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Asphaltene Separation with Designer Solvents for the Deasphaltenes Process-A Quantum Chemical Approach

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Abstract

Significance of Ionic Liquids (ILs), designer solvents, on inhibiting the asphaltene deposition provided the alternative solution to the problem. In this work, 34 anions and 3 cations comprising of 102 combinations of ILs were investigated for a model asphaltene molecule via quantum solvation software tool COSMO-RS (Conductor like Screening for Real Solvents). Validation is done by comparing literature values of activity coefficient at infinite dilution (IDAC) of alkanes, cycloalkanes and aromatic in 3 ILs with 111 data points at 3 sets of different temperatures. Percent relative absolute average deviation (%RAAD) was found to be 10%. Thereafter IDAC values were predicted for model asphaltene compound in the cations and anions combinations for performance analysis. It is found that smaller cation with sterically shielded large anion gave the large performance for removal of upgrading the asphaltenic crude oil.

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1. Introduction

Asphaltene, the most aromatic and the heaviest fraction of crude petroleum, is the most critical to all aspects of upstream and downstream processes due to its nature to self-associate and form clusters[1]. It strongly affects the viscosity, which impacts all areas and causes flow assurance, emulsion stability, low distillate yield unpropitious phase separation and wettability problems [2, 3]. when present in fuel oil, it causes delay in ignition delay, coke formation, fouling in boiler operation, reduced heat transfer, chimney emissions, and rusting [4].

Asphaltenes is considered to be the solubility class fraction in crude oil, is insoluble in short chained alkanes but soluble in aromatic such as toluene [5]. An island type architecture of asphaltene molecule consists of a moderate size polycyclic aromatic hydrocarbon (PAH) ring which is the principal position of intermolecular attraction, along with cycloalkane, normal and branched substituents [1, 3]. In addition, there are some heteroatom contents such as nitrogen is present mostly in the form of pyrrole, sulfur is present in the thiophenic form, oxygen is found in the phenolic form [2]. It is documented that the most apparent number of fused rings (one PAH per molecule) is seven and the type of aromatic carbon is “sextet” [6].

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Nomenclature

$\gamma_{s,i}^{xi}$	activity coefficient (AC) of the pure component xi in solvent S
μ_s^{xi}	chemical potential of the solvent S
μ_{xi}^{xi}	chemical potential of the pure component xi.
C_{∞}	Capacity
S_{∞}	Selectivity
PI_{∞}	Performance index
TZVP	Triple zeta valence potential
T-MOLE	TURBOMOLE

A verity of asphaltene inhibition treatments have been developed to improve the quality of heavy oil: **Carbon rejection** technologies such as solvent deasphalting (SDA) and mild cracking solvent deasphalting (MCSD) are considered to be the most efficient and economical technology available. However, the precipitated pitch is considered as asphaltenes yet it contains maltene and quality of deasphalted oil (DAO) is decreased as temperature decreases. In addition, the process is energy intensive leaving carbon footprints and these solvents are toxic and they cannot be recovered environmentally friendly manner [7]. Hydrogen addition technologies such as aquathermolysis method are the best known to reduce the viscosity and to increase the lighter fractions and decrease resins and asphaltene in heavy oil. However, it is also an energy intensive method and causing severe environmental problems [8, 9]. Therefore, there is a need to develop such a solvent extraction process for asphaltene separation which is efficient, requires less energy, robust and green. The solvent ought to be adequately selective for the separation of asphaltenic component at large capacity. Moreover, recoverability of the solvent should be reasonably easy.

Ionic liquids (ILs) are fit for the purpose solvents for deasphalting process and are modest with compared to the conventional solvents because of its environmentally benign nature, unique thermo physical properties and countless combinations of cation and anion structures allowing them to fine tune their physiochemical properties[10]. Various ILs have been examined in the removal organometallic fraction from heavy oil or model oil and direct coal liquefaction residue, which include ammonium based ILs[11], imidazolium based ILs [12-17], pyridinium based ILs [17], ammonium based ILs [15].

However, research on IL as solvent extractive agent majorly focuses on liquid-liquid extraction (LLE), i.e., extraction of aromatic sulfur from diesel or model oil, the performance of the ILs are unsatisfactory. Data available are scarce and most of the experimental data are found for imidazolium based ILs. There is still less data is available for ILs based on cations: pyridinium, ammonium, and quinolinium. It is a matter of fact that the preliminary experimentations are not only costly but also time consuming. Before going into the detailed analysis for the evaluation of the extractive performance of IL, the screening must be done. IDAC data has the reasonable significance to find the selectivity and capacity of the ILs. The lesser the activity coefficient value from one, the higher is the tendency for the ILs to remove asphaltene components [18]. In this work the aim is to study the interaction between ionic liquid and model asphaltene compound and identify the promising ILs for the separation of asphaltene specie. Asphaltenes are known to have high hydrogen bond donor capability and tetralin also exhibits significant hydrogen bond donor capabilities [2]. Thus, we have chosen aromatic compound as asphaltene model compound i.e. tetra line (THN) (fig 1).

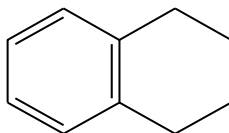


Figure 1 Asphaltene Model Compound

There are 3 cations were chosen i.e pyridinium, imidazolium and quinolinium cations. Anions were chosen with the increase of their Cosmo volume shown in table 1. Group contribution methods (GCMs) such as UNIFAC are not valid for IL systems because large experimental data is required for GMCs to calculate the thermo physical properties. There is no sufficient database of experimental values for finding these parameters for IL systems. Thus, quantum solvation approaches such as COSMO-RS is used because this model predicts the liquid phase non ideal AC of any component in a mixture

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