Solvent Evaluation for Desulfurization and Denitrification of Gas Oil Using Performance and Industrial Usability Indices

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A new strategy for screening of solvents for sulfur, nitrogen, and aromatic compounds removal from gas oil is presented. This ranking is based on comparative assessment of solvents' capacity, selectivity, performance, and newly defined industrial usability indices. Twenty eight solvents comprising of six most widely used industrially proven conventional solvents and 22 imidazolium-based ionic liquids solvents were selected to illustrate the strategy. The solvents were ranked for removal of sulfur compounds namely benzothiophene, dibenzothiophene and their alkylated derivatives, and nitrogenous compounds namely quinoline, indole and carbazole from gas oil. Performance index (P_I) which combines the effect of both capacity and selectivity seems to be better index than individual capacity and selectivity indices to rank the solvents. Industrial usability index (S_{IUI}) of solvents which includes P_I and process complexity factor for solvent recovery section seems more practical and realistic criteria for solvent assessment. © 2015 American Institute of Chemical Engineers *AIChE J*, 61: 2257–2267, 2015

Keywords: solubility parameters, heat of vaporization, performance index, industrial usability index of solvent, desulfurization

Introduction

Gas oil consists of a mixture of paraffins, cycloparaffins, aromatics, sulfur, and nitrogen compounds along with metal impurities. Presence of aromatics, sulfur, and nitrogen compounds in gas oil generate hazardous emissions in environment and adversely affect the performance of emission control technologies during its combustion in the engine.[1–8] This compels the oil industries to produce the sulfur, nitrogen, and polyaromatics free gas oil. Hydroprocessing is most widely used commercial process to remove these impurities. However, the requirement of very severe operating condition and huge investment and operational cost in hydroprocessing stimulate the immense research interest in development of less energy and capital intensive alternative and complementary methods for production of ultraclean gas oil. Extraction method for production of lighter aromatics such as benzene, toluene, and xylene from reformate and pyrolysis gasoline is well-established in hydrocarbon industries. However, its application for removal of sulfur and aromatics from gas oil range hydrocarbon is under research and development stage.

Selection of a suitable solvent is of great importance in this process as it not only governs the quality of products but also controls the initial and operational investment. The success of commercial process depends on the performance of the solvent during the extraction process. Selection of solvent for separation of a specific compound from a mixture depends on its various properties.[9–13] Experimental evaluations of solvents for sulfur and aromatic removal from gas oil is extensively time and resource consuming in comparison to computational methods. There are some computational studies reported for screening the ionic liquid (IL)-based solvents for removal of sulfur and nitrogen compounds from model diesel using the COSMO-RS software from gas oil range material.[14–16] In these studies, effect of type of anions and cations present in ILs on the capacity and selectivity of ILs for removal of sulfur and nitrogen compounds was shown. These studies were performed only for thiophene (boiling point = 84°C), benzothiophene (boiling point = 221°C), and dibenzothiophene (boiling point = 332°C) sulfur compounds. It is important to note that gas oil components having boiling point up to 370°C contain alkylated derivatives of benzothiophene and dibenzothiophene which are more difficult to remove than benzothiophene and

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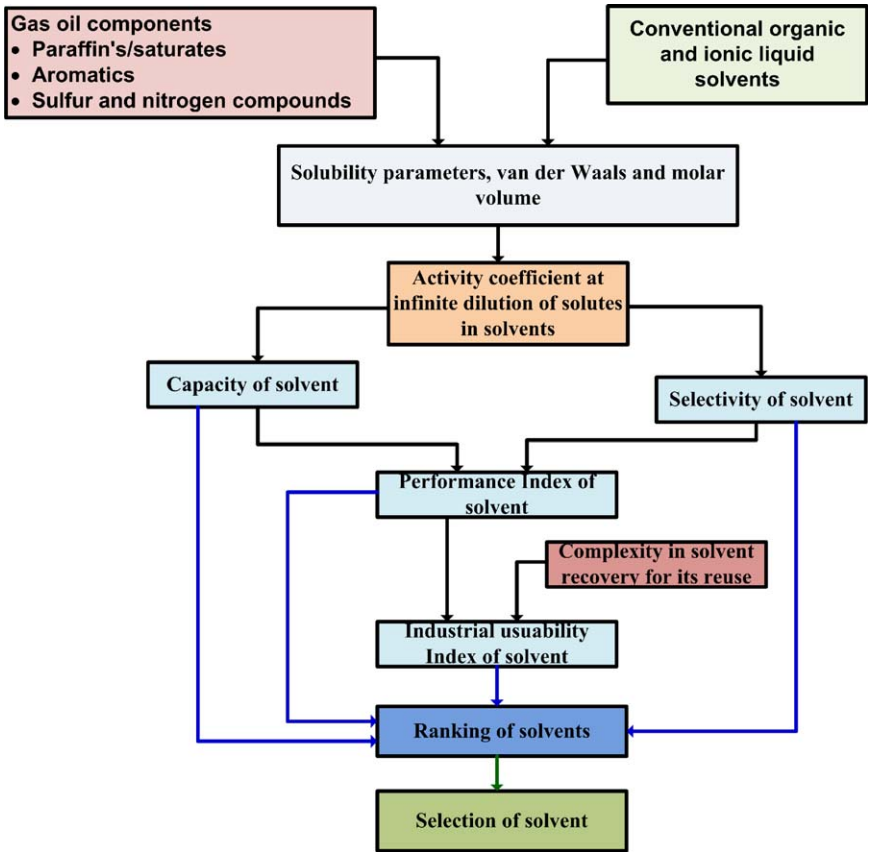

Figure 1. Schematic of strategy for evaluation of solvents for sulfur and nitrogen compounds removal from gas oil.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

dibenzothiophene. It is reported that the hydrotreating difficulty of sulfur compounds increases in the order: benzothiophene < 2/7 methylbenzothiophene < dibenzothiophene < 4 methyldibenzothiophene < 4,6 dimethyldibenzothiophene.[17] Solubility of compounds in solvent depends on their mutual interaction and structures. This suggests that capacity and selectivity of solvent for different sulfur compounds will be different. Moreover, solvent is recovered from raffinate and extract phases in solvent extraction for its reuse in the process. The capital and operational cost for solvent recovery will greatly depend up on simplicity of solvent recovery section design and its operation.

The molar volume (V_m) and solubility parameters (δ) of gas oil compounds are required to estimate their standard heat of vaporization and solubility of these compounds in solvents. Therefore, these parameters are of immense interest to the researchers and have not been reported in the literature. Moreover, capacity, selectivity, and performance (capacity $\times$ selectivity) indexes for alkylated derivatives of benzothiophene and dibenzothiophene which are highly refractive in hydrotreatment have also not been estimated and reported in the literature neither for ILs nor for conventional solvents. Anantharaj and Banerjee[15] used performance index (P_I) of IL solvents only for their rating for sulfur and nitrogen compounds removal and conventional solvents were not included. To the best of authors' knowledge, no study is reported in the literature which considers the effect of complexity of section to be used for solvent recovery for its reuse which affects the extraction process capital and operating cost significantly. It may be the reason that solvent showing better P_I (capacity $\times$ selectivity) than widely used conventional solvents could not be commercialized in the industry. Also, no researcher carried out a computational solvent screening study for sulfur and nitrogen compounds removal from gas oil with industrially proven conventional solvents and IL solvents using the same platform.

Considering these research gaps, a new strategy for a realistic and practical screening of solvents for removal of highly refractory sulfur and nitrogen compounds from gas oil has been evolved (Figure 1) and presented in this study. Two major class of solvents vis a vis conventional organic solvents and ILs are used for aromatic, sulfur, and nitrogen compounds removal from hydrocarbon streams.[18–23] Six most widely used industrially proven conventional organic solvents and 22 imidazolium-based IL solvents were selected for removal of benzothiophene, dibenzothiophene and their alkylated devrivatives, and nitrogen compounds from gas oil. The solubility parameters, molar volume, van der Waals volume of sulfur, aromatics, and nitrogen compounds which can represent the gas oil were estimated using ab initio molecular dynamics method using commercial software material studio 7.0 and Aspen HYSYS software. These parameters were used for estimating the standard heat of vaporization and activity coefficients at infinite dilution of model gas oil compounds in solvents using available correlations. The capacity, selectivity, and P_I of solvents were estimated for selected sulfur and nitrogen compounds. To understand the effect of complexity of solvent recovery section on their industrial utilization, two type of solvent recovery sections were conceptualized for recovering of solvents one having boiling point lower than gas oil and the other for solvents having boiling point in the range gas oil distillation. Based

on complexity of recovery section, a new industrial usability index (S_{IUI}) of solvent was defined and used for their rating for sulfur and nitrogen compounds from gas oil.

Theory

Solubility parameters, activity coefficient at infinite dilution, capacity, and selectivity of solvents

The Hildebrand solubility parameter is derived from the cohesive energy density of the compound, which in turn is derived from the heat of vaporization[24,25]

$$\delta=\sqrt{\Delta E_{\mathrm{ced}}}=\left[\frac{\Delta H_{\mathrm{v}}-RT}{V_{\mathrm{m}}}\right]^{1/2} \tag{1}$$

where, δ is the Hildebrand solubility parameter; ΔE_{ced} is the cohesive energy density; ΔH_{v} is the enthalpy of vaporization; R is the universal gas constant; T is the absolute temperature, and V_{m} is the molar volume.

Activity coefficient at infinite dilution of solute in solvents plays an important role in understanding of solvent extraction process. The correlation of the activity coefficients at infinite dilution is represented by a two-term equation[26,27]

$$\begin{aligned}\ln \gamma_i^{\infty}=\ln \gamma_i^{\infty\mathrm{comb}}+\ln \gamma_i^{\infty\mathrm{res}}=\ln\left(\frac{r_{\mathrm{vwdi}}}{r_{\mathrm{vwds}}}\right)^{2/3}\\ +1-\left(\frac{r_{\mathrm{vwdi}}}{r_{\mathrm{vwds}}}\right)^{2/3}+\left(\frac{V_{\mathrm{mi}}}{RT}\right)(\delta_{\mathrm{i}}-\delta_{\mathrm{s}})^2\end{aligned} \tag{2}$$

where, r_{vwdi} represents van der Waals volume of solute, r_{vwds} represents van der Waals volume of solvent, and V_{mi} represents molar volume of solute.

Capacity (or loading capacity) of the solvent means the maximum concentration of solute that a solvent can contain under specified conditions. The capacity signifies the ability of solvent to dissolve maximum amount of solute.[16] It can be defined in term of activity coefficient at infinite dilution as[15]

$$\begin{aligned}&\text{Capacity of solvent } (C_{\mathrm{i}})\\ &=\frac{\text{Amount of desired impurities removed}}{\text{Amount of solvent}}=\frac{1}{\gamma\infty_{i\mathrm{sp}}}\end{aligned} \tag{3}$$

where, i, sp and γ^{∞} denote the solute name, solvent rich phase, and activity coefficients at infinite dilution.

The selectivity of solvent shows the tendency of component i to be extracted more readily from carrier phase to solvent phase than component j. Selectivity is defined as the ratio of the composition (mole/weight fraction) of solute (sulfur and nitrogen compounds) in the extract rich solvent phase and its composition in raffinate (gas oil) phase. For liquid-liquid extraction process, it can be defined as the ratio of distribution coefficients of components i and j. It is important to mention that if the solvent used is not very soluble in feed phase, the activity coefficients of components i and j in carrier phase will be nearly independent of the nature of the solvent. The selectivity of the solvent for solute i with respect to solute j can be expressed using the equation[15]

$$\begin{aligned}\text{Selectivity}=S_{ij}&=\left(\frac{\gamma\infty_{j\mathrm{sp}}}{\gamma\infty_{i\mathrm{sp}}}\right)^{\text{extract phase}}\left(\frac{\gamma\infty_{j\mathrm{sp}}}{\gamma\infty_{i\mathrm{sp}}}\right)^{\text{raffinate phase}}\\ &=\left(\frac{\gamma\infty_{j\mathrm{sp}}}{\gamma\infty_{i\mathrm{sp}}}\right)^{\text{extract phase}}\approx\frac{\gamma\infty_{j\mathrm{sp}}}{\gamma\infty_{i\mathrm{sp}}}\end{aligned} \tag{4}$$

Here, subscript "i" refers to the sulphur or nitrogen compounds which are to be removed and subscript "j" refers to the gas-oil component. Similarly, yield is defined as

$$\text{Yield}=\frac{\text{Amount of product (solvent free raffinate phase)obtained after extraction}}{\text{Amount of feed (without solvent)}} \tag{5}$$

Performance index (P_I) of solvents

Capacity and selectivity properties of solvent are among the most desired properties. These have been used for screening of solvents for separation of particular compounds.[15–17,27] From the economic point of view, maximization of desulfurized gas oil yield and impurities removal is desired during solvent extraction process for removal of sulfur, nitrogen, and polyaromatics from gas oil. Higher capacity of solvent leads to higher removal of impurities and lower yield of product. This suggests that solvent having higher capacity will result in more loss of desired product with extract, however, require lower solvent to feed ratio (S/F) for same extent of impurities removal.[9] Further, higher selectivity of solvent in gas-oil extraction (tendency of undesired component such as sulfur and nitrogen compounds to be extracted more readily from carrier phase to solvent phase than desired compound such as paraffins) will reduce the loss of desired material with extract but require large amount of solvent for impurities removal. Among, capacity and selectivity, capacity is more important for the selection of an optimum extraction process as it determines the flow rate of the circulating solvent, which in turn governs the size of the reactor and capital and operating cost. However, selectivity is also very important in solvent evaluation. Since, highly selective solvents generally have lower capacity or dissolving power, therefore, large amount of solvent required increases the plant size and operational cost of extraction and solvent recovery equipments. In view of contradictory benefits of these two properties in solvent extraction, the balance of these properties in the solvent is preferred. Therefore, the effect of these two important parameters has been combined in single factor called as performance index (P_{I}) to guide us to select a solvent which has moderate capacity and solubility for an economical solvent extraction process. P_{I} is defined as[9,14]

$$P_{\mathrm{I}}=C_i S_{ij} \tag{6}$$

Industrial usability index (S_{IUI})

In commercial extraction process, solvent is recirculated via its recovery from extract and raffinate phase. Therefore,

the economics of the process is greatly governed by the energy requirement, complexity of solvent recovery section, and capital investment required for solvent recovery. This may be the reason that solvent showing the best capacity and selectivity in the laboratory scale could not be commercialized in the industry. In view of the above, it is essential to integrate above factors with the P_I of solvent for a realistic screening of solvents for a given separation.

The complexity of design of solvent recovery section will largely depend on boiling point difference between solvent and feed. In processes where boiling point of gas oil is 50°C or more above than that of solvent, the solvent recovery is possible using the process design as shown in Supporting Information Figure S1. The feed and solvent come in contact in counter current fashion in an extractor where raffinate and extract phases get generated. The solvent from raffinate phase is removed in raffinate wash column (RWC) using the water. The extract phase is fed to solvent recovery column (SRC) where solvent is vaporized and recovered from the top. The aqueous solvent obtained from RWC and SRC is processed in solvent drying column (SDC) to remove the excess water. The solvent from SDC bottom is sent to the extractor column after recovering its heat in the process. The water vapor from drying column can be partially condensed to meet the requirement of RWC and rest vapor can be superheated for use as stripping steam in SRC.

Further, in the scenario where boiling point of solvent (for most of ILs) is more than that of gas oil or where difference between solvent and gas oil is either not sufficient or has boiling point overlap, highly complicated solvent recovery section with additional secondary solvent is required as shown in Supporting Information Figure S2. In this process, extraction and solvent removal from raffinate phase is similar as described above (Supporting Information Figure S1). The extract phase is routed to re-extraction column where low boiling hydrocarbon (LBH) is used as a secondary solvent to remove the hydrocarbon from extract phase. Hydrocarbon phase obtained from re-extraction column is water washed to remove the solvent. Solvent free extract phase is processed in distillation column to recover the LBH for its reuse. Solvent phase from re-extraction column and water from solvent washing columns are routed to SDC to remove the excess water from the solvent. The solvent from drying column is recirculated to the extraction column. At this point, it is essential to note that aromatic (benzene, toluene and xylene (BTX)) production from liquid-liquid extraction and extractive distillation processes using high boiling and very selective solvent like sulfolane is well-established.

In aromatic extraction process, there is a need of very high purity of aromatics and pure solvent is recovered by vaporizing the aromatics from solvent. This is a reason that use of highly selective solvents having high boiling points are preferable as they provide very pure aromatics and lower reflux rate in SRC to avoid the solvent carry over with vaporized aromatics as a result lower energy requirement in solvent recovery. However, gas oil is a mixture of compounds and has boiling temperature range up to 370°C. This forces the complex design of solvent recovery section for high boiling point solvent (Supporting Information Figure S2) and suggests that best solvent having high boiling point for aromatic extraction may not be the best for gas oil desulfurization. Moreover, for solvent having boiling point less than gas oil, solvent will be vaporized and it is known that process energy required for vaporization is radically higher than sensible heating of a liquid. Thus, process energy consumption in solvent recovery section will depend on the solvent to feed ratio required in the process.

Solvent to feed ratio depends on the capacity and selectivity of solvent. P_I integrates the effect of these both parameters. Therefore, it is a reasonable assumption that process energy requirement has been integrated in performance factor of solvent for lower boiling solvents. It is acknowledged that requirement of more number of separation steps for the production of same products under similar operating conditions of temperature and pressure will increase the complexity of the process. Addition of a new column in process also includes the addition of auxiliary's equipments (pipelines, valves, pump, heater, etc.), their foundations and their operation. This will increase the required capital investment, operational and maintenance complexity. Process design for lower boiling point solvents to be recovered using vaporization route contains three columns for solvent recovery (Supporting Information Figure S1) whereas for high boiling point solvents to be recovered using re-extraction route contains five separation columns (Supporting Information Figure S2).

In view of above, it is clear that complexity of solvent recovery section in term of its operation and capital investment requirements should be integrated for getting realistic evaluation of having lower and higher boiling points. Hence, in present study, industrial usability indexes (S_{IUI}) of solvent is defined as a function of P_I, process complexity factor (P_{cf}) and uncertainty factor (U_f) to undertake the uncertainty in estimation of P_{cf} as

$$S_{IUI}=P_I/(P_{cf}U_f) \tag{7}$$

The process complexity factor (P_{cf}) is the ratio of the number of separation columns required in solvent vaporization (Supporting Information Figure S1) and re-extraction (Supporting Information Figure S2) schemes.

Estimation of van der Waals Volume, Molar Volume, and Solubility Parameters

These parameters for sulfur and nitrogen compounds were estimated using the commercial software, based on quantum mechanics, Materials Studio 7.0. The structure of compound was constructed in the visualizer using builder module of Materials Studio 7.0. Molecule was then geometrically optimized using the forcite module with COMPASS II force field. Smart algorithm was used with convergence tolerances of 0.001 kcal/mol for energy and 0.5 kcal/mol Å for force and maximum iterations was fixed at 500. The van der Waals volume of optimized molecular structure of compound was estimated using atom volumes and surfaces tool. Model system for each compound was constructed using amorphous cell module as an amorphous three-dimensional periodic box. 100 molecules in the cell constructed was selected so that the dimension of the cubic cell be sufficiently more than twice the cut-off distance (12.5 Å) for using the summation method (group based) for the electrostatic term. The initial density of bulk phase is required to build the proper model system. For solvents, nitrogen and certain hydrocarbons whose densities were available in published literature, the reported value was used as initial density input. For sulfur compounds which density is not available in recognized literature, the initial density value input was based on the value reported on www.chemspider.com and dynamic simulation

Table 1. Solubility Parameters at Room Temperature (25°C)

Hydrocarbon Type	Compound Name	Solubility Parameter		% deviation	Reference
		Literature	Predicted		
Paraffin	Hexane	14.90	15.26	−2.4	[31]
Cycloparaffin	Methylcyclohexane	16.00	16.37	−2.3	[31]
Aromatic	Toluene	19.60	19.15	2.3	[29]
	Napthalene	20.30	21.10	−3.9	[31]
Nitrogen	Pyridine	21.80	21.34	2.1	[24]
	Quinoline	22.00	22.28	−1.3	[31]
Sulfur	Carbon disulfide	20.50	20.47	0.1	[31]
Solvents	Dimethyl Formamide	24.43	24.73	−1.2	[29]
	Furfural	24.83	24.45	1.6	[33]
	Dimethyl acetamide	22.08	22.96	−4.0	[29]
	N methyl 2-pyrilidone	23.10	23.75	−2.8	[29]

using constant number of particles, pressure, and temperature (NPT) ensembles to fine tune the density and to minimize the possibility of inaccuracy in reported value.

The cell constructed of known density compounds was then equilibrated using constant number of particles, volume, and temperature (NVT) ensemble and thereafter production run was carried out with the number of particles, volume, and energy (NVE) ensemble using molecular dynamics. The cell constructed of sulfur compounds was equilibrated using NPT; NVT ensembles followed by production run with NVE ensembles using molecular dynamics. The equilibrium and production runs were carried out for 100 ps with time step of 1 fs. Nosé–Hoover–Langevin (NHL) thermostats with Q ratio of 0.01 thermostat and Berendsen barostat were used in the simulation. Group-based summation method with a chosen cut-off distance of 12.5 Å and spline width of 1 Å was used throughout the equilibration steps. The molar volume of compound was estimated using the predicted density of the system after NPT ensemble and molecular weight. The resulting molecular trajectories were then used in the cohesive energy density estimation using the forcite modules of martial studio software.

Results and Discussion

Validation of computation method

It is essential to analyze the accuracy of the value of solubility parameters predicted from the simulation by comparing it with the experimental value reported in literature. To do this, paraffins, cycloparaffins, aromatics, nitrogen, and sulfur compounds which have some structural similarity with gas oil compounds and potential solvents which can be used for desulfurization of gas oil were selected to test the accuracy of simulation method. The results of simulation are presented in Table 1. A good agreement (maximum percent deviation of 4%) between predicted and reported value of solubility parameters was found. This suggests that computational model is capable of predicting the solubility parameters of gas oil model components.

Molar volume (V_m), van der Waals volume (r_{vdw}), solubility parameters

Gas oil is a complex mixture of paraffins, cycloparaffins, aromatics, and sulfur and nitrogen compounds. *N*-tetradecane, 3-ethylbicyclo decane and propyl naphthalene were selected as model compounds to represent the paraffins, cycloparaffins, and aromatics compounds of gas oil, respectively. Benzothiophene, dibenzothiophene, and their derivatives were selected to represent the sulfur compounds. Nitrogen compounds were represented by quinoline, indole, and carbazole. The molar volume (V_m) of *n*-tetradecane, 3-ethylbicyclo decane and propyl naphthalene and nitrogen compounds at 25°C were estimated using ASPEN HYSIS software. The r_{vdw} values for these compounds were estimated using the material studio 7.0. Solubility parameters of aromatics, and sulfur and nitrogen model compounds were also estimated using the material studio 7.0 as per procedure described in section 3.0. Solubility parameter of *n*-tetradecane was estimated using the heat of vaporization value reported in literature[28] as dynamic simulations failed for such a long chains compounds. The solubility parameter of conventional solvents was taken as an average of values reported in literature[29–37] and values of V_m and r_{vdw} were estimated using the ASPEN HYSIS and material studio 7.0. Values of these parameters for IL solvents were taken from literature.[27] Values of above mentioned parameters for gas oil compounds are given in Table 2 and for solvents are in Table 3. Estimated values of standard heat of vaporization of gas oil model compounds using the solubility parameters are also given in Table 2. It is important to note that there is scarcity of the solubility parameters of model compounds representing the gas oil in literature. The V_m, r_{vdw}, and solubility parameters (Table 2) of these compounds can be used for the estimation of activity coefficients. The capacity and selectivity of solvents for given compounds can be estimated using their activity coefficients. Activity coefficients can also be used to regress the interaction parameter of these compounds with the different solvents. These interaction parameters are essential in commercial simulator for simulating the gas oil solvent extraction process to analyze the separation of sulfur and nitrogen compounds and solvent recovery section for its recovery from extract and raffinate phase.

Capacity and selectivity of solvents

Capacity and selectivity are important properties of solvent and can be used as a parameter for their selection in extraction process. Capacity and selectivity of selected solvents were estimated using Eqs. 3–5. The estimated values of capacity of solvents for model compounds are given Supporting Information Table S1 given in (SI). The solubility of model compounds in solvents followed the trend *n*-paraffins < cycloparaffins < aromatic < sulfur compound < nitrogen compounds. It is clear that solubility of undesired compounds (sulfur, nitrogen, and polyaromatics) is significantly higher than the desired compounds. It suggests that

Table 2. Molar Volume (V_m), van der Waals Volume (r_{vdw}), Solubility Parameters (δ), and Heat of Vaporization of Model Gas Oil Compounds

Model hydrocarbon name	Nomenclature	V_m (cm^3/mol)	r_{vdw} (cm^3 /mol)	δ $(j/cm^3)^{1/2}$	Heat of vaporization (kJ/mol)
N-tetradecane*	Ted-NP	260.6	159.2	15.61	67.37
3-Ethylbicycl decane	Ebcd-CP	188.50	115.3	18.30	65.59
1-*n*-propyl napthalene	Npn-A	222.20	107.0	19.44	86.44
Benzothiophene	BT	119.71	71.8	20.32	51.88
3-Methyl Benzothiophene	MBT	138.66	81.7	19.86	57.14
3,5 Dimethylbenzothiophene	DMBT	156.16	91.8	19.43	61.40
2,3,4 trimethylbenzothiophene	TMBT	167.25	101.5	18.88	62.09
Di-benzothiophene	DBT	156.81	98.6	21.04	71.89
4-Methyl-Dibenzothiophene	MDBT	168.32	108.3	20.40	72.54
4,6 Dimethyl-dibenzothiophene	DMDBT	185.10	118.1	19.97	76.27
Quinoline	Quin	118.60	74.0	21.80	58.83
Indole	Indo	106.50	67.6	24.26	65.15
Carbazole	Carba	139.00	103.6	20.38	60.23

refractive sulfur and nitrogen compounds which reduce the desulfurization performance of hydrotreater can be removed using solvent extraction.

In solvent extraction process, it is desirable to minimize the loss of desired compounds with the extract phase. The selectivity of solvent for undesired compound with respect to desired compounds is used to analyze this effect. High value of selectivity of solvent for solute provides better separation between the solute and carrier compounds. In present study, selectivity of solvents for sulfur and nitrogen compounds with respect to *n*-paraffin, cycloparaffin and aromatic were estimated and are given in Supporting Information Tables S2–S4, respectively. Selectivity values of solvent for sulfur and nitrogen compounds w.r.t. paraffins were found drastically higher in comparison to cycloparaffins and aromatic, whereas, w.r.t. cycloparaffins and aromatic are comparable. It is important to note that *n*-paraffins and cycloparaffins are most desirable compounds in gas oil. Considering this, the selectivity of sulfur and nitrogen compounds with respect to cycloparaffins was selected for rating of the solvents.

It is seen that selectivity of DMF, furfural, DMA, DMSO, and NMP solvents for sulfur compounds follow the order: DBT > BT > 4MDBT > 3MBT > 4,6 DMDBT > 3,5DMBT > 2,3,6 DMDBT whereas sulfolane and imidazolium-based IL solvents follow the order: BT > DBT > 3MBT > 4MDBT > 4,6 DMDBT > 3,5 DMBT > 2,3,6 TMDBT. The solvents having high capacity for nitrogen compounds followed the selectivity order: indole > quinoline > carbazole whereas for higher selective solvents the order is: quinoline > indole > carbazole. It is observed that selectivity and capacity values of solvents for nitrogen compounds are higher than most of the sulfur

Table 3. Molar Volumes (V_m), van der Waal Volumes (r_{vdw}), and Solubility Parameters (δ) of Solvents

Full name	Nomenclature	V_m (cm^3/mol)	r_{vdW} (cm^3/mol)	δ (j/cm^3)
N,*N* dimethyl formamide	DMF	77.4	46.00	24.68[(1)]
Furfural	Furfural	85.4	51.4	24.47[(2)]
N,*N* dimethyl acetamide	DMA	93.1	56.2	22.42[(3)]
Dimethyl sulfoxide	DMSO	71.2	43.9	26.55[(4)]
N methyl pyrolidone	NMP	96.7	59.8	23.02[(5)]
Sulfolane	SULFO	95.7	61.6	27.20[(6)]
1-Methacryloyloxyhexyl-1-methylimidazolium Bromide	MIM1[(7)]	362.0	170.0	25.83
1-Propyl-2,3-dimethylimidazolium Tetrafluoroborate	MIM2[(7)]	168.0	197.0	23.99
1-Ethyl-3-methylimidazolium Tetrafluoroborate	MIM3[(7)]	159.0	177.0	24.41
1-Butyl-3-methylimidazolium Tetrafluoroborate	MIM4[(7)]	191.0	197.0	23.78
1-Hexyl-3-methylimidazolium Tetrafluoroborate	MIM5[(7)]	225.0	218.0	22.76
1-Octyl-3-methylimidazolium Tetrafluoroborate	MIM6[(7)]	264.0	238.0	22.00
1-Hexadecyl-3-methylimidazolium Tetrafluoroborate	MIM7[(7)]	577.0	320.0	20.23
1-(2-Hydroxyethyl)−3-methylimidazolium Tetrafluoroborate	MIM8[(7)]	144.0	192.0	24.76
1-Butyl-3-methylimidazolium Hexafluorophosphate	MIM9[(7)]	211.0	143.0	22.06
1-Hexyl-3-methylimidazolium Hexafluorophosphate	MIM10[(7)]	245.0	163.0	22.18
1-Octyl-3-methylimidazolium Hexafluorophosphate	MIM11[(7)]	279.0	184.0	21.19
1-Methyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide	MIM12[(7)]	244.0	154.0	24.71
1-Ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide	MIM13[(7)]	262.0	165.0	22.40
1-Butyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide	MIM14[(7)]	297.0	186.0	23.46
1-Methyl-3-methylimidazolium Dimethylphosphate	MIM15[(7)]	179.0	120.0	25.08
1-Ethyl-3-methylimidazolium Ethylsulfate	MIM16[(7)]	236.0	127.0	24.26
1-Methyl-3-methylimidazolium Methoxyethylsulfate	MIM17[(7)]	195.0	140.0	25.03
1-Butyl-3-methylimidazolium Trifluoromethanesulfonate	MIM18[(7)]	222.0	143.0	25.85
1-Butyl-3-methylimidazolium Diethyleneglycolmonomethylethersulfate	MIM19[(7)]	284.0	194.0	24.80
1-Hexyloxymethyl-3-methyl-imidazolium Bis(trifluoromethylsulfonyl)imide	MIM20[(7)]	350.0	219.0	21.04
1,3-Dihexyloxymethylimidazolium Bis(trifluoromethylsulfonyl)imide	MIM21[(7)]	460.0	284.0	20.59
1-Butyl-3-methylimidazolium Octylsulfate	MIM22[(7)]	328.0	218.0	22.83

(1) to (7) average value of δ reported in References:- (1) : 29–31; (2): 32–33; (3):29,34–35; (4): 30–31; (5):29 (6):24; (7):27.

Table 4. Ranking of Top 10 Solvents Based on Their Capacity Index (Based on Calculation Results Given in Supporting Information Table S1)

BT	MBT	DMBT	TMBT	DBT	MDBT	DM DBT	Quin	Indo	Carba
MIM7	MIM7	MIM7	MIM7	MIM7	MIM7	MIM7	MIM6	MIM2	MIM7
MIM21	MIM21	MIM21	MIM21	MIM21	MIM21	MIM21	MIM7	MIM4	MIM21
MIM20	MIM20	MIM20	MIM20	MIM20	MIM20	MIM20	MIM21	MIM19	MIM20
MIM11	MIM11	MIM11	MIM11	MIM6	MIM11	MIM11	MIM20	MIM8	MIM11
MIM6	MIM6	MIM6	MIM6	MIM11	MIM6	MIM6	MIM5	MIM3	MIM6
MIM10	MIM9	MIM9	MIM9	MIM10	DMA	DMA	MIM22	MIM14	MIM9
MIM9	MIM10	MIM10	MIM10	MIM9	MIM9	MIM9	MIM11	MIM22	DMA
MIM5	MIM13	MIM13	DMA	DMA	MIM10	MIM10	MIM10	MIM5	MIM10
MIM13	MIM5	DMA	MIM13	MIM13	MIM13	MIM13	MIM13	MIM12	MIM13
MIM22	MIM22	MIM5	MIM5	MIM5	MIM5	MIM5	MIM9	MIM16	MIM5

compounds. This suggests that nitrogen compounds are easier to remove than sulfur compounds and will remove simultaneously.

The ranking of solvent based on their capacity shown in Table 4 reveals that top five solvents for all sulfur and nitrogen compounds are all ILs. It is observed that position of solvents other than top five changes with respect to the type of sulfur compounds. However, for nitrogen compounds, position of all the solvent changes with respect to the type of nitrogen compounds which suggests that one solvent can be the best for either quinoline or indole or carbazole removal and not for removal of all nitrogen compounds.

Anantharaj and Banerjee[15] reported the capacity and selectivity trend of 1-Ethyl-3-methylimidazolium Tetrafluoroborate (MIM3); 1-Ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide (MIM13), and 1-Ethyl-3-methylimidazolium Ethylsulfate (MIM16) ILs for removal of benzothiophene and dibenzothiophene sulfur compounds. In these studies, capacity ranking of these solvents for benzothiophene and dibenzothiophene was in the same order: MIM13 > MIM3 $\approx$ MIM16. In the present study, capacity ranking of these solvents for benzothiophene also followed the same order MIM13 > MIM3 $\approx$ MIM16 and for dibenzothiophene MIM13 > MIM16 $\approx$ MIM3. Anantharaj and Banerjee[15] reported the selectivity ranking of these solvents for benzothiophene in order: MIM3 > MIM3 $\approx$ MIM16 and for dibenzothiophene in the order: MIM13 $\approx$ MIM3 > MIM16. In the present study, the selectivity ranking of these solvents for benzothiophene and dibenzothiophene followed the order MIM3 $\approx$ MIM16 > MIM13 which is different than that reported by Anantharaj and Banerjee.[15,16] However, the ranking order in the present study seems realistic in view of the fact that for solvents having different capacities, selectivity generally follows the reverse order of capacity.

The analysis of top five solvents in Table 5 indicates that solvents such as sulfolane, DMSO, MIM1, MIM18, and MIM15 which are of lower capacity show higher selectivity. This clearly suggests that there is reverse trend between capacity and selectivity of solvents. Hence, selection of solvents cannot be done either based on capacity or selectivity.

Performance index (P_I) and industrial usability index (S_{IUI}) of solvents

P_I values of solvents were estimated for all model sulfur and nitrogen compounds using the Eq. 5. Solvents ranking based on their P_I values for sulfur and nitrogen compounds is given in Table 6. This reveals that MIM1 for BT, MIM22 for MBT and MDBT, MIM7 for DMBT and TMBT, MIM 19 for DBT, DMA for DMDBT, sulfolane for indole and quinoline, DMF for carbazole are the best solvent on P_I scale. It is important to note that all top five solvents for benzothiophenic sulfur compounds are ILs. Whereas for removal of dibenzothiophenic sulfur compounds, conventional solvents also are among the top five solvents and there ranking are: DMF, fifth for DBT; NMP, third for MDBT; and DMA, first for DMDBT. For nitrogen compounds, ranking of conventional solvents are: sulfolane, first and DMSO, fourth for quinoline; sulfolane, first and DMSO, second for indole; DMF, first and furfural, fifth for carbazole. Ranking of solvents based on P_I implies that solvents showing highest capacity or selectivity may not be best solvent for different sulfur and nitrogen compounds removal. It is also clear that there is no single solvent which performs best for removal of all sulfur and nitrogen compounds; and solvent selection can only be done based on detailed sulfur and nitrogen compounds analysis of gas oil.

In view of solvents' industrial application, industrial usability index (S_{IUI}) of solvents was estimated using Eq. 6.

Table 5. Ranking of Top 10 Solvents Based on Their Selectivity for Sulfur Compounds and Nitrogen Compounds with Respect to 3-ethylbicycl decane (Based on Calculation Results Given in Supporting Information Table S3)

BT	MBT	DMBT	TMBT	DBT	MDBT	DM DBT	Quin	Indo	Carba
SULFO	SULFO	SULFO	SULFO	SULFO	SULFO	SULFO	SULFO	SULFO	SULFO
DMSO	DMSO	DMSO	DMSO	DMSO	DMSO	DMSO	DMSO	DMSO	DMSO
MIM1	MIM1	MIM1	MIM1	MIM18	MIM18	MIM18	MIM1	MIM1	MIM18
MIM18	MIM18	MIM18	MIM18	MIM1	MIM1	MIM1	MIM18	MIM18	MIM1
MIM15	MIM15	MIM15	MIM15	MIM15	MIM15	MIM15	MIM15	MIM15	MIM15
MIM17	MIM17	MIM17	MIM17	MIM17	MIM17	MIM17	MIM17	MIM17	MIM17
MIM19	MIM19	MIM19	MIM19	MIM19	MIM19	MIM19	MIM19	MIM19	MIM19
MIM8	MIM8	MIM8	MIM8	MIM8	MIM8	MIM8	MIM8	MIM8	MIM8
MIM12	MIM12	MIM12	MIM12	MIM12	MIM12	DMF	MIM12	MIM12	MIM12
MIM3	MIM3	MIM3	MIM3	DMF	DMF	MIM12	MIM3	MIM3	DMF

Table 6. Ranking of Top 10 Solvents Based on Their Performance Index (Based on Calculation Results Given in Supporting Information Table S5)

BT	MBT	DMBT	TMBT	DBT	MDBT	DM DBT	Quin	Indo	Carba
MIM1	MIM22	MIM7	MIM7	MIM19	MIM22	DMA	SULFO	SULFO	DMF
MIM19	MIM5	MIM21	MIM21	MIM8	MIM5	MIM6	MIM1	DMSO	MIM19
MIM8	MIM6	MIM20	MIM20	MIM3	NMP	MIM21	MIM18	MIM1	MIM8
MIM18	MIM4	MIM6	MIM11	MIM1	MIM6	MIM20	DMSO	MIM18	MIM2
MIM3	MIM2	MIM11	MIM6	DMF	MIM14	MIM11	MIM19	MIM17	Furfu
MIM2	MIM14	MIM5	MIM9	MIM2	DMA	MIM7	MIM8	MIM15	MIM3
MIM12	MIM21	MIM22	MIM10	MIM12	MIM4	MIM10	MIM17	MIM19	MIM4
MIM17	MIM13	MIM10	MIM13	MIM17	MIM2	NMP	MIM15	MIM8	MIM12
MIM4	MIM3	MIM13	DMA	MIM4	MIM13	MIM9	MIM12	MIM12	DMSO
MIM15	MIM7	MIM9	MIM5	MIM18	DMF	MIM5	MIM3	MIM3	MIM17

The process complexity factor (P_{cf}) of 1.0 was used for solvents having boiling point less than gas oil and can be recovered using the solvent recovery section shown in Supporting Information Figure S1. However, for solvents having boiling point more than gas oil, P_{cf} value of 1.67 was used. S_{IUI}-based ranking of solvents is shown in Table 7. It can be seen clearly that dominance of conventional solvents increases in the top five solvents against the predominance of IL solvents on P_I index scale. This implies that complexity in solvent recovery is very important aspect to be included in solvent screening and evaluation.

Further, it is understood that there are chances of uncertainty in P_{cf} estimations which need detail and rigorous simulations and costing of the solvent recovery section. Rigorous simulations and exact costing can be done only after extensive experimental and engineering work. Considering the approximation of $\pm 20\%$, S_{IUI} were also estimated with $\pm 20\%$ value of uncertainty factor (U_f). The ranking of solvents for $U_f = 0.8$ and $U_f = 1.2$ are given in Supporting Information Tables S5 and S6, respectively. It can be seen that as the weightage to complexity in solvent recovery increase, preference to chose the conventional organic solvents having boiling point less than gas oil increases.

The 4,6 DMDBT and quinoline are most refractive sulfur and nitrogen compound selected in the study. For easy understanding of the study results, the solvent ranking based on all the indexes scale for 4,6 DMDBT and quinoline is given in Table 8. There is no single solvent which seems the best for all the indexes. The C_i showed MIM7, S_{ij} showed sulfolane, P_I and S_{IUI} showed DMA as the best solvent for removal of 4,6 DMDBT from gas oil. C_i showed MIM6, S_{ij} and P_I showed sulfolane, and S_{IUI} showed DMSO are the best solvents for removal of quinoline.

Further, in commercial process there will always be slight loss of solvent and expenditure required for its makeup in the process would also increase the operating cost significantly. There is also reasonable amount of solvent stored as an inventory in the plant. Considering above, the price of solvent parameter could also be included in the estimation of S_{IUI}. The cost of conventional solvents which are used in the industry is almost comparable. However, cost of IL given in open literature are not true representative of their price as they are manufactured in very small quantity for either specific use or for lab scale utilization. The price of ILs may reduce drastically when they will be produced in bulk and their production technologies will get more mature. Hence, cost index of solvent has not been included in S_{IUI} in present study.

Still in light of the current price of IL and conventional solvents, the number of conventional solvents among top five solvents based on C_i, S_{ij}, P_I, and S_{IUI} are 0, 2, 1, and 4, respectively, for 4,6 DMDBT removal; and 0, 2, 2, and 3 for quinoline removal. It is important to note that on S_{IUI} scale, DMA ranked first and 20th for 4,6 DMDBT and quinoline removal, DMSO solvent ranked 25th and first for 4,6 DMDBT and quinoline removal. DMF is the only solvent which is common among the top five solvents for 4,6 DMDBT and quinoline. Overall, DMF and DMA seem to be the best solvents for simultaneous desulfurization and denitrogenation of gas oil.

In this study, relationship between rankings and various parameters such as van der Waals volume, molar volume, and solubility parameters was also explored. No relationship was obtained between various rankings (based on capacity, selectivity, performance index, and industrial usability index) of solvents for removal of benzothiophene,

Table 7. Rating of Top 10 Solvents Based on Their Industrial Usability Index (S_{IUI}) with $U_f = 1.0$ (Based on Calculation Results given in Supporting Information Table S6)

BT	MBT	DMBT	TMBT	DBT	MDBT	DM DBT	Quin	Indo	Carba
DMSO	NMP	DMA	MIM7	DMF	NMP	DMA	DMSO	SULFO	DMF
DMF	DMA	NMP	MIM21	Furfu	DMA	NMP	SULFO	DMSO	Furfu
MIM1	Furfu	MIM7	DMA	DMSO	DMF	Furfu	MIM1	MIM1	DMSO
Furfu	DMF	MIM21	MIM20	NMP	Furfu	DMF	MIM18	MIM18	NMP
MIM19	MIM22	MIM20	MIM11	DMA	MIM22	MIM6	DMF	MIM17	DMA
MIM8	MIM5	MIM6	NMP	MIM19	MIM5	MIM21	MIM19	MIM15	MIM19
MIM18	MIM6	MIM11	MIM6	MIM8	MIM6	MIM20	Furfu	MIM19	MIM8
MIM3	MIM4	MIM5	MIM9	MIM3	MIM14	MIM11	MIM8	MIM8	MIM2
MIM2	MIM2	MIM22	MIM10	MIM1	MIM4	MIM7	MIM17	DMF	MIM3
MIM12	MIM14	MIM10	MIM13	MIM2	MIM2	MIM10	MIM15	MIM12	MIM4

Table 8. Rating of Solvents Based on Selected Indexes (C_i, S_{ij}, P_I, and S_{IUI}) for 4,6 DMDBT and Quinoline Removal from Gas Oil

4,6 DMDBT						Quinoline					
C_i	S_{ij}	P_I	S_{IUI} $U_I = 0.8$	S_{IUI} $U_I = 1.0$	S_{IUI} $U_I = 1.2$	C_i	S_{ij}	P_I	S_{IUI} $U_I = 0.8$	S_{IUI} $U_I = 1.0$	S_{IUI} $U_I = 1.2$
MIM7	SULFO	DMA	DMA	DMA	DMA	MIM6	SULFO	SULFO	DMSO	DMSO	DMSO
MIM21	DMSO	MIM6	NMP	NMP	NMP	MIM7	DMSO	MIM1	SULFO	SULFO	SULFO
MIM20	MIM18	MIM21	MIM6	Furfu	Furfu	MIM21	MIM1	MIM18	MIM1	MIM1	MIM1
MIM11	MIM1	MIM20	MIM21	DMF	DMF	MIM20	MIM18	DMSO	MIM18	MIM18	MIM18
MIM6	MIM15	MIM11	MIM20	MIM6	MIM6	MIM5	MIM15	MIM19	MIM19	DMF	DMF
DMA	MIM17	MIM7	MIM11	MIM21	MIM21	MIM22	MIM17	MIM8	MIM8	MIM19	Furfu
MIM9	MIM19	MIM10	MIM7	MIM20	MIM20	MIM11	MIM19	MIM17	MIM17	Furfu	MIM19
MIM10	MIM8	NMP	MIM10	MIM11	MIM11	MIM10	MIM8	MIM15	MIM15	MIM8	MIM8
MIM13	DMF	MIM9	MIM9	MIM7	MIM7	MIM13	MIM12	MIM12	MIM12	MIM17	MIM17
MIM5	MIM12	MIM5	MIM5	MIM10	MIM10	MIM9	MIM3	MIM3	DMF	MIM15	MIM15
MIM22	Furfural	MIM13	MIM13	MIM9	MIM9	MIM14	DMF	MIM2	MIM3	MIM12	MIM12
NMP	MIM3	MIM22	MIM22	MIM5	MIM5	DMA	MIM16	MIM16	Furfu	MIM3	MIM3
MIM14	MIM16	MIM14	Furfu	MIM13	MIM13	MIM4	Furfu	MIM4	MIM2	MIM2	MIM2
MIM4	MIM2	MIM4	DMF	MIM22	MIM22	MIM2	MIM2	DMF	MIM16	MIM16	MIM16
MIM2	MIM4	MIM2	MIM14	MIM14	MIM14	NMP	MIM4	Furfu	MIM4	MIM4	MIM4
Furfu	MIM14	Furfu	MIM4	MIM4	MIM4	MIM3	MIM14	MIM14	MIM14	MIM14	NMP
MIM16	NMP	DMF	MIM2	MIM2	MIM2	MIM16	MIM22	MIM22	MIM22	NMP	MIM14
DMF	MIM22	MIM16	MIM16	MIM16	MIM16	MIM8	MIM5	MIM5	MIM5	MIM22	DMA
MIM3	MIM5	MIM3	MIM3	MIM3	MIM3	MIM19	NMP	NMP	NMP	MIM5	MIM22
MIM12	DMA	MIM8	MIM8	MIM8	MIM8	MIM12	MIM13	MIM13	MIM13	DMA	MIM5
MIM8	MIM13	MIM12	MIM12	MIM12	MIM12	Furfu	MIM10	MIM6	DMA	MIM13	MIM13
MIM19	MIM10	MIM19	MIM19	MIM19	MIM19	DMF	MIM6	MIM10	MIM6	MIM6	MIM6
MIM17	MIM9	MIM17	MIM17	MIM17	DMSO	MIM17	DMA	MIM9	MIM10	MIM10	MIM10
MIM15	MIM6	MIM15	MIM15	MIM15	MIM17	MIM15	MIM9	DMA	MIM9	MIM9	MIM9
MIM1	MIM11	MIM1	DMSO	DMSO	MIM15	MIM1	MIM11	MIM11	MIM11	MIM11	MIM11
MIM18	MIM20	MIM18	MIM1	MIM1	MIM1	MIM18	MIM20	MIM20	MIM20	MIM20	MIM20
DMSO	MIM21	DMSO	MIM18	MIM18	MIM18	DMSO	MIM21	MIM21	MIM21	MIM21	MIM21
SULFO	MIM7	SULFO	SULFO	SULFO	SULFO	SULFO	MIM7	MIM7	MIM7	MIM7	MIM7

dibenzothiophene, and their alkylated derivatives sulfur compounds, quinoline, indole, and carbazole nitrogen compounds with respect to van der Waals volume and molar volume. When solubility parameter of all solvents (six conventional solvents and 22 imidazolium-based ILs solvents) was correlated with the various rankings of solvents, again no trend was observed. However, when conventional and ILs solvent were categorized and correlated separately for 4,6 DMDBT sulfur compound removal with respect to rankings based on selectivity and capacity, a linear trend was observed. It was found that the selectivity and solubility parameter follow same trend whereas solubility parameter of solvent and its capacity have exactly opposite trend. Thus, rankings based on selectivity and capacity correlated well with the solubility parameter. Since, performance index and industrial usability index represent the combined effect, no trend was observed for these rankings.

Kumar et al.[9] used various solvents namely acetonitrile, *N-N*-dimethyl formamide, furfural, *N-N*-dimethyl acetamide, and dimethyl sulfoxide were used for extraction of sulfur and polyaromatic impurities from actual straight run gas oil (SRGO) containing 1.3 wt % sulfur. Performance of solvent extraction process was evaluated in terms of a performance factor which was governed by degree of sulfur removal and yield of ESRGO. DMF was found to be the best solvent. In the present study also, DMF was found to be the best solvent for desulfurization of gas oil. This demonstrates that the screening strategy adopted in this work has high significance.

This study reveals that IL solvents may be preferred based on their individual capacity and selectivity values over lower boiling point conventional organic solvents for removal of sulfur compounds from gas oil. However, complexity in their recovery brings their ranking lower than the conventional organic solvents. This strongly suggests that ILs-based solvents which can be very selective could have great chances in recovery of pure aromatic extraction which are to be vaporized for solvent recovery and small scale, pharmaceutical, specific chemical manufacturing industries where the quality of product is of predominant importance and even small loss of product can overcome the additional expenditure involved in its recovery.

Conclusion

Presented study established a new strategy for screening of solvents for sulfur, nitrogen, and aromatic compounds removal from gas oil. A new industrial usability index was defined which included performance factor (product of solvent capacity and selectivity) and process complexity factors for solvent recovery. Twenty eight solvents comprising of six most widely used industrially proven conventional solvents and 22 imidazolium-based ILs solvents were assessed and ranked based on their capacity, selectivity, performance, and newly defined industrial usability index. For assessing these indices, first solubility parameters, molar volume, van der Waal volume of sulfur, nitrogen, and aromatic compounds of gas oil were estimated. These properties were used to estimate the standard heat of vaporization and activity coefficient at infinite dilution of gas oil compounds in various solvents. It was observed that selectivity and capacity values of solvents for nitrogen compounds are higher than most of the sulfur compounds. Rankings based on selectivity and capacity correlated well with the solubility parameter. It was also observed that ranking of solvents strongly depends on the parameter/index selected for the ranking. Performance index seemed to be better parameter

than capacity and selectivity parameters, however, industrial usability index was found to be more practical and realistic criteria for ranking of solvents. The 4,6 DMDBT sulfur and quinoline are most refractive compounds to be removed. Overall, DMF and DMA were found to be better solvents for desulfurization and denitrogenation of gas oil. There was no single solvent which ranked first for all sulfur and nitrogen compounds removal from gas oil. Therefore, the detail sulfur component wise analysis of gas oil played an important role in selection of solvent. Moreover, it seems that solvent having very high capacity and selectivity are not the best solvents. The best solvent should have moderate capacity, selectivity, and lower boiling point than gas oil.

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Notation

BT = benzothiophene
Carba = carbazole
C_i = capacity of solvent for component, i
DBT = di-benzothiophene
DMA = *N*,*N*-dimethyl acetamide
DMBT = 3,5 dimethylbenzothiophene
DMDBT = 4,6 dimethyl-dibenzothiophene
DMF = *N*,*N* dimethyl formamide
DMSO = dimethyl sulfoxide
Ebcd-CP = 3-ethylbicycl decane
Furfu = furfural
γ^{∞} = activity coefficients at infinite dilution
Indo = Indole
MBT = 3-methyl Benzothiophene
MDBT = 4-methyl-Dibenzothiophene
MIM1 = 1-methacryloyloxyhexyl-1-methylimidazolium Bromide
MIM2 = 1-propyl-2,3-dimethylimidazolium Tetrafluoroborate
MIM3 = 1-ethyl-3-methylimidazolium Tetrafluoroborate
MIM4 = 1-butyl-3-methylimidazolium Tetrafluoroborate
MIM5 = 1-hexyl-3-methylimidazolium Tetrafluoroborate
MIM6 = 1-octyl-3-methylimidazolium Tetrafluoroborate
MIM7 = 1-hexadecyl-3-methylimidazolium Tetrafluoroborate
MIM8 = 1-(2-hydroxyethyl)−3-methylimidazolium Tetrafluoroborate
MIM9 = 1-butyl-3-methylimidazolium Hexafluorophosphate
MIM10 = 1-hexyl-3-methylimidazolium Hexafluorophosphate
MIM11 = 1-octyl-3-methylimidazolium Hexafluorophosphate
MIM12 = 1-methyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide
MIM13 = 1-ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide
MIM14 = 1-butyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide
MIM15 = 1-methyl-3-methylimidazolium Dimethylphosphate
MIM16 = 1-ethyl-3-methylimidazolium Ethylsulfate
MIM17 = 1-methyl-3-methylimidazolium Methoxyethylsulfate
MIM18 = 1-butyl-3-methylimidazolium Trifluoromethanesulfonate
MIM19 = 1-butyl-3-methylimidazolium Diethyleneglycolmonomethylethersulfate
MIM20 = 1-hexyloxymethyl-3-methyl-imidazolium Bis(trifluoromethylsulfonyl)imide
MIM21 = 1,3-dihexyloxymethylimidazolium Bis(trifluoromethylsulfonyl)imide
MIM22 = 1-butyl-3-methylimidazolium Octylsulfate
NMP = *N* methyl pyrolidone
Npn-A = 1-*n*-propyl napthalene
P_{cf} = process complexity factor
P_I = performance index of solvent
Quin = quinoline
R = universal gas constant,j/k/mol
r_{vdw} = van der Waals volume,cm^3/mol
S_{ij} = selectivity of solvent for component i with respect to j
SI = supporting information
S_{IUI} = industrial usability index of solvent
sp = solvent rich phase
SULFO = 2,3,4,5-tetrahydrothiophene-1,1-dioxide (Sulfolane)
Ted-NP = *N*-tetradecane
TMBT = 2,3,4 trimethylbenzothiophene
U_f = uncertainty factor
V_m = molar volume, cm^3/mol
δ = Hildebrand solubility parameter $(j/cm^3)^{1/2}$
ΔE_{ced} = cohesive energy density, j/cm^3
ΔH_v = enthalpy of vaporization, j/mol

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