrations of $\mathrm{C}_{n}\mathrm{MPY}\cdot\left[(\mathrm{CH}_3)_2\mathrm{PO}_4\right]$ and $\mathrm{C}_{n}\mathrm{MPY}\cdot\mathrm{C}_{n}\mathrm{H}_2\mathrm{SO}_4$ are maximum (i.e., $\gamma < 1$), which implies that they have maximum possibility to act as a potential IL and form strong bonds with butanol. As can be seen in Figure 11c,d, the pyrrolidinium-based ionic liquids such as $\mathrm{C}_{n}\mathrm{MPYR}\cdot[(\mathrm{CH}_3)_2\mathrm{PO}_4]$...
and \([\text{C}_8\text{MIM}]\)[\(\text{C}_4\text{H}_9\text{SO}_4\)] and the phosphonium-based ionic liquids such as [THP][(CH3)2PO4] and [THP][CH4SO4] have the activity coefficient less than 1 \((\gamma < 1)\), indicating favorable interactions between ILs and butanol. From Figure 11e, ammonium-based ionic liquids such as [B4AMM][(CH3)2PO4] and [B4AMM][CH4SO4] show favorable interactions with butanol because of their activity coefficient less than 1 \((\gamma < 1)\). It is remarkable to see that these systems present different trends in butanol activities and activity coefficients with ILs.

6. CONCLUSIONS

The COSMO-RS model is the most effective and fastest method for screening and identifying the potential and effective ionic liquid as an entrainer for the butanol—water azeotrope breaker. The suitable ionic liquids for the separation are proposed with the help of global scalar properties, sigma profile, sigma potential, and activity coefficient. The HF, DFT, and TZVP are the basis set used for the overall computation process, and the order of selective ionic liquid combinations is as follows: imidazolium: [C6H4BO8][C4MPYR][C4H9SO4]; pyrrolidinium: [C4MPYR][C4H9SO4]; pyridinium: [C4MPYR][CH4SO4]. Further, from these data, vapor—liquid and vapor—liquid—liquid equilibrium experiments can be performed and residue curves can be plotted.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02086.

Optimized structure; COSMO file; sigma profile; and sigma potential of all of the studied species in the standard format (ZIP)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Janakey Devi, V. K. P.; Sai, P. S. T.; Balakrishnan, A. R. Experimental Studies and Thermodynamic Analysis of Isobaric Vapor-Liquid-Liquid Equilibria of 2-Propanol + Water System Using n-Propyl Acetate and Isopropyl Acetate as Entrainers. Fluid Phase Equilib. 2017, 454, 22–34.
(2) Janakey Devi, V. K. P.; Sai, P. S. T.; Balakrishnan, A. R. Screening of Ionic Liquids as Entrainers for the Separation of 1-Propanol + Water and 2-Propanol + Water Mixtures Using COSMO-RS Model. Chem. Eng. Commun. 2018, 205, 772–788.
(3) Wen, G.; Bai, W.; Zheng, F.; Reyes-Labarta, J. A.; Ma, Y.; Wang, Y.; Gao, J. Ternary Liquid–Liquid Equilibrium of an Azeotropic Mixture (Hexane + Methanol) with Different Imidazolium-Based Ionic Liquids at \(T = 298.15\) K and 101.325 KPa. Fluid Phase Equilib. 2018, 461, 51–56.
(4) Anantharaj, R.; Banerjee, T. Evaluation and Comparison of Global Scalar Properties for the Simultaneous Interaction of Ionic Liquids with Thiophene and Pyridine. Fluid Phase Equilib. 2010, 293, 22–31.
(5) Tan, X.-C.; et al. Pyrolysis of Heavy Oil in the Presence of Supercritical Water: The Reaction Kinetics in Different Phases. AIChE J. 2015, 61, 857–866.
(6) Hajipour, A. R.; Rafiee, F. Basic Ionic Liquids. A Short Review. J. Iran. Chem. Soc. 2009, 6, 647–678.
(7) Ilawe, N. V.; Fu, J.; Ramanathan, S.; Wong, B. M.; Wu, J. Chemical and Radiation Stability of Ionic Liquids: A Computational Screening Study. J. Phys. Chem. C 2016, 120, 27757–27767.
(8) Klamt, A.; Eckardt, F. Erratum: COSMO-RS: A Novel and Efficient Method for the a Priori Prediction of Thermophysical Data of Liquids (Fluid Phase Equilibria (2000) 172 (43–72)). Fluid Phase Equilib. 2003, 205, 357.
(9) Klamt, A. Conductor-like Screening Model for Real Solvents: A New Approach to the Quantitative Calculation of Solvation Phenomena. J. Phys. Chem. A 1995, 99, 2224–2235.
(10) Vivek, M. S.; Anantharaj, R.; Shyam, S.; Mayuri, N. Evaluation of Molecular Behaviour of Priority of Water Pollutants with Ionic Liquids: COSMO Based Approach. Ind. Eng. Chem. Res. 2019, 58, 316–333.
(11) Zhao, X.; Wu, H.; Duan, M.; Hao, X.; Yang, Q.; Zhang, Q.; Huang, X. Fluid Phase Equilibria Liquid-Liquid Extraction of Lithium from Aqueous Solution Using Novel Ionic Liquid Extractants via COSMO-RS and Experiments. Fluid Phase Equilib. 2018, 459, 129–137.
(12) Hizaddin, H. F.; Anantharaj, R.; Hashim, M. A. A Quantum Chemical Study on the Molecular Interaction between Pyrrole and Ionic Liquids. J. Mol. Liq. 2014, 194, 20–29.
(13) Rajalakshmi, K.; Nayak, D. HOMO–LUMO Analysis of Dasatinib. Int. J. Mater. Sci. 2017, 12, 32–37.
(14) Pilli, S. R.; Banerjee, T.; Mohanty, K. HOMO-LUMO Energy Interactions between Endocrine Disrupting Chemicals and Ionic Liquids Using the Density Functional Theory: Evaluation and Comparison. J. Mol. Liq. 2015, 207, 112–124.
(15) Asghar, A.; Abdul Raman, A. A.; Wan Daud, W. M. A.; Ramalingam, A. Reactivity, Stability, and Thermodynamic Feasibility of H2O2/H2O at Graphite Cathode: Application of Quantum Chemical Calculations in MFCs. Environ. Progress Sustainable Energy 2018, 37, 1291–1304.
(16) Klamt, A. Comments on “A Priori Phase Equilibrium Prediction from a Segment Contribution Solvation Model” (Multiple Letters). Ind. Eng. Chem. Res. 2002, 41, 2330–2334.
(17) Man, M. S.; Abdullah, M. A. M.; Abdullah, S. B.; Yaacob, Z. Screening Cation and Anion of Ionic Liquid for Dissolution of Silicon Dioxide Using COSMO-RS. Indian J. Sci. Technol. 2017, 10, 1–6.
(18) Gruber, D.; Langenheim, D.; Gmeling, J.; Moollan, W. Measurement of Activity Coefficients at Infinite Dilution Using Gas...
Liquid Chromatography. 6. Results for Systems Exhibiting Gas-Liquid Interface Adsorption with 1-Octanol. *J. Chem. Eng. Data* 1997, 42, 882−885.

(19) Gerber, R. P.; Soares, R. D. P. Prediction of Infinite-Dilution Activity Coefficients Using UNIFAC and COSMO-SAC Variants. *Ind. Eng. Chem. Res.* 2010, 49, 7488−7496.