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Fast Solvent Screening for the Simultaneous Hydrodesulfurization and Hydrodenitrification of Diesel Oil Using Ionic Liquids

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S *Supporting Information*

ABSTRACT: 1-Ethyl-3-methylimidazolium [EMIM], 1-ethylpyridinium [EPY], 1-ethyl-1-methylpyrrolidinium [EPYRO], 4-ethyl-4-methylmorpholium [EMMOR], 1-ethyl-1-methylpiperidinium [EMPIP], and 1,2,4-trimethylpyrazolium [TMPYZO] based cations along with 25 anions have been investigated as possible solvents for the simultaneous hydrodesulfurization (HDS) and hydrodenitrification (HDN) of diesel oil at $T = 298.15$ K. The infinite dilution activity coefficient (IDAC) of thiophene (TS), benzothiophene (BTS), dibenzothiophene (DBTS), pyrrole (PYR), indole (IND), indoline (INDI), carbazole (CAR), benzocarbazole (BCAR), pyridine (PY), quinoline (QU), and benzoquinoline (BQU) was predicted via the quantum chemical based COSMO-RS (**CO**nductor like **S**creening **MO**del for **R**eal **S**olvents) model. Subsequently, the selectivity and capacity at infinite dilution were used as indicators for the possible screening of ionic liquids (ILs). [EMMOR], [EMPYRO], and [EMPIP] based cations gave lesser activity coefficient values at infinite dilution as compared to [EMIM], [EPY], and [TMPYZO] based cations. It was noted that [DMP], [BTA], [OcSu], and [MSACN] anions, having a different electronegative atom such as N (nitrogen), O (oxygen), and S (sulfur), respectively, play a significant role in increasing the selectivity. High activity coefficients at infinite dilution values were observed for basic nitrogen compounds as compared to the nonbasic nitrogen compounds irrespective of the cation and anion. Evidently, [EMMOR] and [EPYRO] gave higher solvent capacity values at infinite dilution irrespective of the aromatic nitrogen and sulfur compounds.

INTRODUCTION

Diesel oil is one of the most important energy sources, and it is directly derived from crude oil by an atmospheric distillation unit. The diesel oil is a complex mixture of several saturated, unsaturated, and aromatic hydrocarbons. However, the presence of pollutant contributors such as refractory sulfur and aromatic nitrogen compounds adds to environmental pollution. These compounds are difficult to remove because of its higher molecular weight and higher boiling point. Additionally these compounds are known to inhibit the hydrodesulfurization (HDS) process. Some of sulfur species have been acknowledged by Whitehurst et al.,[1] while the aromatic nitrogen compounds were identified by Shin et al.[2] and Wiwel et al.[3]

The sulfur species has been classified as non acidic and acidic sulfur compounds like thioles (RSR), sulfides (RSR′), disulfides (RSSR′), cyclicsulfides (CS), thiophene (TS), benzothiophene (BTS), and dibenzothiophene (DBTS). The nonbasic and basic nitrogen compounds are classified as: pyrrole (PYR), indole (IND), indoline (INDI), carbazole (CAR), benzocarbazole (BCAR), pyridine (PY), quinoline (QU), and benzoquinoline (BQU). They are all present with diesel oil and thus are responsible for SO_X and NO_X emission to atmospheric during the combustion process. SO_X is the major contributor for acid rain and global warming.[4,5] NO_X is converted into nitrogen dioxide and is an important contributor for the troposphere ozone formation.[6]They further cause environmental pollution and air quality degradation.[4] Nitrogen compounds having nonheteroaromatic or heteroaromatic structure with multiple ring compounds adversely affect the stability of diesel oil during its storage.[7]This reduces the efficiency of hydrodenitrification (HDN) process due to the poisoning of the catalyst.[8]

The development of HDS process for the removal of sulfur content from diesel oil are previously reported using a conventional solvent,[10] zeolite process (CuNaY zeolite, etc.), and via a catalyst.[11−13] Other processes include use of highly active absorbent such as fly ash and γ-Al_2O_3.[12,14,15] The HDS process has worked well for the removal of thioles, sulfides,[15] and cyclic sulfides.[5]But it fails to remove aromatic sulfur compounds such as TS, BTS, and DBTS.[13] The boiling points of sulfur compounds are 357.37 K (TS), 472.85 K (BTS), and 588.33 K (DBTS), respectively. Even processes conducted at high temperatures (> 500 K),[16] high hydrogen pressures ((20 to 100) atm of H_2), higher active catalyst,[17] longer residence time,[13] and heavier hydrogen consumption have failed to remove the aromatic sulfur compounds.

Nitrogen is present in diesel oil in the form of both nonheterocyclic organo-nitrogen (amines, nitriles) and heterocyclic aromatic compounds.[7]A heterocyclic aromatic compound with multiple rings includes compounds such as five-membered pyrrolic (non basic or neutral) and six-membered pyridinic ring (basic) systems,[18] for example, for PYR, IND, INDI, CAR, BCAR, PY, QU, and BQU. The conventional HDN process is used to remove the organo-nitrogen and heterocyclic aromatic compounds from diesel oil using methanol[19] or via catalysts such

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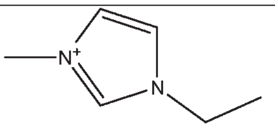
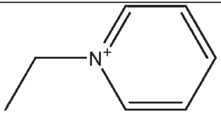
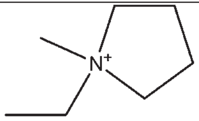
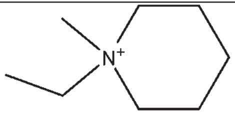
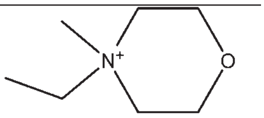
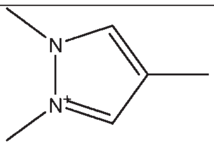
Table 1. List of Studied Cations

S.No	Name	Molecular Formula	Acronym	Structure
01	1-Ethyl-3-Methylimidazolium	$C_6H_{11}N_2$	[EMIM]	
02	1-Ethylpyridinium	$C_7H_{10}N$	[EPY]	
03	1-Ethyl-1-Methylpyrrolidinium	$C_7H_{16}N$	[EPYRO]	
04	1-Ethyl-1-Methylpiperidinium	$C_8H_{18}N$	[EMPIP]	
05	4-Ethyl-4-Methylmorpholinium	$C_7H_{16}NO$	[EMMOR]	
06	1,2,4-Trimethylpyrazolium	$C_6H_{11}N_2$	[TMPYZO]	

as zeolite[18] and NiMo/Al_2O_3.[7] Thus they are unable to remove all the heteroaromatic nitrogen compounds up to the maximum level, even at a high operating temperature (> 500 K)[7] and pressure (12.8 MPa).[20] The maximum boiling point of five-membered ring heteroaromatic nitrogen compound is 627.84 K (CAR), whereas the six-membered ring is 620.51 K (BQU). Therefore, the heteroaromatic nitrogen compounds forms a product with undesirable characteristics during the HDS process. However, there is an increasing need for the removal of both the nitrogen compounds (neutral and basic) from diesel oil.

The inhibiting role of nitrogen (basic and neutral) and refractory sulfur compounds on the conventional HDN and HDS processes has already been studied by various authors.[9,18,21] However, the effective removal of such species from diesel oil is not achievable due to the wide variation of the operating cost and process. Ionic liquids (ILs), better known as green solvents, might provide an important alternative in removing such compounds by liquid−liquid extraction (LLE). ILs are attractive solvents for desulfurization and denitrification[17,22−24,26−30] and are competitive with molecular solvents with respect to the following properties: (a) environmentally benign and designable, (b) nonvolatile, nonflammable, highly solvating, and noncoordinating medium having a high thermal stability over a wide liquid range, (c) higher sulfur extracting ability and virtually immiscibility with diesel, preventing cross contamination, and (d) recovery and regeneration involves using back extractant to recover the sulfur/nitrogen compounds intact. In one such study Huh et al.[22] conducted the regeneration of ILs using diethyl ether as the back extractant. They used the extractant to extract QU from the IL. The IL was able to retain its chemical structure for eight cycles. In another work by Zhang et al.[23,24] the IL [EMIM][BF_4] was quantifiably regenerated from TS by simple distillation using water.

Several studies have also been reported recently for the removal of aromatic sulfur and nitrogen species from diesel oil.[11,13,25−31] However few data are available for the nitrogen compound elimination.[22,26,31] The simultaneous removal of sulfur and nitrogen compounds from diesel oil is still not reported. This is essential for the future refinery process since nitrogen compounds are the major inhibitors for HDS processes. The advantages of ILs as solvents are that they have low energy cost, eliminate the need of hydrogen consumption, and retain the chemical structure of the diesel oil with higher octane values. ILs have a higher density than organic solvent and thus exist as two different phases during the separation process.[32] Apart from these properties, each IL has a unique chemical and physical property based on their cation and anion combination.[26]

In our previous study we have observed that the smaller size cation have a higher selectivity but low capacity for the removal of TS.[33] The aim of this work is to screen the potential cations (Table 1) and anions (Table 2) for the simultaneous removal of aromatic nitrogen and sulfur species by tuning the cation and anion combination. This tuning is very difficult to perform experimentally since limited data are available in literature with respect to different classes of cations. It should be noted that, without the screening of potential ILs, experimental studies are not possible because of the high cost and time involved. It is a well-known fact that the most challenging and difficult parts are in removing the last traces of nitrogen/sulfur species from diesel oil. The infinite dilution activity coefficient (IDAC) is an

Table 2. List of Studied Polynuclear and Mononuclear Anions

serial no.	anion name	molecular formula	acronym	COSMO volume ($Å^3$)	COSMO area ($Å^2$)
1	bromide	Br	[Br]	284	209.37
2	nitrate	NO_3	[NT]	366.72	269.87
3	thiocyanate	SCN	[SCN]	465.9	309.73
4	acetate	CH_3COO	[Ac]	475.39	324.56
5	bisulfate	HSO_4	[BiSu]	514.95	346.73
6	tetrafluoroborate	BF_4	[BF_4]	567.46	384.80
7	methylsulfonate	CH_3SO_3	[MeSul]	588.65	383.90
8	trifluoroacetate	CF_3COO	[TfAc]	621.01	403.68
9	methyl sulfate	CH_3SO_4	[MeSu]	658.09	420.30
10	hexafluorophosphate	PF_6	[PF_6]	674.69	430.83
11	triflate	CF_3SO_3	[TfO]	734.15	462.25
12	ethyl sulfate	$C_2H_5SO_4$	[EtSu]	793.51	491.58
13	dimethyl phosphate	$(CH_3)_2PO_4$	[DMP]	827.84	516.63
14	methylsulfonylacetamide	$C_3H_7NO_3S$	[MSACN]	923.2	557.06
15	tetracyanoborate	$B(CN)_4$	[TCNB]	975.27	584.76
16	salicylate	$C_7H_5O_3$	[Scy]	995.26	564.18
17	bis(methylsulfonyl)amide	$(CH_3\ SO_2)_2N$	[BMA]	1036.03	605.84
18	bisoxaloborate	$B(C_2O_4)_2$	[BOB]	1056.41	619.64
19	diethyl phosphate	$(C_2H_5)_2PO_4$	[DEP]	1101.36	664.86
20	*o*-toluenesulfonate	$C_7H_7SO_3$	[TSy]	1197.11	678
21	*p*-toluenesulfonate	$C_7H_7SO_3$	[TOS]	1197.19	678.49
22	bis(trifluoromethylsulfonyl)amide	$(CF_3SO_2)_2N$	[BTA]	1328.92	771.91
23	2-(2-methoxyethoxy)ethyl sulfate	$C_5H_{11}SO_6$	[Me-Et-EtSu]	1340.19	765.83
24	decanoate	$C_{10}H_{19}O_2$	[DeC]	1565.97	925.51
25	octylsulfate	$C_8H_{17}SO_4$	[OcSu]	1610.46	945.45

important indicator which quantifies this very phenomenon. The lesser the IDAC values from unity, the greater are the tendencies for the IL to remove nitrogen species. The selectivity and capacity at infinite dilution, which are functions of IDAC values, quantify and screen the potential ILs. Quantum chemical based approaches such as COSMO (**CO**nductor like **S**creening **MO**del)[34] along with its extension to RS (**R**eal **S**olvent)[35−40] clearly demonstrate the rapid progress in this area. An important advantage of the COSMO-RS model is that it predicts a priori the liquid phase nonideal activity coefficient of any component in a mixture without using any experimental data. It uses the molecular structure of the solute/component as the only initial input. Thus it directly predicts the IDAC values which are measurable and thereby used to calculate the selectivity and capacity at infinite dilution. Therefore, in this work we have used the COSMO-RS model for the a priori prediction of IDAC values of the above-mentioned nitrogen and sulfur species in both IL and diesel oil.

Computational Details. A comprehensive description of the COSMO-RS theory is given by Klamt et al.[34−38,40] Lin et al.[39] and also reported in our previous work[41−43] on IL systems. The physical parameters such as $a_{\mathrm{eff}} = 6.25$ $Å^2$ (surface area of a standard segment), $\alpha' = 8896$ $(\mathrm{kcal}\cdot Å^4)\cdot(\mathrm{mol}\cdot e^2)^{-1}$ (misfit constant for misfit energy interaction), $c_{\mathrm{hb}} = 54874$ $(\mathrm{kcal}\cdot Å^4)\cdot(\mathrm{mol}\cdot e^2)^{-1}$ (constant for hydrogen-bonding interaction), and $\sigma_{\mathrm{hb}} = 0.0085$ $e\cdot Å^{-2}$ (the a cutoff value for hydrogen-bonding interactions) were taken from Klamt and Schüürmann.[34]

The initial structures of all nitrogen based compounds comprised of a five-membered ring (PYR, IND, INDI, CAR, and BCAR) and a six-membered ring (PY, QU, and BQU) were drawn with the help of MOLDEN freeware.[44] Additionally different cations ([EMIM], [EPY], [EPYRO], [EMMOR], [EMPIP], and [TMPYZO]; Table 1) with 25 anions (Table 2) were also drawn in a similar fashion. The molecular geometries were fully optimized by Hartree−Fock theory with the 6-31G* basis set via GAUSSIAN03.[45] To detect the presence of any negative or imaginary frequencies, a frequency optimization was done using the *freq* keyword in GAUSSIAN03 using the same level of theory.

GAUSSIAN03 was used to generate the COSMO files. The first step for COSMO-RS calculation is to estimate the σ profile of each species. The equilibrium geometry of the molecules in the ideal gas phase is first obtained using the density functional theory of P86.[46] The triple zeta valence potential (TZVP)[47] basis set has then been used in combination with the density fitting basis set of DGA1.[48] The ideal screening charges on the molecular surface are then computed using the same level of theory [PBV86] (P86 written as PBV86 in Gaussian) via the keyword scrf=COSMORS. The radii of the elements are used to define the cavity for the molecule. The radii of the nine components are taken from Klamt.[35]For the prediction involving ILs, the complete dissociation is taken to be equal to the dissociation of cation and anion.[49]The σ profile (charge distribution of screening charge densities)[41−43] of the IL is simply the algebraic sum of the σ profile of cation and anion (eq 1).

$$p_{\mathrm{ionicliquid}}(\sigma) = p_{\mathrm{cation}}(\sigma) + p_{\mathrm{anion}}(\sigma) \qquad (1)$$

where $p_{\mathrm{cation}}(\sigma)$ and $p_{\mathrm{anion}}(\sigma)$ are the σ profiles for cation and anion, respectively. After the addition, the σ profile has been

Table 3. Mole Fraction of Diesel (PIONA Series),[51] Sulfur, and Nitrogen Compounds

simulated diesel oil	until C_5	C_6	C_7	C_8	C_9	C_{10}	$C_{11}+$
n-paraffins (C_nH_{2n+2})	0.0032 (pentane)	0.006 (hexane)	0.003 (heptane)	0.004 (octane)	-	-	0.3663 (undecane)
isoparaffins (C_nH_{2n+2})	0.003 (isopentane)	0.0181 (isohexane)	0.0562 (isoheptanes)	0.013 (iso-octane)	0.17 (isononane)	-	0.109 (iso-undecane)
olefins (C_nH_{2n})	0.003 (pentene)	0.011 (hexene)	0.0162 (heptene)	0.012 (octane)	0.004 (nonene)	-	-
naphthenes (C_nH_{2n})	0.0051 (cyclopentane)	0.0162 (cyclohexane)	0.002 (cycloheptane)	0.001 (cyclo-octane)	-	-	-
aromatics (C_nH_{2n-6})	-	0.067 (benzene)	0.0041 (toluene)	0.0132 (ethylbenzene)	0.025 (propylbenzene)	0.067 (butylbenzene)	0.0006 (pentylbenzene)
nonbasic nitrogen species	0.001 (PYR)	-	-	0.001, 0.001 (IND, INDI)	-	-	0.001,0.001 (CAR, BCAR)
basic nitrogen species	0.001 (PY)	-	-	-	0.001 (QU)	-	0.001 (BQU)
acidic sulfur species	0.001 (TS)	-	-	-	0.001 (BTS)	-	0.001 (DBTS)

normalized. This is equivalent in calculating the σ profile of a mixture consisting of a cation and anion. Along with the profile, the COSMO volume and COSMO area also get added linearly. Thus, the mixture will now act as a single component of IL.

Solvent Selectivity and Capacity. The technical and economical feasibility of ILs for the removal of aromatic nitrogen and refractory nitrogen species is via the LLE process. Selectivity is the most important property for separation of aromatic nitrogen and refractory sulfur species from diesel oil using ILs. Diesel oil is defined using the composition as given in Table 3.[50] σ profiles of all the components are calculated and further linearly added as:

$$p_S(\sigma) = \sum_{i \in S} x_i p^{X_i}(\sigma) \tag{2}$$

Table 3 also gives the composition in mole fraction of aromatic sulfur and nitrogen composition. Here x_i and $p^{X_i}(\sigma)$ are the mole fractions and normalized σ profile of each component i present in diesel. Thus, $p_S(\sigma)$ represents the σ profile of diesel component and will be used in our predictions. The selectivity is defined as the ratio of the composition of nitrogen/sulfur species in the IL-rich phase (extract) and its composition in model diesel-rich phase (raffinate). The operational expression can be written as:

$$S_{12,\max} = S_{12}^{\infty} = \left(\frac{\gamma_2^{\infty}}{\gamma_1^{\infty}}\right)^{\text{ILphase}} \tag{3}$$

where γ_1^{∞} is the activity coefficient of nitrogen species at infinite dilution and γ_2^{∞} activity coefficient of model diesel oil at infinite dilution. Usually γ_1^{∞} or γ_2^{∞} is defined as

$$\gamma_1^{\infty} \text{ or } \gamma_2^{\infty} = \lim_{x \to 0} \gamma_i^{\infty} \tag{4}$$

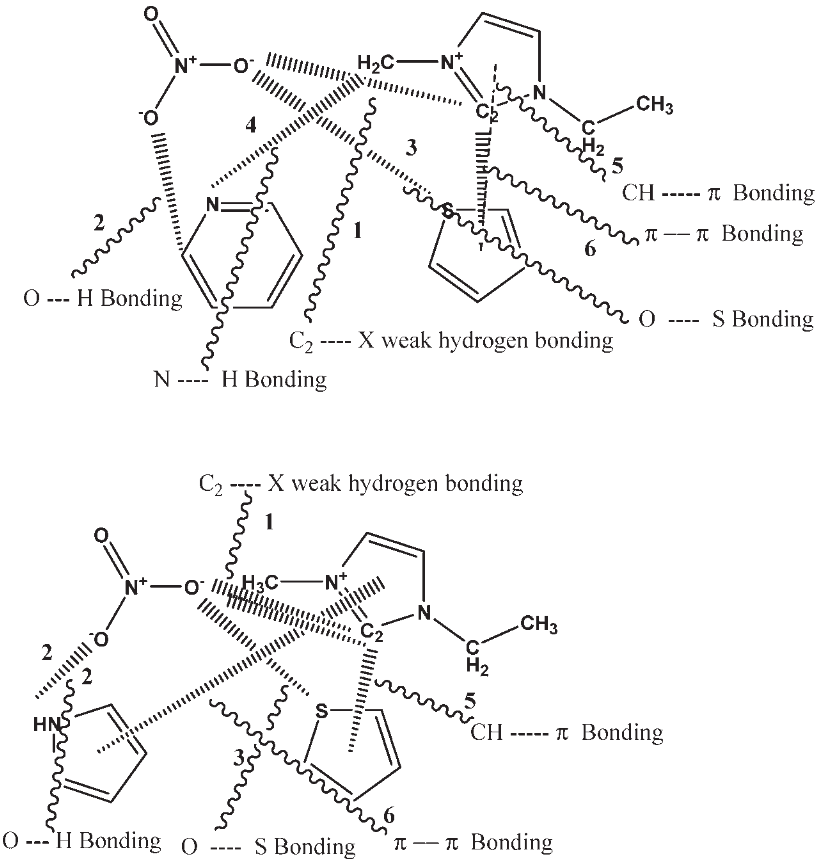
The capacity is directly related for evaluating the amount of ILs required for the removal of nitrogen/sulfur species.[51] It signifies the ability to dissolve maximum amount of nitrogen species in the solvent. The capacity can be expressed in terms of activity at infinite dilution:

$$C_{12}^{\infty} = \left(\frac{1}{\gamma_1^{\infty}}\right)^{\text{ILPhase}} \tag{5}$$

The subscripts 1 and 2 indicate the IL and nitrogen species, respectively. The selectivity and capacity strongly depend on the solvent−solute interaction effect.[52−54] In general, the extraction capacity depends on the anion volume and the interaction energy between cation and anion.[55−59] In our earlier work we have successfully benchmarked the IDAC predictions of sulfur compounds,[33,56] PY,[57] and other solutes[43] in ILs. So benchmarking studies are not carried out in this work.

■ RESULTS AND DISCUSSION

There are several possible contributing factors for simultaneous desulfurization and denitrification of diesel oil. They can be classified as (Figure 1): (a) hydrogen-bonding effect, (b) CH−π-bond interaction between cation and aromatic sulfur compounds,[55,57,59] (c) aromatic ring current effect, (d) dilution effect,[58] (e) electrostatic field effect,[59] (f) N (heteroaromatic)−H (imidazolium) hydrogen-bond interaction,[55−57] (g) S (heteroaromatic)−H (imidazolium) hydrogen-bond interaction,[55,56] and (h) anion effect.[59] Furthermore, there are anion effects which influences the structural phenomena such as the F (anion)−H (aromatic sulfur/nitrogen) interaction,[59] NH



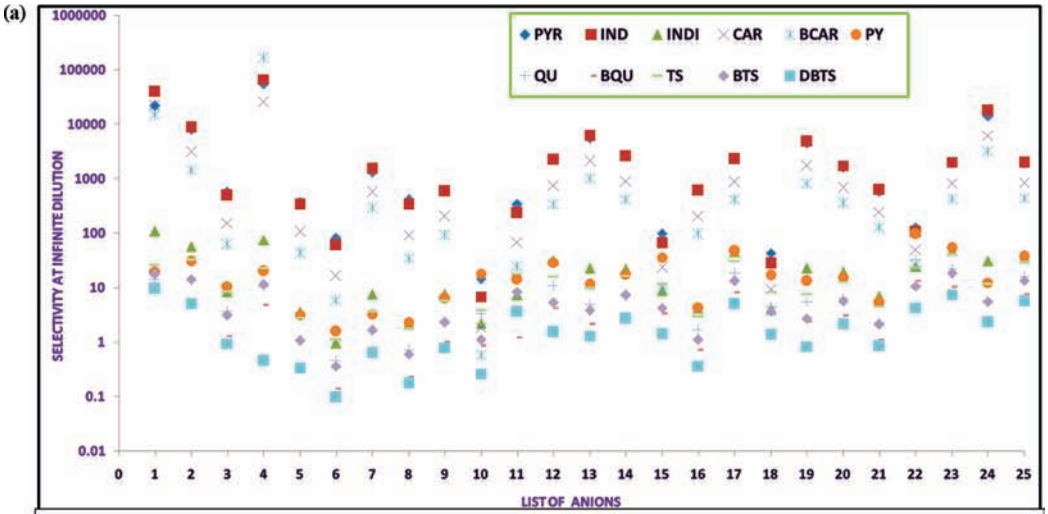
Specific simultaneous interaction forces for acidic sulfur and basic/non-basic nitrogen compounds with 1-ethyl-3-methylimidazolium nitrate ionic liquid

1]. C_2 (Cation) --- X (Anion) weak hydrogen bond interaction
2]. O (Anion) ----- H (Non-Basic/Basic Nitrogen)
3]. O (Anion) ----- S (Acidic Sulfur)
4]. H (Cation) ----- N (Basic Nitrogen)
5]. CH (Cation) ---- π (Acidic Sulfur)
6]. π (Cation) ----- π (Non Basic Nitrogen)

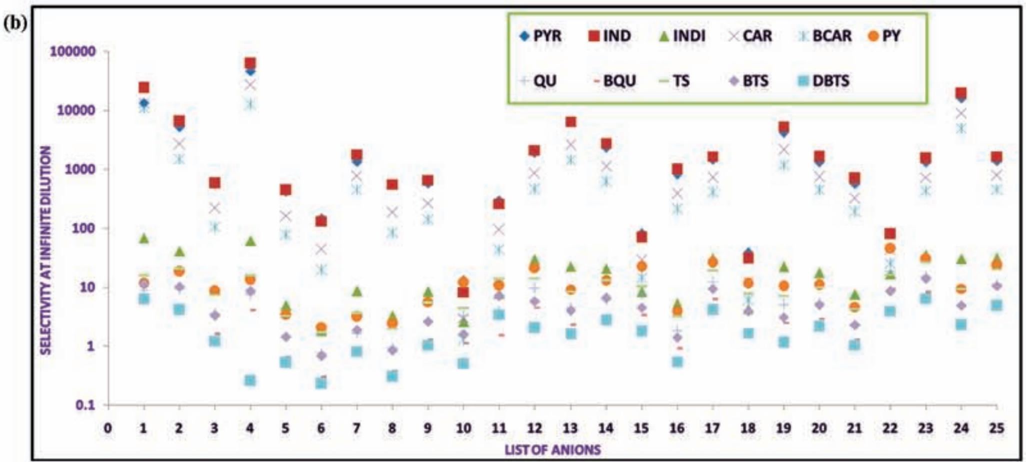
Figure 1. Schematic representation of specific interaction forces between IL ([EMIM][NT]) and acidic sulfur or basic and/or nonbasic nitrogen compounds (TS, PYR, PY); the arrow denotes the direction of electron cloud transfer.[56−58]

(aromatic nitrogen)−F (anion) interaction, higher sterical shielding effect,[56,60−62] and the presence of highly electronegative anions such as Cl and Br. The dilution effect refers to the weak ionic interaction between cation and anion due to the insertion of PY and TS molecules. Both of the molecules resemble the structure of the cation such as imidazolium. However, the dilution of IL by a neutral molecule such as TS is not expected to break apart the strong Coulombic interaction between cations such as [EMIM] and [PF_6]. It requires favorable molecular interaction between the dissolved molecules (TS and PY) and the ILs.[58] The following sections discuss the importance of various interaction factors for the simultaneous desulfurization and denitrification of diesel oil using ILs.

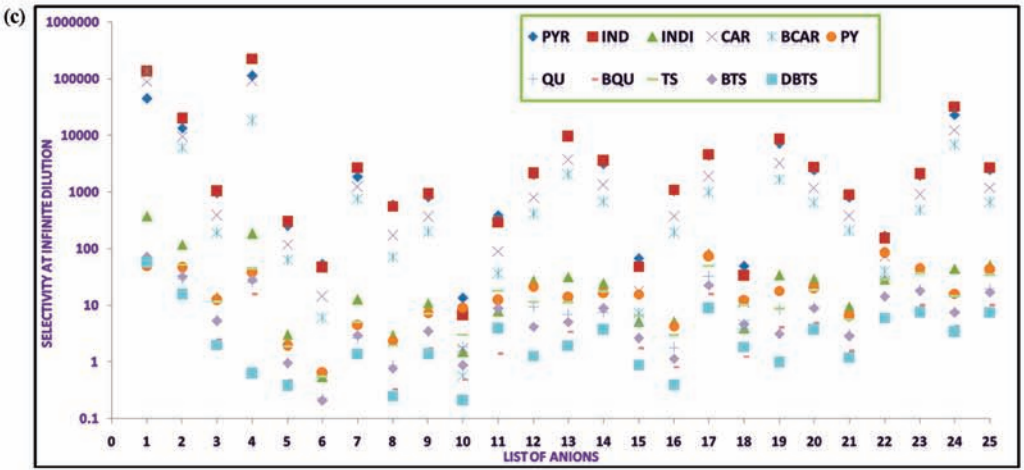
Benchmarking Using the Infinite Dilution Coefficient (IDAC). The comparison between experimental and predicted IDAC values has not been performed as it has been carried out extensively in our previous work.[33,55,57]In one of our earlier works[55] we have predicted the IDACs of TS in eight ILs, namely: [BMIM][BF_4], [BMIM][OSu], [BMIM][SCN], [OMIM][BF_4], [OMIM][Tf_2N], [BMIM][TFO], [BMIM][PF_6], and [EMIM][TOS] at various temperatures. We have calculated the root-mean-square (rms) error between reported and predicted selectivities for 20 points or solutes. The rms error was equal to 11 %. The equation for the rms values are the same as used by Klamt et al.[63] in his predictions of IDAC of solutes in ILs. It should be noted that the method is a priori and there will be deviation in selectivity; however, the change will be not significant. Further the observed rmsd is more consistent with the reported values of Klamt et al.[63]In our previous work[33] we have successfully compared and predicted the ternary LLE of 15 TS based IL systems with an average absolute deviation in rmsd of 10 %. With respect to nitrogen heterocyclic compounds in our prior work[57]



1. [Br], 2. [NO_3], 3. [SCN], 4. [CH_3COO], 5. [HSO_4], 6. [BF_4], 7. [CH_3SO_3], 8. [CF_3COO], 9. [CH_3SO_4], 10. [PF_6], 11. [CF_3SO_3], 12. [$C_2H_5SO_4$], 13. [$(CH_3)_2PO_4$], 14. [$C_3H_7NO_3S$], 15. [$B(CN)_4$], 16. [$C_7H_5O_3$], 17. [$(CH_3SO_2)_2N$], 18. [BC_2O_4], 19. [$C_4H_{10}O_4P$], 20. [$C_7H_7SO_3$], 21. [$C_7H_7SO_3$], 22. [$CF_3SO_2)_2N$], 23. [$C_5H_{11}SO_6$], 24. [$C_{10}H_{19}O_2$], 25. [$C_8H_{18}O_4S$].

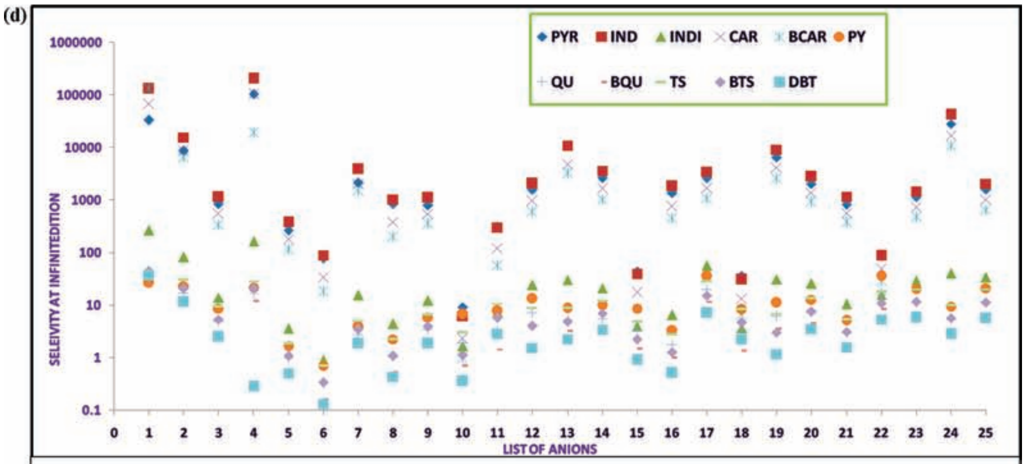


1. [Br], 2. [NO_3], 3. [SCN], 4. [CH_3COO], 5. [HSO_4], 6. [BF_4], 7. [CH_3SO_3], 8. [CF_3COO], 9. [CH_3SO_4], 10. [PF_6], 11. [CF_3SO_3], 12. [$C_2H_5SO_4$], 13. [$(CH_3)_2PO_4$], 14. [$C_3H_7NO_3S$], 15. [$B(CN)_4$], 16. [$C_7H_5O_3$], 17. [$(CH_3SO_2)_2N$], 18. [BC_2O_4], 19. [$C_4H_{10}O_4P$], 20. [$C_7H_7SO_3$], 21. [$C_7H_7SO_3$], 22. [$CF_3SO_2)_2N$], 23. [$C_5H_{11}SO_6$], 24. [$C_{10}H_{19}O_2$], 25. [$C_8H_{18}O_4S$].



1. [Br], 2. [NO_3], 3. [SCN], 4. [CH_3COO], 5. [HSO_4], 6. [BF_4], 7. [CH_3SO_3], 8. [CF_3COO], 9. [CH_3SO_4], 10. [PF_6], 11. [CF_3SO_3], 12. [$C_2H_5SO_4$], 13. [$(CH_3)_2PO_4$], 14. [$C_3H_7NO_3S$], 15. [$B(CN)_4$], 16. [$C_7H_5O_3$], 17. [$(CH_3SO_2)_2N$], 18. [BC_2O_4], 19. [$C_4H_{10}O_4P$], 20. [$C_7H_7SO_3$], 21. [$C_7H_7SO_3$], 22. [$CF_3SO_2)_2N$], 23. [$C_5H_{11}SO_6$], 24. [$C_{10}H_{19}O_2$], 25. [$C_8H_{18}O_4S$].

Figure 2. Continued



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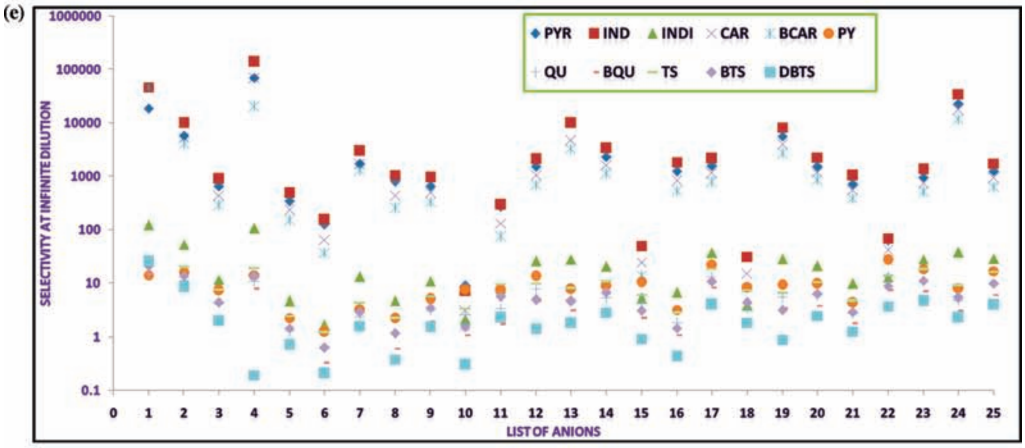

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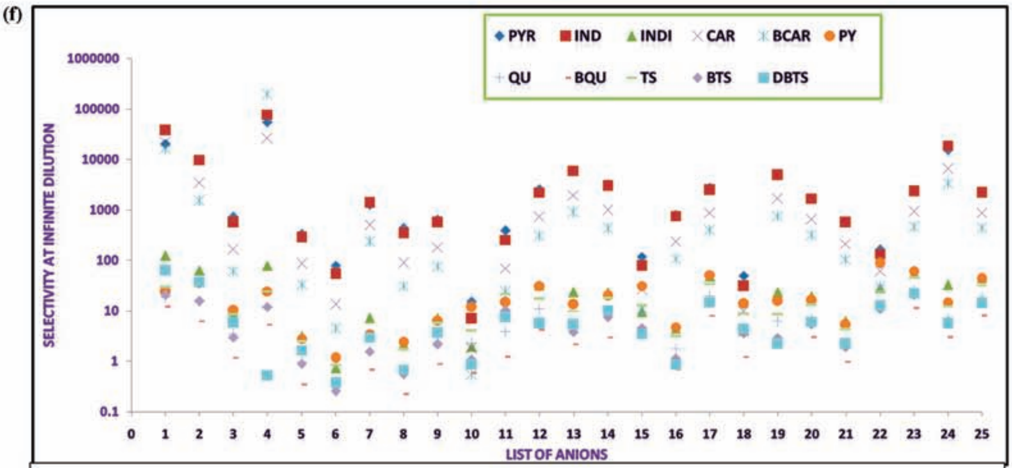

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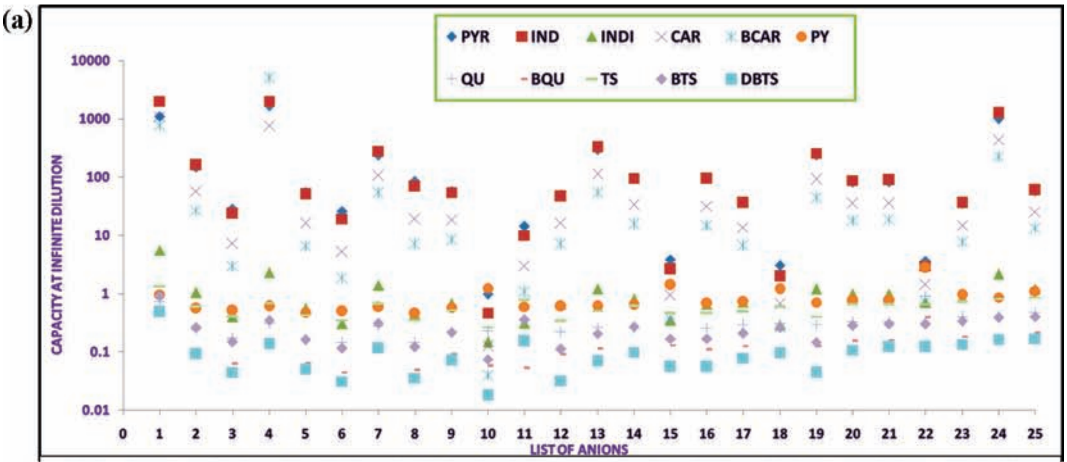
Figure 2. Selectivity at infinite dilution of aromatic nitrogen and refractory sulfur species in (a) [EMIM] cation-based ILs, (b) [EPY] cation-based ILs, (c) [EMMOR] cation-based ILs, (d) [EPYRO] cation-based ILs, (e) [EMPIP] cation-based ILs, and (f) [TMPYZO] cation-based ILs. *X*-axis legend: Anion numbers mentioned are as per Table 3.

(a)



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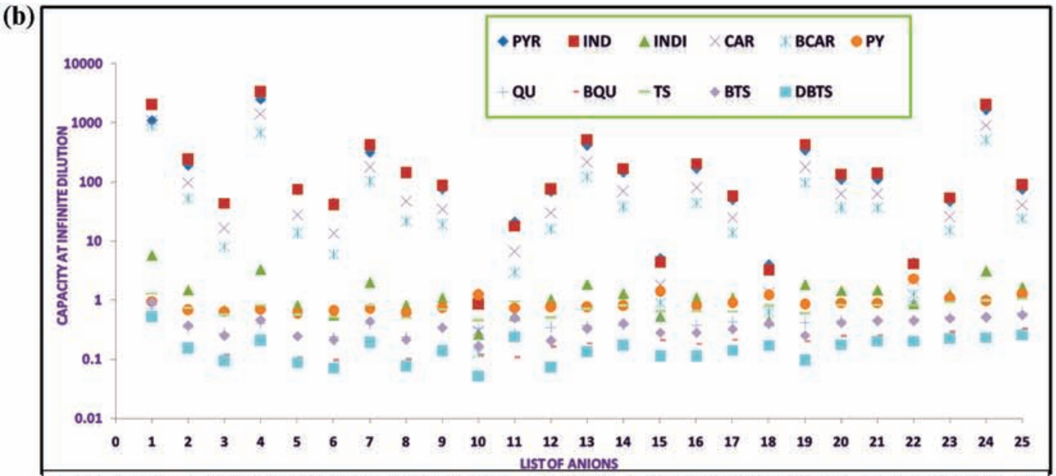
(b)



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(c)

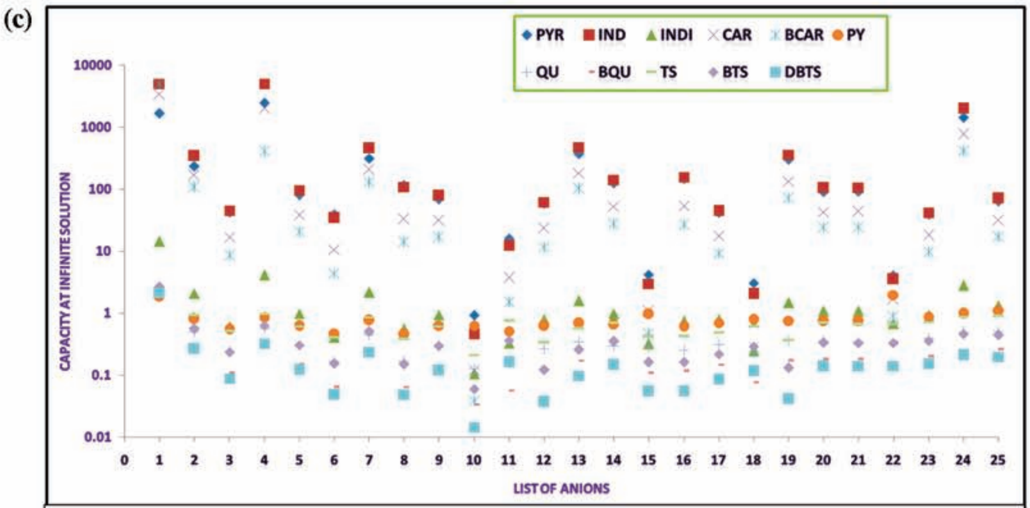

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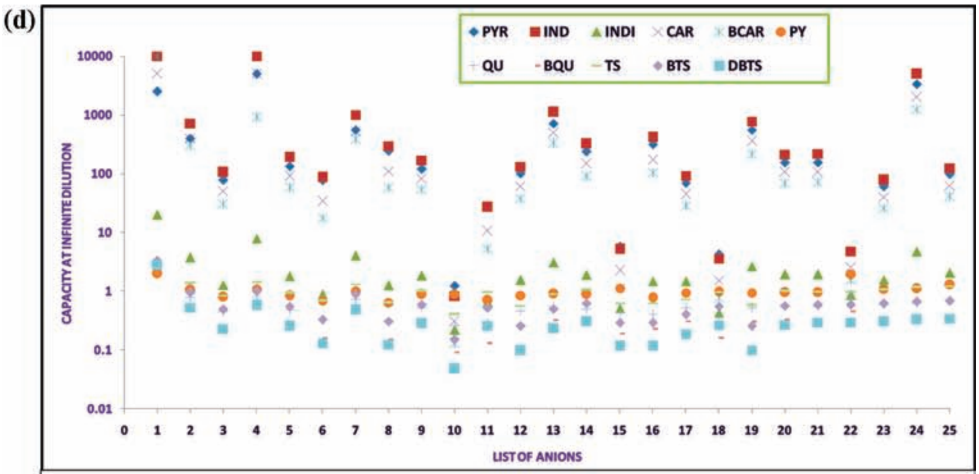
Figure 3. Continued



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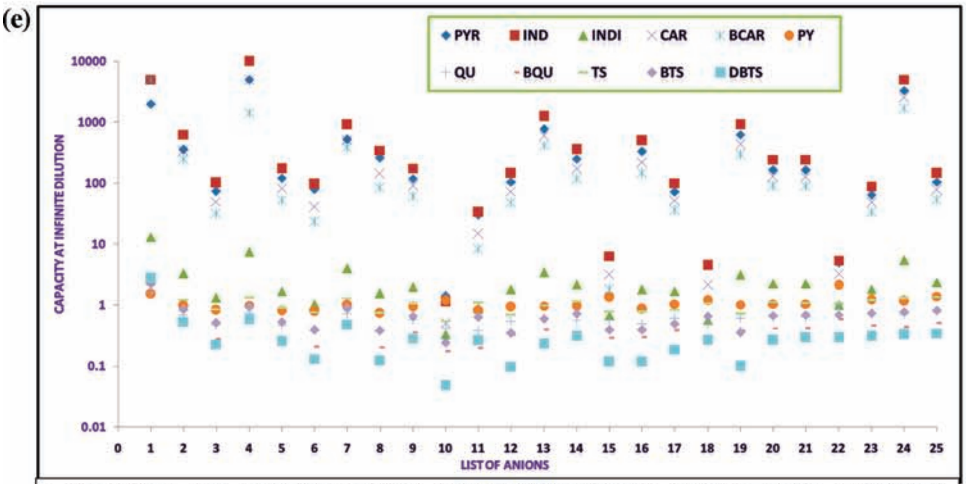

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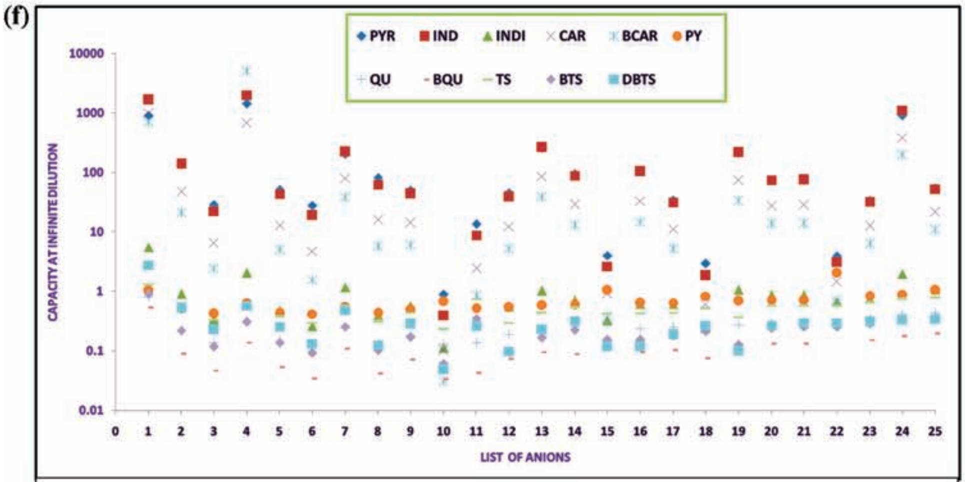

1. [Br], 2. [NO_3], 3. [SCN], 4. [CH_3COO], 5. [HSO_4], 6. [BF_4], 7. [CH_3SO_3], 8. [CF_3COO], 9. [CH_3SO_4], 10. [PF_6], 11. [CF_3SO_3], 12. [$C_2H_5SO_4$], 13. [$(CH_3)_2PO_4$], 14. [$C_3H_7NO_3S$], 15. [$B(CN)_4$], 16. [$C_7H_5O_3$], 17. [$(CH_3SO_2)_2N$], 18. [BC_2O_4], 19. [$C_4H_{10}O_4P$], 20. [$C_7H_7SO_3$], 21. [$C_7H_7SO_3$], 22. [$CF_3SO_2)_2N$], 23. [$C_5H_{11}SO_6$], 24. [$C_{10}H_{19}O_2$], 25. [$C_8H_{18}O_4S$].

Figure 3. Capacity of (a) [EMIM] cation-based ILs, (b) [EPY] cation-based ILs, (c) [EMMOR] for cation-based ILs, (d) [EPYRO] cation-based ILs, (e) [EMPIP] cation-based ILs, and (f) [TMPYZO] cation-based ILs for the removal of aromatic nitrogen and refractory sulfur species at infinite dilution. *X*-axis legend: Anion numbers mentioned are as per Table 3.

the IDAC values of PY in (1-butyl-3-methylimidazolium tetrafluoroborate) [BMIM][BF_4] and (1-ethyl-3-methylimidazolium tosylate) [EMIM][TOS] at various temperatures have been compared and predicted. The average rms error for all four points was equal to 15 % for [BMIM][BF_4] and 0.85 % for [EMIM] [TOS]. With the combined and extensive benchmarking we will now proceed in the screening of other potential ILs for simultaneous desulfurization and dinitrification studies.

Effect of Selectivity at Infinite Dilution. *Cation Influence.* The selectivity at infinite dilution of unsaturated acidic sulfur and basic/nonbasic nitrogen compounds in [EMIM] (Figure 2a), [EPY] (Figure 2b), [EMMOR] (Figure 2c), [EPYRO] (Figure 2d), [EMPIP] (Figure 2e), and [TMPYZO] (Figure 2f) with 25 anions was calculated using eq 3. The selectivity at infinite dilution was determined from the IDAC values of studied sulfur and nitrogen compounds in simulated diesel as well as ILs, respectively. We have chosen a smaller cation in our predictions, since these are proven to give high values of selectivity.[33,62]

It has been realized that the variation of the cationic core is a very valuable approach for tuning the behavior and structural phenomena of these compounds in a liquid mixture. In general [EMMOR], [EPYRO], and [EMPIP] based ILs gave lesser IDAC values as compared to [EMIM], [EPY], and [TMPYZO] based cations when compared with 25 anions (Figure 2a−f). This is due to the fact that [EMIM], [EPY], and [TMPYZO] consist of aromatic rings which possess aromatic steric hindrance toward similar aromatic ring structure of nitrogen species.[55,60,61] It should be noted that the cations possess higher π electron density. In the same manner the positive charge of nitrogen atom in the cation is delocalized over the aromatic ring. Both of the effects thus contribute to an increase in π electron density. In case of PY, the lone pair on the nitrogen atom is localized around their aromatic ring (PY).[64] Thus, when these two molecules comes close together then their higher π electron density increases the sterical hindrance. Thus the sterical hindrance arises from contribution ascribed to strain as the sum of (1) same charges repelling each other, (2) $\pi-\pi$ stretches or compression, and (3) maximum Coulomb effect.[59] This steric hindrance lowers the strength of N (heteroaromatic)−H (cation) hydrogen bond which ultimately decreases the selectivity. Further the electron-donating tendency through higher alkyl substitution in cations increases the delocalized π electron density within the cations, thereby providing a higher selectivity for the removal of nitrogen species. Thus, as discussed earlier the factors such as (a) electron donor tendency of [EMMOR], [EPYRO], [EMPIP], [EMIM], [EPY], and [TMPYZO] cations, (b) the aromatic structure of the cation without a hetero-ring, and (c) the number of electronegative atom (N, O, and S; similar or different) located on the aromatic structure of the cation are the deciding factors for IDAC values.

[EMIM], [EPY], or [TMPYZO] cations do exhibit higher aromaticity around their heterocyclic structure; however, the positive charges are spread over the aromatic ring.[60,64] From our previous work[56] the NBO (normal bonded orbital) analysis is used as an excellent tool for the investigation of partial charge transfer interaction within the parent compounds. On the basis of these partial charges, the difference in the hydrogen-bonding, electrostatic interaction, and CH−π bonding interaction is considered. Therefore, on the basis of the quantum chemical investigation, the CH groups can participate and play an important role in the simultaneous interaction of π based compounds such as TS and PY. The number of stable sites (i.e., hydrogen atom) having positive charges on the cation is 19, 16, and 13 for 1-butyl-4-methylpyridinium [BUMPY], 1-butyl-1-methylpyrolidinium [BUMPYR], and 1-benzyl-3-methylimidazolium [BeMIM] cations, respectively.

[EPYRO] and [EMPIP] cations do not exhibit high aromaticity due to the absence of a hetero-ring, but the positive e charge is localized on the nitrogen atom of the five- and/or six-membered heterocyclic [EPYRO] and [EMPIP] ring, respectively. [EMMOR] has a similar trend as [EPYRO] and [EMPIP], but there are two different electronegative atoms (N and O) located over the six-membered heterocyclic morpholinium ring.[60,61] An NBO calculation using HF/6-31G* for the morpholinium cation ([EMMOR]) gave a positive charge (0.65675) for the nitrogen atom and a negative charge (−0.3534) for the oxygen atom. Both of the opposing charges are delocalized in the ring which thus stabilizes and lowers the sterical hindrance effect. This agrees well with the work of Lava et al.[64] Therefore [EMMOR] (Figure 2c), [EPYRO] (Figure 2d), and [EMPIP] (Figure 2e) based ILs gave lower IDAC values, while higher IDAC values were observed by [EMIM] (Figure 2a), [EPY] (Figure 2b), and [TMPYZO] (Figure 2f) based cations. Thus, [EMMOR], [EPYRO], and [EMPIP] based ILs are the best choice for the removal of all kinds of aromatic nitrogen and sulfur compounds from diesel oil.

Anion Influence. The anion also plays an important role in increasing the selectivity and capacity of the ILs. There are several types of anions investigated in this work, such as halogenated, fluorinated, alkyl sulfonates, organo borates, alkyl sulfates, and heterocyclic (Table 2). It was found that the anion not only affects the selectivity but also affects the capacity of the ILs. It can be seen that the selectivity increases with increasing capacity (Figure 3a−f) by a given cation with all anions irrespective of nitrogen and sulfur compounds. The favorable anions are those having (a) highly electronegative nature, (b) a different number of electronegative atoms at the anion structure, and (c) symmetry with high negative charges or higher basicity. Additional factors such as anion structure with longer alkyl substitution and higher sterical shielding effect around the anion charge center are also pivotal in the anion performance.[65] Anions such as [SCN], [BF_4], [PF_6], [BiSu], [Ac], and [MeSu] (Figure 2a−f) increase the hydrogen-bond acceptors, though not significantly. Tosylate [TSy] and salicyclate [SCy] anions having alkyl substitution at the aromatic anion structure should be favorable in increasing the overall performance of the IL. The addition of the methyl group at tosylate and salycilate anion structure enhances the van der Waals repulsive force in which the interaction between cation and anion is decreased. The hydrogen atom of anion interacts with the nitrogen atom of PY and with the sulfur atom of TS molecules. Further the partial charge of the hydrogen atom is delocalized over the aromatic ring structure of tosylate and salycilate anions which leads to an increase in the possibility of $\pi-\pi$ stacking or interaction between similar structures of anion (tosylate and salycilate) with TS/PY molecules. It is observed that the methyl group substitution at anion structure has a significant influence on the overall performance of the ILs. This agrees well with the study of Lei et al.[65] The effect of aromaticity is higher in ILs with a similar structure of PY/TS molecules. Further the partial charge of hydrogen, sulfur, and oxygen atoms are not completely delocalized over the anion structure, thereby reducing the interactions between the cation and the anion with sulfur/nitrogen species. This decreases the selectivity and capacity for these anions.

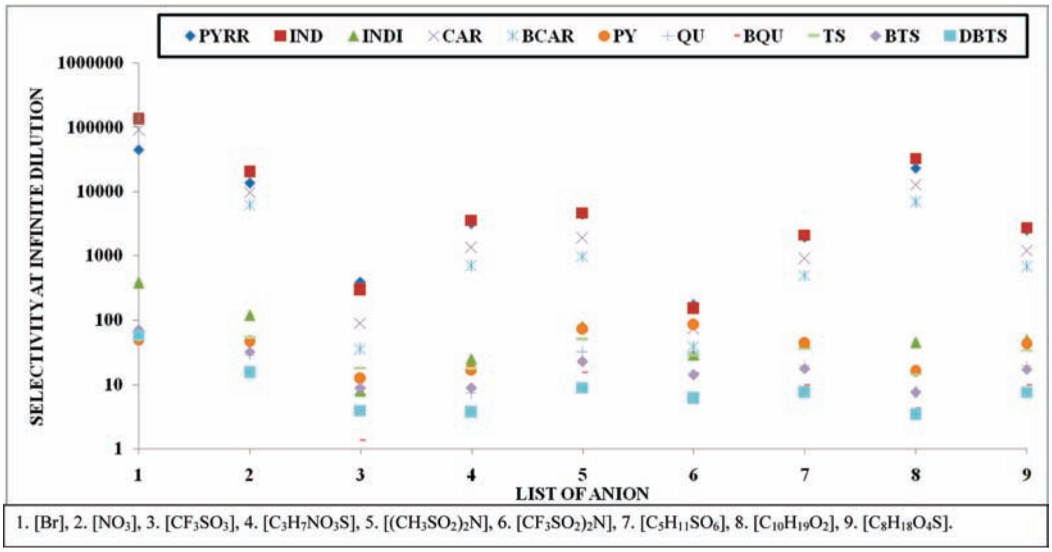

Figure 4. Selectivity at infinite dilution of aromatic nitrogen species and refractory sulfur species in [EPYRO] based ILs.

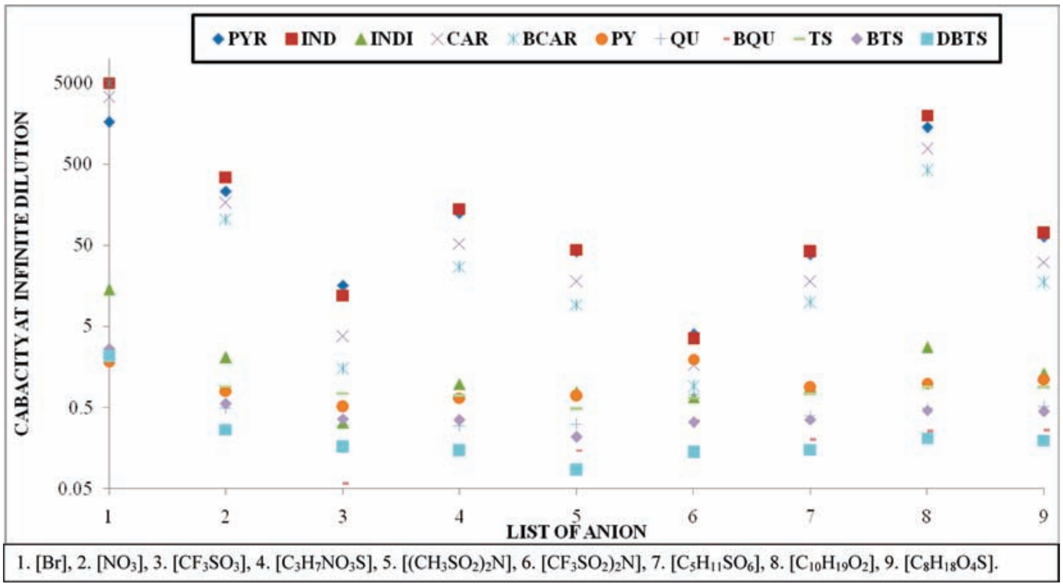

Figure 5. Capacity at infinite dilution of aromatic nitrogen species and refractory sulfur species in [EPYRO] based ILs.

The selectivity at infinite dilution of the five-membered ring of sulfur and nitrogen species in ILs strongly depends on the charge center of the anion. The anion charge center is known to exhibit a higher sterical shielding effect.[65] The shielding effect of anion decreases in the following order:[57] [Br] > [NT] > [TfO] > [MS-ACN] > [BMA] > [Tfi] > [Me-Et-EtSu] > [DeC] > [OcSu]. It is noted that the halogenated ILs gave the highest selectivity. However the fluorinated ILs produce HF at moderate temperatures when in contact with water or moisture. This limits their application in processes which uses high temperatures or in aqueous solution. So we would not recommend such an IL for desulfurization or denitrification.

In the nitrate ([NT]) anion, the central atom of nitrogen has a charge of +1.272 (obtained via ESP or CHELPG fit via HF/6-31G* theory), while the oxygen has a charge of −0.757 each oxygen atom. This is higher than that of fluorine atom in [BF_4] (B = 1.225715, F = −0.556151) and [PF_6] (P = 1.721851, F = −0.454266).[59] In the case of the [NT] anion, the positive charge of nitrogen atom is delocalized with three oxygen atoms, and therefore the negative charge of oxygen atom is −0.757 as compared to the fluorine atom in [BF_4] (−0.556151) and [PF_6] (−0.454266). Therefore, cations with [NT] possess higher selectivity as compared to cations with [BF_4] or [PF_6]. Thus with a higher negative charge it can form O(anion)−H(PY/TS) interactions more strongly as compared to [BF_4] or [PF_6] (Figure 2a−f).

On the basis of the above factors, anions such as [Br], [NT], [TfO], [MSACN], [BMA], [Tfi], [Me-Et-EtSu], [Dec], and [OcSu] gave high values of selectivity and capacity irrespective of cations. To compare the performance, the selectivity and capacity has been plotted with respect to the potential cation, that is, [EMMOR] cation as obtained earlier (Figures 4 and 5). It can be seen that the selectivity/capacity increases from [Br] to [TfO] due to the shielding effect of the anions which decreases

Table 4. Maximum and/or Minimum Selectivity and Capacity for Studied ILs

name	limitation	selectivity (S)	capacity (C)	better ILs for aromatic nitrogen and refractory sulfur species removal in single step	
				selectivity (S)	capacity (C)
PYR	maximum	44651	1667	[EMIM][Br]	[EMMOR][Br]
	minimum	63	4	[EMIM][BTA]	[EMIM][BTA]
IND	maximum	46639	10000	[EMPIP][Br]	[EPYRO][Br]
	minimum	69	3	[EMPIP][BTA]	[EMIM][BTA]
INDI	maximum	380	14	[EMMOR][Br]	[EMMOR][Br]
	minimum	7	1	[EMIM][TfO]	[TMPYZO][BTA]
CAR	maximum	89303	5000	[EMMOR][Br]	[EPYRO][Br]
	minimum	41	2	[EMPIP][BTA]	[EMIM][BTA]
BCAR	maximum	133955	10000	[EMMOR][Br]	[EPYRO][Br]
	minimum	24	1	[TMPYZO][TfO]	[EMIM][BTA]
PY	maximum	97	3	[EMIM][BTA]	[EMIM][BTA]
	minimum	8	0.21	[EMPIP][TfO]	[EMIM][NT]
QU	maximum	56	3	[EMMOR][Br]	[EPYRO][Br]
	minimum	3	0.10	[EPYRO][TfO]	[EMIM][NT]
BQU	maximum	56	3	[EMMOR][Br]	[EPYRO][Br]
	minimum	2	0.21	[EMIM][TfO]	[EMIM][NT]
TS	maximum	66	3	[EMMOR][Br]	[EPYRO][Br]
	minimum	10	0.53	[EMPIP][TfO]	[TMPYZO][BMA]
BTS	maximum	70	3.5	[EMMOR][Br]	[EPYRO][Br]
	minimum	5	0.21	[EPY][Dec]	[EMIM][BMA]
DBTS	maximum	58	3	[EMMOR][Br]	[EPYRO][Br]
	minimum	2	0.07	[EMPIP][Dec]	[EMIM][BMA]

via [Br] > [NT] > [TFO] (refer Figure 1). However for [$C_3H_7NO_3S$] ([MSACN]) and [$(CH_3SO_2)_2N$]([BMA]) the selectivity increases since an extra alkyl group is added which increases the shielding effect or increases the electronegativity. Similarly for [$(CF_3SO_2)_2N$]([BTA]) and [$C_5H_{11}SO_6$] ([Me-Et-EtSu]), the alkyl group vanishes, and the selectivity again is lowered because of decrease in shielding effect. The only exception is [OcSu] having higher alkyl substitution, which thus contributes to higher selectivity via dominant H-bonding.

Heterocyclic Structure Influence. Unsaturated nonbasic nitrogen compounds (Figure 2a−f) gave a higher selectivity at infinite dilution as compared to unsaturated acidic (BTS) and basic (BQU) compounds. It can also be observed that sulfur compounds having a similar structure with heterocyclic cations like [EMIM] and [EPYRO] do not show any significant increase in selectivity with sulfur or nitrogen compounds. The anion selection plays a significant role within the cation, for example, the maximum selectivity at infinite dilution of PYR is 44651 in [EMIM][Br], whereas the minimum value of PYR is 63 in [EMIM][BTA] (Table 4). The maximum and minimum values of selectivity for all of the sulfur/nitrogen species are summarized in Table 4. In Figure 2a−f it is seen that the selectivity of nonbasic nitrogen such as INDI, PYR, CAR, and BCAR is quite higher than that of the six-membered nitrogen ring such as PY, QU, and BQU (Figure 4). The suphur species in general show a lesser selectivity as compared to six- or five-membered nitrogen species.

Basic nitrogen compounds like PY structurally related to benzene have a smaller π-delocalized electron density where the negative charge is localized on the nitrogen atom. Therefore, high IDAC values were observed as compared to the nonbasic nitrogen compounds irrespective of the size of the cation and anion (Figure 2a−f). It was noted that [DMP], [BTA], [OcSu], and [MSACN] anions having different electronegative atom such as N (nitrogen), O (oxygen), and S (sulfur), and therefore the anions play a significant role in increasing the selectivity. This is because of their ability in forming different hydrogen bonds such as N−H and O−H between the nitrogen heterocyclic and the anion, especially when the cation structure (cation−anion interaction) influence is weak (Figure 1). Table 4 shows that [EMIM] based cation gave higher selectivity for PY as compared to other cations, while the [EMMOR] cation shows higher selectivity for QU, BQU, TS, BTS, and DBTS. Their maximum selectivity values are: S_{QU} = 56, S_{BQU} = 56, S_{TS} = 66, S_{BTS} = 70, S_{DBTS} = 58. The minimum selectivity values are as follows: S_{QU} = 3 ([EPYRO][TfO]), S_{BQU} = 2 ([EMIM][TfO]), S_{TS} = 10 ([EMIM][TfO]), S_{BTS} = 5 ([EPY][Dec], S_{DBTS} = 2 ([EMPIP][Dec]).

Effect of IL Capacity at Infinite Dilution. The IL capacity at infinite dilution was compared among [EMIM] (Figure 3a), [EPY] (Figure 3b), [EMMOR] (Figure 3c), [EPYRO] (Figure 3d), [EMPIP] (Figure 3e), and [TMPYZO] (Figure 3f) based cations with 25 anions. The capacities at infinite dilution were predicted using eq 5, and the results are shown in Figure 3a−f. Evidently, [EMMOR] (Figure 3c) and [EPYRO] (Figure 3d) have a higher solvent capacity at infinite dilution irrespective of the aromatic nitrogen and sulfur compounds. It should be noted that [EPYRO] (Figure 3d) consists of low π-delocalized electron clouds with a positive charge localized on the nitrogen atom of the five-membered heterocyclic pyrrolidinium ring. This enables to retain a significant amount of sulfur/nitrogen species within its interstitial volume. In a similar manner, [EMMOR] (Figure 3c) has a low π-delocalized electron density. Thus, the positive and negative charges are localized on both the nitrogen and oxygen atom of the six-membered heterocyclic morpholinium ring.[64]

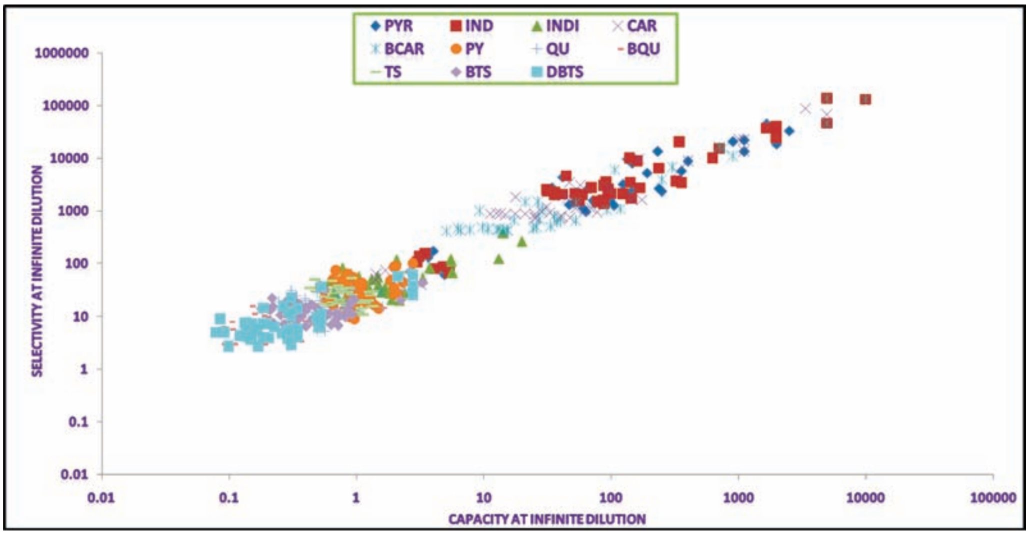

Figure 6. Selectivity versus solvent capacity at infinite dilution for [EMIM], [EPY], [EMMOR], [EPYRO], [EMPIP], and [TMPYZO] based cations with the combination of [Br], [NT], [TFO], [MSACN], [BMA], [BTA], [Me-Et-EtSu], [Dec], and [OcSu] based anions.

Thus it can easily form weak hydrogen bond interaction as well as CH−π bond interaction between cation and different aromatic ring of nitrogen and sulfur compounds.

It can be seen that under a given anion the capacity decreases in the order of: [EPYRO] ≈ [EMMOR] < [EMPIP] < [EMIM] < [TMPYZO] < [EPY]. However, it can be seen that the favorable anions are those having a higher electron acceptor tendency and highly electronegative nature such as halogenated ions [Br] and [NT]. On the other hand, the unfavorable anions are those where sterical shielding effect around their charge centers do not exist or is very less,[65] for example, for [TfO], [MSACN], [BMA], [BTA], [Me-Et-EtSu], [Dec], and [OcSu]. However, the anion without a hetero-ring such as [Dec] and [OcSu] increases the capacity (Figures 4 and 5) irrespective of the nitrogen and sulfur compounds. This is due to the fact that they inhibit the positive charges of cation to approach the negative charges of anions in the IL itself. They allow the negative charges of anion to approach the positive charge of hydrogen atom on the aromatic ring of PYR/PY/TS.[55−57] As discussed earlier, the salicylate [Scy] and tosylate [TSy] anions, being aromatic in nature, possess methyl substitution in its ring. This is unfavorable in increasing the selectivity and capacity.

The results obtained for removal of aromatic nitrogen and sulfur from model diesel oil are given in Table 4. [EMMOR][Br] and [EPYRO][Br] IL show the maximum capacity for all of the studied compounds. Figure 6 shows that the comparison between capacity and selectivity of the potential cation, that is, [EPYRO] (obtained in the section 2.2 Effect of Selectivity at Infinite Dilution) when combined with potential anions such as [Br], [NT], [TfO], [MSACN], [BMA], [BTA], [Me-Et-EtSu], [Dec], and [OcSu] anions. All of the effective cation and anion combinations of ILs show a linear trend, which indicates that IL identification requires knowledge of structural phenomena as well as the location of alkyl substitution at the cations or anions. Thus, [EPYRO][Br] is the best among all of the solvents investigated from the viewpoint of capacity, but there is not much difference between[EPYRO], [EMMOR], and [EMPIP] based ILs for the simultaneous removal of sulfur and nitrogen.

Effect of Heteroatom of Pyrrole, Thiophene, and Pyridine. It was found that among all the three compounds, PYR has higher interaction with all studied ILs because of its hydrogen bond donor tendency toward the aprotic anions and comfortable packing with the polar or protic cation of an IL.[60,61] It should be noted that the lone pair of electrons of the nitrogen atom is delocalized and is contributed over the whole aromatic ring. For TS, the lone pair of electron is delocalized over the five-membered TS ring, and it is responsible for higher acidity of these homologues species. For PY, the lone pair of electrons is localized on the nitrogen atom of the six-membered pyridinium ring and can extend in the plane of the ring. This delocalized electron is responsible for the basicity of these nitrogenous bases. [54] Like TS, PY can also form hydrogen bonding, CH−π bonding, and π−π interaction. But when TS and PY molecules are compared with PYR, the interactions are very less in magnitude. For example, the selectivity of PYR is higher for those cations having lower steric hindrance, namely, [EPYRO] (Figure 2d), [EMPIP] (Figure 2e), and [EMMOR] (Figure 2c).

The addition of one or two six-membered benzene rings fused on either side of PYR or TS and/or PY ring induce more sterical hindrance due to the additional π delocalized electron clouds. The higher sterical hindrance of the substituted six-membered ring is a disadvantage over their structural relationship with heterocyclic ring cations such as [EMIM], [EPY], [TMPYZO], [EPYRO], [EMPIP], and [EMMOR]. These planar fused structures reduce the highly localized electron tendency on nitrogen atom and/or sulfur atom of the six-membered PY and five-membered TS ring. Thus a combination of weak structural and intramolecular interaction results in a lower selectivity and capacity at infinite dilution of IL (Figure 2a−f; Figure 3a−f). For example, QU, BQU, BTS, and DBTS with higher steric hindrance and highly delocalized π electron clouds have low IDAC values when compared with cations such as [EPYRO] (Figure 2d), [EMPIP] (Figure 2e), and [EMMOR] (Figure 2c). It was found that the nonsubstituted hetero-ring, that is, [EPYRO], [EMPIP], and [EMMOR] cations show strong interaction since the positive charge of the cation is more localized on the nitrogen and/or oxygen atom of the five/six-membered ring of [EPYRO], [EMPIP], and [EMMOR] cations.

CONCLUSION

In this work, we have investigated six different types of heterocyclic cations, such as [EMIM], [EPY], [TMPYZO], [EPYRO], [EMPIP], and [EMMOR]. These cations are combined with several types of anions, namely, halogenated, fluorinated, alkyl sulfonates, organoborates, alkyl sulfates, and heterocyclic anions. [EPYRO], [EMPIP], and [EMMOR] based ILs showed higher selectivity and capacity for the simultaneous removal of acidic heterocyclic sulfur and basic and nonbasic heterocyclic nitrogen compounds from simulated diesel oil. The lower steric hindrance of the nonsubstituted hetero-ring such as [EMMOR] increases its ability to accept/donor hydrogen bonds. Thus [EPYRO], [EMPIP], and [EMMOR] cations form hydrogen bonds with other aromatic acidic, basic, and nonbasic compounds. On other hand, the halogenated anions, that is, [Br] or [Cl] and anions such as [$EtSO_4$] and [NT] possessing more heteroatoms gave a higher selectivity and capacity. Anions with longer alkyl chains (i.e., [Dec] or [OcSu]), with or without heterocyclic anions, gave low values of selectivity and capacity. Moreover, it is observed that the molecular rearrangement in the ILs strongly depends on the possibility of hydrogen bond formation between the cationic rings themselves and with other heterocyclic compounds. Thus the potential ILs chosen for simultaneous desulfurization and dinitrification are: [EPYRO], [EMPIP], and [EMMOR] cations with the combination of [Br], [NT], [TfO], [MSACN], [BMA], [BTA], [Me-Et-EtSu], [Dec], and [OcSu] anions. With respect to environmental considerations, the fluorinated and nitrated anions are of limited use in industrial applications due to its hydrolytical instability. Therefore, the recommended IL should consist of nonfluorinated and nitrated anions such as alkyl acetates, alkyl sulfonates, alkyl sulfates, and organoborates for the large scale production of nitrogen and sulfur free diesel oil.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Physical and chemical properties of aromatic nitrogen and sulfur compounds. The infinite dilution activity coefficients (IDACs) of all of the compounds in 6 cations and 24 anions are also given. This material is available free of charge via the Internet at http://pubs.acs.org.

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NOMENCLATURE: LIST OF SYMBOLS

[EMIM]	1-ethyl-3-methylimidazolium
[EPY]	1-ethylpyridinium
[EPYRO]	1-ethylpyrrolidinium
[EMMOR]	4-ethyl-4-methylmorpholinium
[EMPIP]	1-ethyl-1-methylpiperidinium
[TMPYZO]	1,2,4-trimethylpyrazolium
C	solvent capacity
S	solvent selectivity
PI	performance index
a_{eff}	effective contact surface area of a segment in $Å^2$
c_{hb}	hydrogen bonding coefficient
$p_i(\sigma)$	probabilistic surface charge distribution for pure component (i)
$p_s(\sigma)$	probabilistic surface charge distribution for mixture (s)
T	temperature in K
x	mole fraction in liquid phase

GREEK SYMBOLS

σ	screening charge density in $e \cdot Å^{-2}$
α'	misfit constant in $kJ \cdot mol^{-1} \cdot Å^{-2}$
σ_{hb}	cut-off screening charge density for hydrogen bonding in $e \cdot Å^{-2}$

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