

## Supporting information

# Experimental and Simulation Studies of Imidazolium Chloride Ionic Liquids with Different Alkyl Chain Lengths for Viscosity Reductions in Heavy Crude Oil: The Effect on Asphaltene Dispersion

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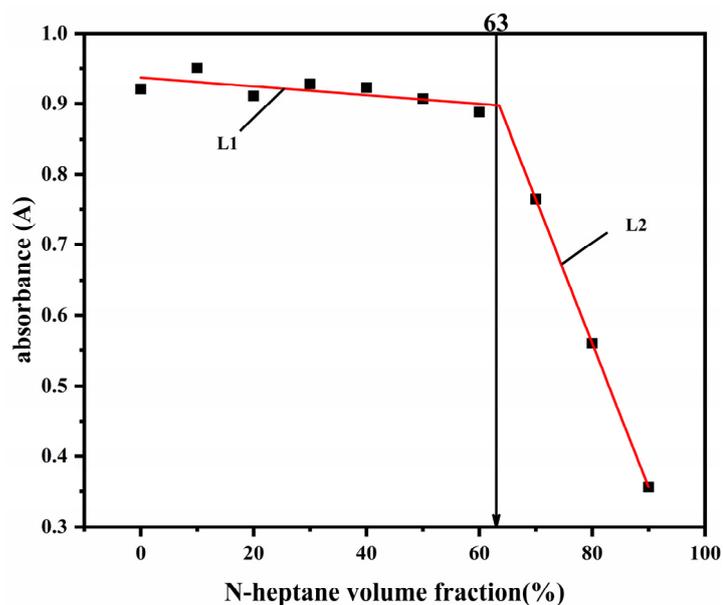
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## Text S1

### The initial deposition point of asphaltene method

The deposition of asphaltene was evaluated by measuring the absorbance using a UV spectrophotometer. The decrease in absorbance indicated the onset of asphaltene deposition. The initial point of asphaltene deposition was determined as the volume fraction of n-heptane at which the absorbance began to decrease. 9 mL of n-heptane:toluene mixtures (0:9, 1:8, 2:7, 3:6, 4:5, 5:4, 6:3, 7:2, 8:1, and 9:1 vol/vol), 0.6 mL of heavy crude oil toluene solution (30 g/L), and 0.4 mL of ionic liquid ethanol solution (25 g/L) were mixed and kept at 25°C for 24 hours. Subsequently, the absorbance of each solution was measured at 620 nm using a 752N UV-visible spectrophotometer. As can be seen in Fig. S1, the absorbance starts to decrease rapidly when the volume fraction of n-heptane exceeds 60% without the addition of ionic liquids. One curve is plotted for the points where the n-heptane volume fraction is less than 60% and another curve is plotted for the points where the n-heptane volume fraction is greater than 60%. From the intersection of the two curves, it can be concluded that the initial deposition point of asphaltenes in a heavy crude oil solution is 63%.



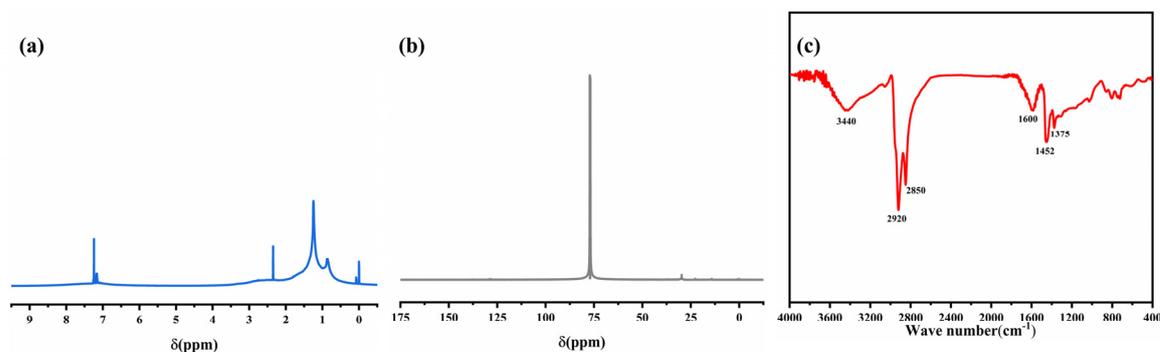
**Figure S1.** Variation of absorbance of heavy crude oil solution with n-heptane volume fraction

## Text S2

### Characterization of asphaltene structure

**Table S1.** Relative molecular weight and elemental analysis results of asphaltenes

	Result
M <sub>w</sub>	5414
C (%)	79.46
H (%)	7.18
S (%)	3.14
N (%)	1.35
O (%)	8.87
C/H	0.92



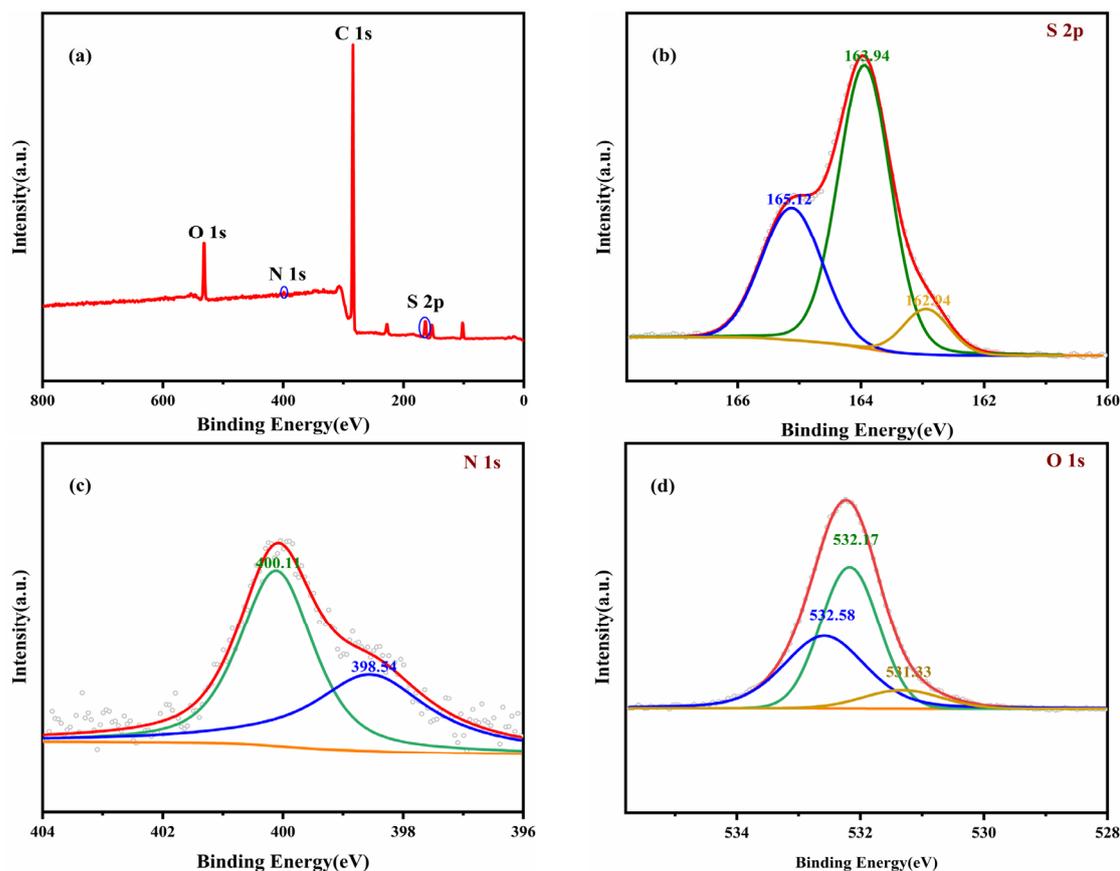
**Figure S2.** Asphaltene characterization results: (a) the <sup>1</sup>H NMR spectrum, (b) the <sup>13</sup>C NMR spectrum, (c) the infrared spectra

**Table S2.** Asphaltene <sup>1</sup>H NMR results

Parameters	Types of hydrogen	peak ranges (ppm)	Ratios (%)
H <sub>A</sub>	Aromatic hydrogen	6.0~9.0	12.15
H <sub>α</sub>	Alpha hydrogen in aromatic side chain	2.0~4.0	19.07
H <sub>β</sub>	Beta hydrogen in aromatic side chain	1.0~2.0	51.40
H <sub>γ</sub>	Gamma position and farther hydrogen in aromatic side chain	0.5~1.0	17.38

**Table S3.** Asphaltene <sup>13</sup>C NMR results

	<b>Types of carbon</b>	<b>peak ranges (ppm)</b>	<b>Ratios (%)</b>
<b>Aromatic carbon (100~150)</b>	Protonated aromatic carbon	100~127.1	18.03
	Aromatic bridgehead carbon	127.1~133	3.59
	CH <sub>3</sub> alkylated aromatic carbon	133~135	2.14
	cycloalkyl-arylene carbon	135~137	7.00
	≥C <sub>2</sub> alkylated aromatic carbon	137~150	8.89
<b>Saturated carbon (10~66)</b>	γ-CH <sub>3</sub>	10~15	5.00
	β-CH <sub>3</sub>	15~18	2.88
	α-CH <sub>3</sub> , branched CH <sub>3</sub>	18~22.5	6.29
	α-CH <sub>2</sub> , β-CH <sub>3</sub> , Aliphatic CH	22.5~37	25.55
	α-CH	37~66	20.63



**Figure S3.** XPS characterization results

### Text S3

#### Calculation method for solubility parameters

It is necessary to determine the density before calculating the solubility parameters of ionic liquids using the group contribution method. While experimental values for the densities of [BMIM]Cl and [OMIM]Cl are available, those for [C12-MIM]Cl and [C16-MIM]Cl are not[1,2]. Therefore, the latter must be calculated using the group contribution method [3]. To calculate the density of the ionic liquids, use Eq. S1, while Eq. S2 can be used to determine the molar volume. Finally, Eq. S3 is used to calculate  $\rho$ , and the contribution values of the atoms and functional groups in the cations and anions of the ionic liquids can be found in Appendices 1 and 2, respectively.

$$\rho = \frac{M}{V_m} \quad (\text{S1})$$

Where:  $\rho$  was the density of the ionic liquid, ( $\text{g}/\text{m}^3$ );  $M$  was the molecular mass of the ionic liquid, ( $\text{g}/\text{mol}$ );  $V_m$  was the molar volume, ( $\text{m}^3/\text{mol}$ ).

$$V_m = dm + \frac{N_{at}}{100}(c + aT + bP) \quad (S2)$$

$$dm = V_0 + n_r V_r + \sum n_i V_{c_i} + \sum m_j V_{a_j} \quad (S3)$$

Where:  $V_0$ ,  $V_r$  were constants;  $n_r$  denotes the total number of rings in the ionic liquid (including anions and cations);  $V_c$ ,  $V_a$  were the contribution values of the functional groups in the cations and anions, respectively (check Appendices 1 and 2);  $n_i$ ,  $m_j$  were the number of functional groups in the cations and anions, respectively;  $N_{at}$  was the total number of atoms in the ionic liquid;  $T$  was the temperature (K);  $P$  was the pressure (KPa).

The density value calculated using this method was denoted as  $\rho_{cal}$ , and the experimental value identified from the literature was denoted as  $\rho_{exp}$ , defining RE as the relative error between the calculated value  $\rho_{cal}$  and the experimental value  $\rho_{exp}$  as shown in Equation S4

$$RE = \frac{|\rho_{cal} - \rho_{exp}|}{\rho_{exp}} \quad (S4)$$

Where RE was the relative error;  $\rho_{cal}$  was the calculated value of density;  $\rho_{exp}$  was the experimental value of density.

Table S4 displays the calculated value  $\rho_{cal}$  of the ionic liquids, the experimental value  $\rho_{exp}$  obtained from the literature, and the corresponding relative error RE. It can be seen that the relative errors between the calculated ionic liquid density value  $\rho_{cal}$  and the experimental value  $\rho_{exp}$  are all within 1%. Therefore, we utilized the calculated values  $\rho_{cal}$  of the density for [C12-MIM]Cl and [C16-MIM]Cl and the experimental values  $\rho_{exp}$  of the density for the remaining ionic liquids in computing the ionic liquid solubility parameters.

**Table S4.** Density of ionic liquids

<b>Ionic liquid</b>	<b><math>\rho_{cal}</math> (g/cm<sup>3</sup>)</b>	<b><math>\rho_{exp}</math> (g/cm<sup>3</sup>)</b>	<b>RE(%)</b>
[BMIM]Cl	1.0881	1.0816	0.60
[OMIM]Cl	1.0118	1.0096	0.22
[C12-MIM]Cl	0.9704	/	/
[C16-MIM]Cl	0.9444	/	/

We employed the group contribution method developed by Trevor K. Carlisle et al. to determine the solubility parameters of the ionic liquids[4]. This involved

computing the molar volume of the ionic liquid using Equation S5 and, subsequently, utilizing Equation S6 to derive its solubility parameter.

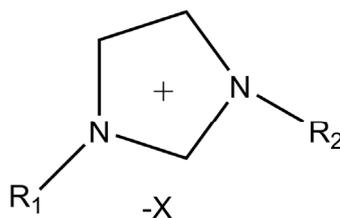
$$V_m = \frac{M}{\rho} \quad (\text{S5})$$

Where  $V_m$  was the molar volume of the ionic liquid ( $\text{cm}^3/\text{mol}$ );  $M$  was the molar mass of the ionic liquid ( $\text{g/mol}$ );  $\rho$  was the density of the ionic liquid ( $\text{g/cm}^3$ ).

$$\delta_{IL} = \frac{\sum_j F_j}{V_m} \quad (\text{S6})$$

Where  $\delta_{IL}$  was the solubility parameter of the ionic liquid ( $\text{MPa}^{1/2}$ );  $F_j$  was the molar attraction constant of the ionic liquid group ( $\text{MPa}^{1/2} \cdot \text{cm}^3 \cdot \text{mol}^{-1}$ );  $V_m$  was the molar volume of the ionic liquid ( $\text{cm}^3/\text{mol}$ ).

To categorize the imidazole ionic liquids used in this study, they were first divided based on their respective functional groups and structures, illustrated in Fig. S4. The imidazole ionic liquids were then separated into three parts, with  $R_1$  and  $R_2$  comprising one part each and the imidazole ring and anion forming the third part. Analysis of the imidazolium ionic liquids in this study revealed that the main functional groups of  $R_1$  and  $R_2$  were  $-\text{CH}_3$ ,  $-\text{CH}_2-$ , and phenyl, each displaying varying molar attraction constants as outlined in Table S5. The molar attraction constants of the imidazole ring and  $\text{Cl}^-$  were determined through back-calculation using the solubility parameter of 1-butyl-3-methylimidazolium chloride salt [BMIM]Cl ( $\delta_{IL}=24.14\text{MPa}^{1/2}$ ).



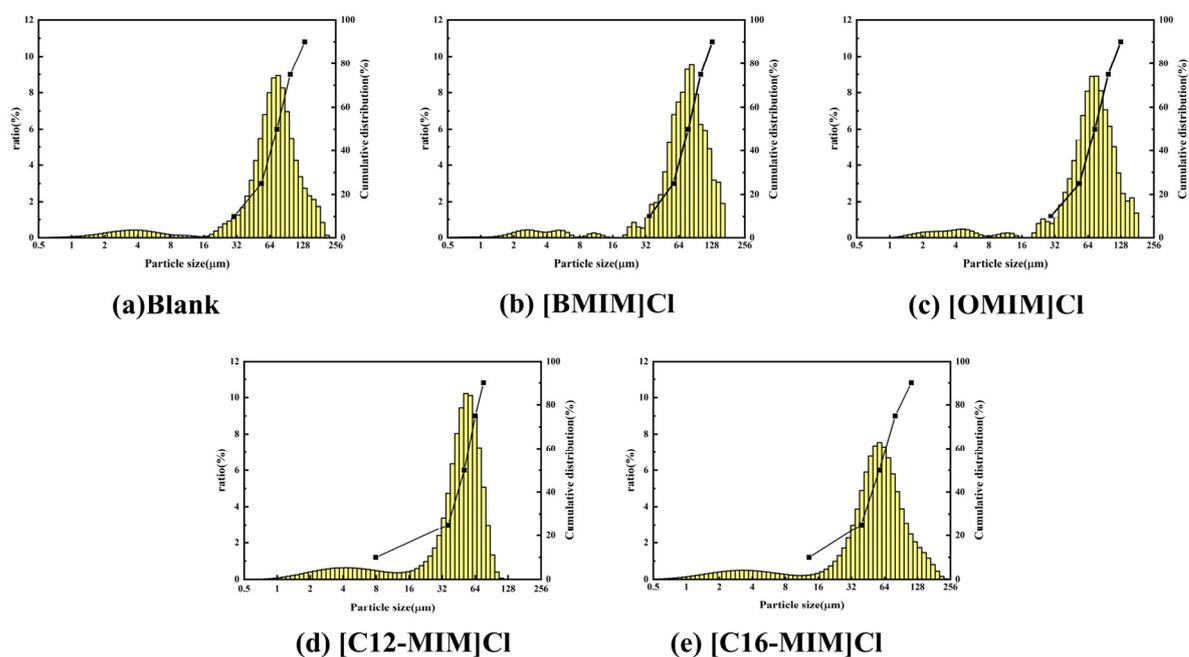
**Figure S4.** Group decomposition of imidazole-based ionic liquids

**Table S5.** Molar attraction constants of functional groups <sup>[124]</sup>

Group	F ( $\text{MPa}^{1/2} \cdot \text{cm}^3 \cdot \text{mol}^{-1}$ )
$-\text{CH}_3$	303
$-\text{CH}_2-$	269
Phenyl	1400

## Text S4

### Particle Size of asphaltene



**Figure S5.** Effect of ionic liquids on particle size distribution of asphaltene sediment particles: (a) blank, (b) [BMIM]Cl, (c) [OMIM]Cl, (d) [C12-MIM]Cl, (e) [C16-MIM]Cl

**Table S6.** Contributions of atoms and functional groups in cations[3]

Group		$V_c(\text{cm}^3/\text{mol})$
<b>Atomic contribution</b>		
N		12.0965
C		12.2105
H		0.9746
O		0.6759
F		0.7919
Si		27.2494
P		14.5812
S		17.5598
Br		5.9869
Fe	$m=1^a$	-81.9660
Cl	$m=1$	82.7637
I		20.4978
<b>Functional group contribution<sup>b</sup></b>		
=C< (ring) <sup>c</sup>		-3.4898
NH (ring)		9.3246

>CH <sup>-d</sup>		2.7969
CO		14.3775
COO		5.4468
OH		2.0058
C≡N		-11.8741
COOH		11.9135
Rn <sup>e</sup>	n>2	0.0851

a: m was the number of times the atom appears in the cation;

b: Those groups not represented by the symbols > or - (e.g., NH (ring), CO, COO) can also be connected to atoms (including H) or functional groups by double or single bonds;

c: (ring); It indicates that the group is in the ring structure;

d: The > or - symbols indicate groups linked to functional groups or atoms other than H;

e: n-alkyl chains with n carbon atoms, e.g. butyl or pentyl.

**Table S7.** Contributions of atoms and functional groups in anions[3]

Group	V <sub>a</sub> (cm <sup>3</sup> /mol)
<b>Atomic contribution</b>	
Cl	21.6536
Br	29.6404
I	46.3084
O	6.2398
B	20.3946
F	6.2740
N	8.4436
S	23.3129
C	11.1926
P	25.6053
H	1.2163
Al	18.7904
Nb	42.3397
Ta	39.0276
W	32.3795
Ga	19.3993
Fe	18.6362
In	26.2812
<b>Functional group contribution</b>	
CN	1.7655

=C<(ring) <sup>a</sup>	-1.1086
CO	-12.6131
COO	8.0128
COOH	-22.7409
OH	-6.6065

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a: (ring); It indicates that the group is in the ring structure.

## References

1. He, R.-H.; Long, B.-W.; Lu, Y.-Z.; Meng, H.; Li, C.-X., Solubility of Hydrogen Chloride in Three 1-Alkyl-3-methylimidazolium Chloride Ionic Liquids in the Pressure Range (0 to 100) kPa and Temperature Range (298.15 to 363.15) K. *Journal of Chemical & Engineering Data* **2012**, 57, (11), 2936-2941.
2. Mac Dowell, N.; Llovel, F.; Sun, N.; Hallett, J. P.; George, A.; Hunt, P. A.; Welton, T.; Simmons, B. A.; Vega, L. F., New experimental density data and soft-SAFT models of alkyimidazolium ([C(n)C(1)im](+)) chloride (Cl(-)), methylsulfate ([MeSO(4)](-)), and dimethylphosphate ([Me(2)PO(4)](-)) based ionic liquids. *J Phys Chem B* **2014**, 118, (23), 6206-21.
3. Taherifard, H.; Raeissi, S., Estimation of the Densities of Ionic Liquids Using a Group Contribution Method. *Journal of Chemical & Engineering Data* **2016**, 61, (12), 4031-4038.
4. Carlisle, T. K.; Bara, J. E.; Gabriel, C. J.; Noble, R. D.; Gin, D. L., Interpretation of CO<sub>2</sub> Solubility and Selectivity in Nitrile-Functionalized Room-Temperature Ionic Liquids Using a Group Contribution Approach. *Industrial & Engineering Chemistry Research* **2008**, 47, (18), 7005-7012.