Engineered Science
DOI: https://dx.doi.org/10.30919/es1102

Deep Eutectic Solvents for Sustainable Management of Asphaltene Deposition in Oil Production

Salimat Ryspaeva,[1] Aigul Kerimkulova,[1,*] Khadichakhan Rafikova,[1] Saule Nauryzova,[1] Sholpan Islam,[1] Murat Aydemir[2] and Madina Kozhaisakova[3]

Abstract

Deep Eutectic Solvents (DES) offer a sustainable solution to mitigating asphaltene deposition in oil production, minimizing environmental impact and enhancing the operational efficiency in the petroleum industry. The paper investigates the sustainable management of asphaltene deposition in oil production through the application of Deep Eutectic Solvents (DESs). Three DES formulations were prepared: DES1 (Citric acid:Glycerin, 1:4 ratio), DES2 (Citric acid:Ethylene Glycol, 1:4 ratio), and DES3 (Choline chloride:Glycerin, 1:2 ratio). The physical properties (pH, density, and viscosity) of these DESs were measured. The study utilized Karazhanbas crude oil from Western Kazakhstan, characterized by distinct hydrocarbon groups. The weight composition was as follows: Paraffin-naphthenic 17.2%, Aromatic (light) 10.2%, Aromatic (medium) 8.1%, Aromatic (heavy) 28.2%, Total resins 24.1%, and Asphaltenes 12.2%. The FTIR spectrum of the received DES and asphaltene was also determined. Asphaltene deposition was studied both with and without DES inhibitors. Microscopic tests revealed that DES3 exhibited superior results, as evidenced by significantly smaller asphaltene particle sizes compared to other DES formulations and the control without DES. The findings suggest that DES3 holds promise as an effective inhibitor for asphaltene deposition in oil production, offering a sustainable and environmentally friendly approach to address challenges associated with asphaltene-related issues in the petroleum industry.

Keywords: Asphaltenes; Deep eutectic solvents; Asphaltene deposition inhibitor; Agglomeration trend; Absorbance spectra.
Received: 22 December 2023; Revised: 30 December 2023; Accepted: 31 January 2024.
Article type: Research article.

1. Introduction

Crude oil is a flammable, oily liquid of natural origin found in the Earth's sedimentary shell. Its main components include water, mechanical impurities, asphaltene-resin, hydrocarbon and ash compounds, as well as small percentages of sulfur and oxygen compounds. [1]

Among these, asphaltenes have the highest molecular weight fraction, consisting of mixtures of polycyclic aromatic and naphthenic-aromatic structures, which include heteroatoms, metal complexes, and aliphatic substituents.[2] The quantity and characteristics of asphaltene components in crude oil depend to a greater or lesser extent on the oil's source.[3] During oil refining, asphaltene components cannot be distilled and remain in the residual fuel as the distilled fractions are removed. Therefore, the content of asphaltenes is of paramount importance.[4] Asphaltene components are loose solids ranging from dark brown to black in color. They do not have a specific melting point and typically foam and swell when heated, leaving behind a carbonaceous residue.[5]

The structure of the asphaltene molecule, which determines its properties, can be represented by two models according to literature data: the "continent" and the "archipelago" models.[6] The "continent" model suggests that the molecule consists of a large polycondensed core of 6-17 rings surrounded by several aliphatic tails and heteroatoms (Fig. 1).

According to the second model, the “archipelago”, asphaltene molecules are many separate groups of 5-7

[1] *Department of Chemical and Biochemical Engineering, Satbayev University, Almaty, Satbayev 22, Kazakhstan.*
[2] *Department of Chemistry, Faculty of Science, Dicle University, Diyarbakir 21280, Turkey.*
[3] *Department of Chemistry, Chemical Technology and Ecology, Almaty Technological University, Almaty, Tole by 100, 050012, Kazakhstan.*
**Email:* kerimkulova07@mail.ru (A. Kerimkulova)

condensed rings connected by aliphatic and heteroatomic bridges. Side substituents are also present in such molecules, represented by aliphatic and heteroatomic sites (Fig. 2).

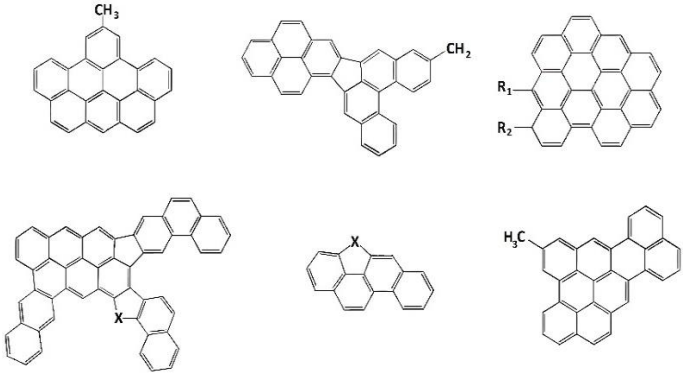


Fig. 1 Asphaltene molecules of the “continent" type.

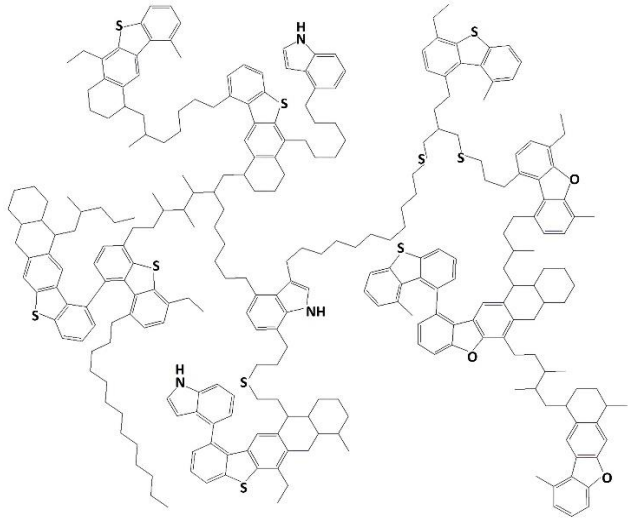


Fig. 2 Asphaltene molecules of the “archipelago" type.

The predominant type of “continent” molecules precipitates from oil with minimal addition of n-alkane and represents the heaviest and most polar part of asphaltenes. The second type of molecules, the “archipelago”, precipitates from oil when the maximum amount of n-alkane is added and constitutes a lighter and less polar part that dissolves better in low molecular weight arenas compared to the first type. Consequently, molecules of the “continental” fraction act as aggregation accelerators. Their high content in raw materials leads to the instability of the dispersed system and precipitation of asphaltene aggregates with minimal changes in external conditions. In contrast, the predominance of molecules of the "archipelago” fraction increases the system's resistance to asphaltene deposition.[6,7]

The propensity of asphaltenes to form aggregates is a crucial characteristic, complicating numerous technological procedures involving oil and petroleum products.[8] Asphaltenes can exist in production under high pressure as single molecules or as nanoaggregates.[9] However, changes in the system's conditions, such as pressure loss in the reservoir during production, mixing of different oils, temperature changes, adjustments to the flow pattern, and the addition of foreign chemicals to the oil can cause them to aggregate or become unstable.[10] This agglomeration increases operating expenses and causes production losses, pipeline, and filter blockages. The two main approaches to mitigate this problem are to either remove the formed aggregates from the oil or to use a variety of inhibitors and solvents to prevent their formation in the first place.[11]

Recent research has extensively investigated asphaltene deposition and the development of effective solutions.[7] Asphaltene deposition is commonly prevented by using asphaltene dispersants[8] or additives that modify the dispersion state of asphaltene to stabilize it. Polymer and low-molecular-weight asphaltene dispersants are commonly employed today. Examples of low molecular weight asphaltene dispersants include ionic liquids, amides, imides, and acidic amphiphilic molecules.[12] These dispersants can inhibit asphaltene aggregation by creating acid-base interactions and enhance crude oil fluidity by forming hydrogen bonds with asphaltene molecules.[13] However, they are associated with drawbacks such as high preparation costs and poor compatibility with different crude oils. Polymer asphaltene dispersants offer more adsorption sites and improved interaction with asphaltene molecules.[14] Polymethacrylate, polystyrene/maleate copolymer, alkylene/maleate copolymer, and other polymer asphaltene dispersants are commonly used.[15,16] These polymers exhibit better compatibility with crude oil due to chemical modifications in their polar groups.[17] However, it is important to note that the chemical composition of asphaltene molecules varies significantly between samples and even within an oil field, making it challenging to identify a universal inhibitor for this purpose.

Thus, the development and utilization of new deposition inhibitors that are efficient, cost-effective, and environmentally friendly are crucial. Recent data from several authors suggest that deep eutectic solvents (DES) have been examined as potential deposition agents for this purpose.[12,15] "Deep eutectic solvents" (DES), a novel class of solvents that had many physicochemical characteristics with ionic liquids, were discovered in the early 2000s.[18,19] The formation of a deep eutectic solvent is based on the establishment of hydrogen bonds, or Van der Waals interactions, between the donor and the acceptor of hydrogen bonds.[20] Organic acids, alcohols, and sugars usually act as donors, and quaternary ammonium salts act as acceptors.[21] The most common components of "green" solvents are shown in Table 1. To

create a eutectic combination with a melting point lower than the melting point of the individual components, quaternary ammonium salt (HBD) is typically complexed with a metal salt or a hydrogen-bond acceptor (HBA). Since the process is straightforward and leaves no by-products, it can be regarded as an environmentally benign synthesis because there are no emissions or waste products, and the finished combination contains 100% of the original atoms.[22,23]

Table 1. Donors and acceptors of hydrogen bonds, most often forming Deep Eutectic Solvents.

Hydrogen bond acceptors	Donors of hydrogen bonds
Choline chloride	Malic acid
Choline bitartrate	Oxalic acid
Acetylcholine chloride	Glucose
L-Proline	Glycerin
L-Alanine	Ethylene Glycol
L-Histidine	Propylene Glycol

Most DESs are biodegradable, have low toxicity, and are volatile, making them suitable for various industries, including pharmaceuticals.[25] Many DESs are also liquid at room temperature.[24] Unlike ionic liquids, deep eutectic liquids are easy to create and can exhibit a wide range of physicochemical properties depending on their constituents, molar ratios, and water content. DESs are typically viscous liquids with minimal vapor pressure. Their viscosity can be significantly reduced by increasing the temperature or adding a small amount of water.[26]

According to Dwamena, A. K.,[27] most of the DESs developed and studied at that time were hydrophilic. However, there was a need to develop hydrophobic DESs to extract nonpolar organic and inorganic molecules, as hydrophilic DESs interacted theoretically only with polar compounds.

This research aims to explore the potential of deep eutectic solvents (DESs) for the sustainable management of asphaltene deposition in oil production. By leveraging the tunable properties of DESs, we investigate their efficacy in preventing asphaltene agglomeration, promoting enhanced oil recovery, and enhancing the overall efficiency and environmental sustainability of oil production processes. The environmentally benign nature of DESs aligns with the growing global emphasis on sustainable practices within the oil and gas industry.[12]

In this study, three different types of deep eutectic solvents were obtained, and their potential as inhibitors of asphaltene deposition was studied using UV-visible spectroscopy and microscopic observation.

2. Experimental section

2.1 Materials

Deep eutectic solvents were synthesized using citric acid (Sigma-Aldrich, >99%), glycerin (Sigma-Aldrich, >99%), ethylene glycol (Sigma-Aldrich, >99%) and choline chloride (Merck, >99%). Toluene (Merck, >99%) and n-heptane (Merck, >99%) were used as a solvent. Before use, choline chloride was dried for 48 hours under vacuum conditions, and other reagents were used for additional purification. In many studies, choline chloride (ChCl) is widely used as HBA, given its cheapness, low toxicity, biodegradability and biocompatibility.[18]

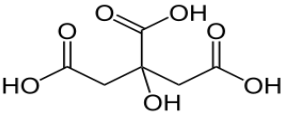
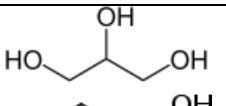
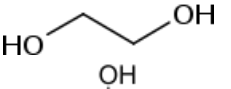
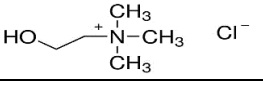
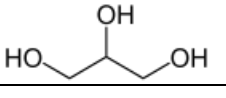
2.2 Preparation of DES

The eutectic mixtures were prepared by mixing the two components in the appropriate molar ratios (refer to Table 2) at 80 °C and normal pressure until a homogeneous, colorless liquid was formed. Following the formation of the DESs, their density, viscosity, and pH were analyzed. Density was measured at 25 °C using a density meter with a vibrating tube (Excellence D6, Mettler Toledo), viscosity was determined using an Ostwald viscometer (China), and pH was measured using a pH meter (HM Digital HM-200, USA). Additionally, the functional groups present in the DESs were analyzed using Fourier-transform infrared spectroscopy (FTIR).

2.3 Asphaltene extraction and sample preparation

In accordance with the procedure outlined in API IP143, asphaltenes were extracted from a sample of Karazhanbas crude oil (Western Kazakhstan) by precipitating them with the

Table 2. Structural formulas of starting substances and their mass ratio.

DES model No.	HBA	Structural formula	HBD	Structural formula	Molar ratio
DES1	Citric acid		Glycerin		1:4
DES2	Citric acid		Ethylene Glycol		1:4
DES3	Choline chloride		Glycerin		1:2

addition of n-heptane to the oil at a volume ratio of 40:1. Subsequently, Fourier-transform infrared spectroscopy (FTIR) was conducted using an FTIR-8400S spectrometer from Shimadzu, Japan, to study the structure of the asphaltenes. Elemental analyses were also performed using a Unicube Elemental Analyzer from Belgium to determine the composition of the asphaltenes.

The group composition of Karazhanbas crude oil was also studied by elemental analysis to show the mass fraction of asphaltenes in oil (Table 3). As can be seen from Table 3, the asphaltene content is 12.2%, which proves the high viscosity of the selected raw materials.

Table 3. Group composition of Karazhanbas crude oil.

The content of individual groups of hydrocarbons	% by weight
Paraffin-naphthenic	17.2
Aromatic (light)	10.2
Aromatic (medium)	8.1
Aromatic (heavy)	28.2
Total resins	24.1
Asphaltenes	12.2

Toluene was mixed with 0.5 weight percent of asphaltenes to create the model oil for this investigation. The mixture was then stirred for two hours to ensure the complete dissolution of the asphaltenes and to prevent any asphaltene precipitation.[12] This concentration was selected to facilitate the study of the onset of asphaltene deposition.

2.4 Investigation of the deposition starting point by UV spectrometry

The onset of asphaltene deposition, with and without inhibitors (DES), was measured using a UV-Vis spectrophotometer (Lambda 25, Perkin Elmer). Quartz cuvettes with a path length of 10 cm were used for the measurements. Initially, model oil and n-heptane were tested separately in pure form using air as a medium in the wavelength range of 700 to 900 nm. Subsequently, samples of deep eutectic solvents were tested. Several compositions of the model oil were created by titrating with n-heptane. A wavelength of 850 nm was selected to observe the behavior of asphaltene samples based on information from the literature.[15] The results of the experiments were used to create curves for the kinetic deposition of asphaltenes.

2.5 Microscopic test

Visual observations with a microscope were performed using a QUANTA 3D 200i microscope (FEI, USA) to demonstrate the deposition of asphaltenes in the presence and absence of inhibitors. Local analysis of the chemical composition of the samples was conducted using a microscope equipped with an energy dispersive X-ray spectrometer (EDAX) and a semiconductor detector with an energy resolution of 128 eV. Cover glasses measuring 20 × 20 mm^2 and microscope slides measuring 76 = 26 mm^2 were used for sample preparation.

3. Results and discussion

3.1 Characteristics of deep eutectic solvents

In this study, choline chloride and citric acid served as the hydrogen bond acceptors (HBA), while glycerin and ethylene glycol acted as the hydrogen bond donors (HBD). As previously noted, the pH, density, and viscosity of the produced DES samples were examined (refer to Table 4). The pH value is a crucial factor to consider when creating novel solutions, as it can impact chemical reactions. In this regard, the obtained DESs can be considered as media that do not significantly affect the acidity of the reagents, as the pH of the solvents was found to be nearly neutral, ranging from 6.7 to 7.15.

Density is a significant physical indicator of intermolecular interactions and plays a crucial role in the development and execution of technological processes. In this investigation, the densities of the DESs at 25 °C were found to be 1.03 g/cm^3, 1.12 g/cm^3, and 1.207 g/cm^3, respectively. According to published data, the majority of DESs have densities between 1.0 and 1.35 g/cm^3 at 25 °C. It is observed that DESs have a denser structure than water, which can be attributed to the formation of hydrogen bonding that increases the material's density.

When designing equipment and calculating fluid flow, it is crucial to consider the viscosity of DESs. Due to the extensive network of hydrogen bonds that connect each component, DESs typically exhibit high viscosity values (> 100 cP).[22] This high viscosity limits the mobility of molecular compounds within DESs. In this study, the DESs produced had viscosities of 133.1 cP, 138.5 cP, and 148.99 cP, respectively. High viscosity in DESs can also result from large ion sizes, Van der Waals forces, or limited unfilled volumes.

The FTIR spectrum of the resulting DESs was obtained and analyzed to identify and explain conformational changes and interactions between the functional groups HBA and HBD (refer to Fig. 3). By examining the related peaks, it was possible to determine the interactions of hydrogen bonds between HBD and HBA in the DESs. Peaks at approximately 3400, 3392, and 3355 cm^{-1} in all DES models can be attributed to the stretching vibration of the O-H functional group, indicative of hydrogen bonds. The C-H bond also exhibits characteristic peaks at 2929 and 2878 cm^{-1}, while the C-N stretching modes are represented by bands at 955 and 923

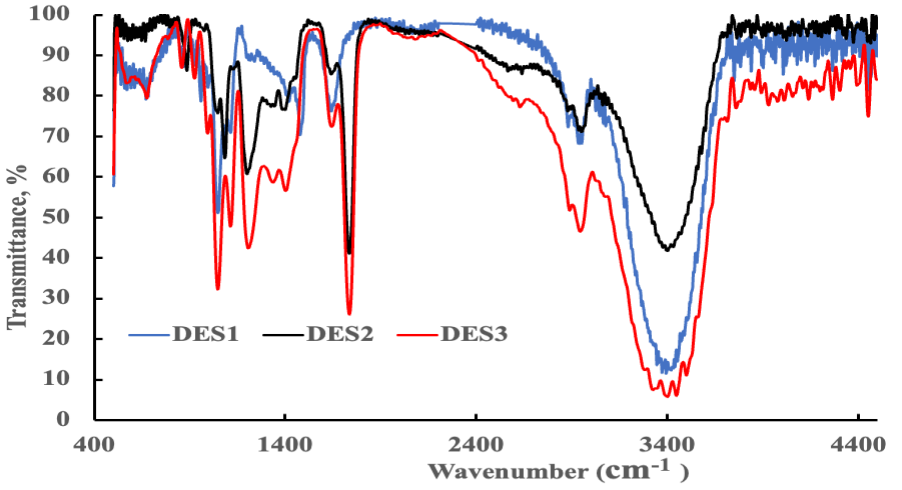


Fig. 3 FTIR spectrum of the received DES.

cm^{-1}, respectively.

Table 4. Physical properties of the obtained deep eutectic solvents.

DES model No.	Parameter	Meaning
DES №1. CA:Gl [1:4]	pH	6.75
DES №2. CA:EG [1:4]	pH	7.01
DES №3. ChCl:Gl [1:2]	pH	7.15
DES №1. CA:Gl [1:4]	Density, g/cm^3	1.03
DES №2. CA:EG [1:4]	Density, g/cm^3	1.12
DES №3. ChCl:Gl [1:2]	Density, g/cm^3	1.207
DES №1. CA:Gl [1:4]	Viscosity, cP	133.1
DES №2. CA:EG [1:4]	Viscosity, cP	138.5
DES №3. ChCl:Gl [1:2]	Viscosity, cP	148.99

3.2 Characteristics of extracted asphaltenes from oil

The FTIR spectrum of asphaltenes extracted from Karazhanbas crude oil (Western Kazakhstan) is shown in Fig. 4. The analysis of the obtained FTIR spectra shows that the main structural elements of asphaltenes are methylene and methyl groups. The characteristic bands observed on the spectrum corresponding to certain structural groups have the following maxima: 1380-1370 cm^{-1} (C-H bond in CH_3 groups), 1470-1460 cm^{-1} (C-H bond in CH_2 groups), 1605-1640 cm^{-1} (aromatic CH). Several bands in the range of 870 – 750 cm^{-1} correspond to fluctuations in the C–H bond of mono- and polycyclic aromatic hydrocarbons and their substituted ones. The absorption bands with maxima of 2849, and 2918 cm^{-1} corresponding to valence vibrations of C-H bonds of methyl and methylene groups and 3480 cm^{-1} valence vibrations of -OH groups of phenols are the most intense in the studied FTIR spectrum.

Elemental analysis was conducted to assess the elemental content and group composition of asphaltene (refer to Table 5). The strong aromaticity of asphaltene is indicated by the molar ratio of H/C, which is close to 1 in this table. Additionally, asphaltene has a higher sulfur (S) content compared to other types of oil.

Table 5. Elemental chemical composition of asphaltene.

The content of the elements	% by weight
Carbon	82
Hydrogen	8
Sulfur	7.2
Nitrogen	1.5
Oxygen	1.2

3.3 Results of asphaltene deposition tests by UV spectrometry

The main objectives of this research were to determine the origins of asphaltene deposition and to evaluate the effectiveness of DESs in inhibiting it using UV-vis spectrometry. The amount of n-heptane required to reach the onset of deposition was compared between samples with and without DES inhibitors under the same conditions. A greater amount of n-heptane was needed in the presence of DESs, indicating their beneficial effect in inhibiting asphaltene deposition. It was expected that samples with inhibitors would have smaller asphaltene particle sizes than those without inhibitors at the initial n-heptane/model oil ratio.

Using a UV-vis spectrophotometer (Lambda 25, Perkin Elmer), the behavior of asphaltene during agglomeration and the onset of deposition were evaluated by measuring the amount of precipitation after adding varying amounts of n-heptane to the model oil without inhibitors and with DES inhibitors, followed by mixing (Fig. 5).

The absorption intensity decreases as the samples used for the n-heptane titration become more diluted until precipitation occurs. From a physics standpoint, precipitation begins when aggregate formation outweighs the dilution effect.[21,22] Fig. 5

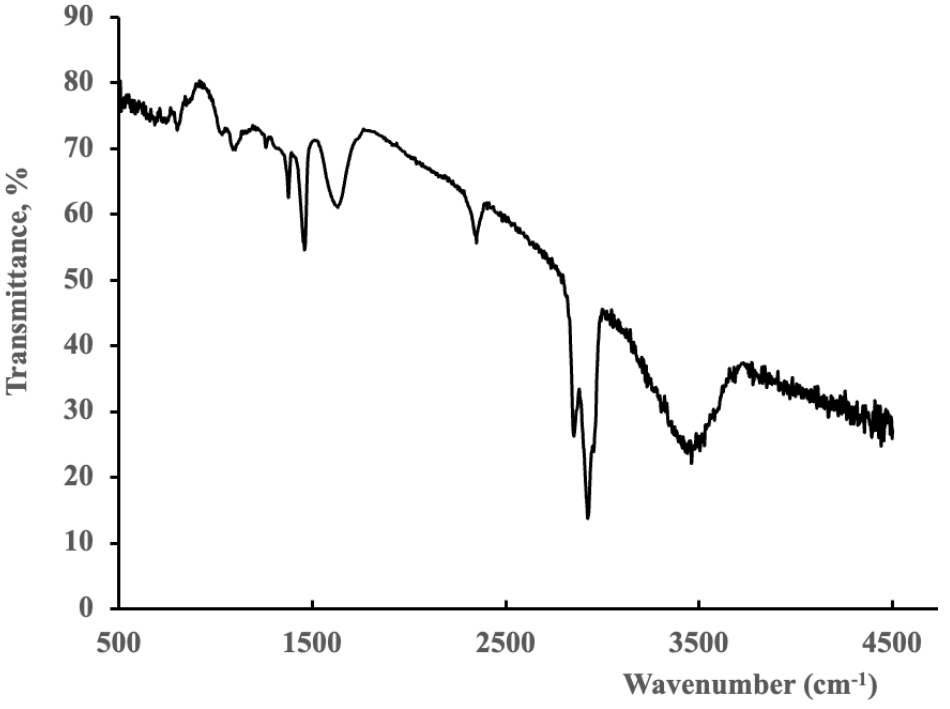


Fig. 4 The FTIR spectrum of asphaltene.

illustrates the trend in absorption intensity (vertical axis) of samples titrated with n-heptane. The graph shows the absorption intensity against the ratio of n-heptane to model oil (horizontal axis), both with and without the addition of three samples of inhibitors. The starting point is considered the point at which the horizontal trend diverges. All groups exhibit the same upward trend, but the addition of n-heptane reduces the absorption intensity despite this trend. The onset of the process was successfully delayed by DES3 to approximately 60% by weight of n-heptane compared to the sample without inhibitors and other DES samples. Three repetitions of each measurement resulted in an average deviation of less than 1%. All samples had absorption intensities higher than 0.5 before the addition of n-heptane, but this intensity sharply dropped after its addition due to the diluting effect of n-heptane. At a ratio of 2, the absorption coefficient for the sample containing

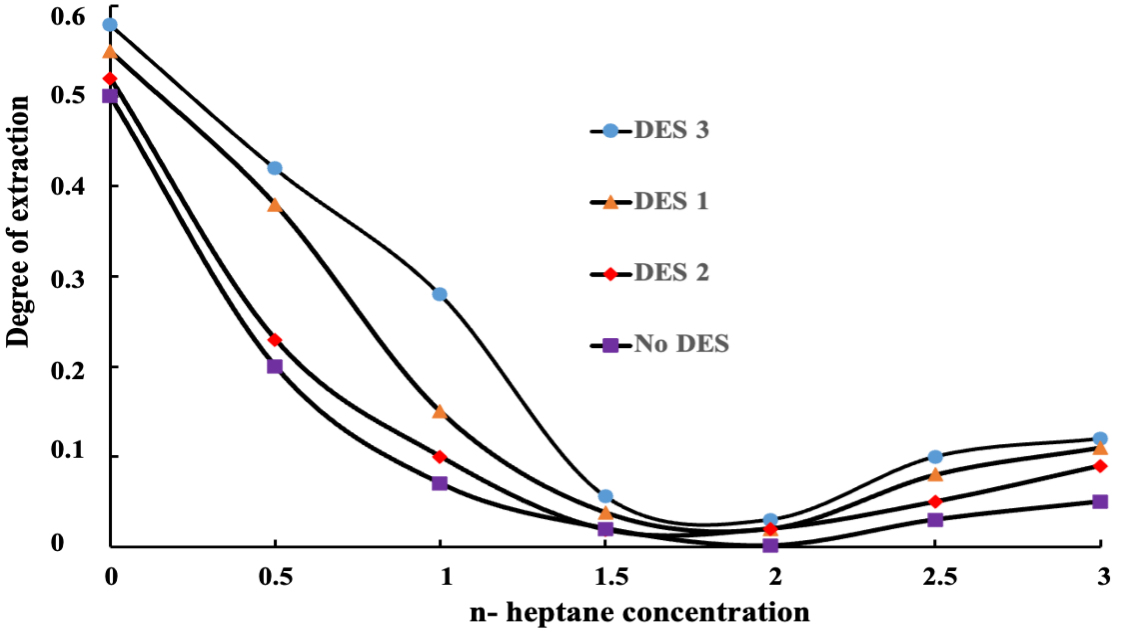


Fig. 5 Intensity curve based on the result of UV spectrometry at the beginning of asphaltene deposition (ratio of model oil with n-heptane without and with inhibitors).

DES3 dropped to less than 0.03, while at a ratio of 1.5, the absorption coefficient for the sample without inhibitors was approximately 0.02. Although precipitation occurred due to the continued addition of n-heptane, the formed asphaltene particles overcame the dilution effect of n-heptane, leading to an increase and peak in absorption intensity. For the model oil sample, the absorption coefficient was 0.03 at a ratio of 2.3, and for the DES3 group, it was 0.1 at a ratio of 2.5 with n-heptane.

3.4 Microscopic test results

The microscopic method allows us to take images and visually track the study. Fig. 6 shows four ratios with n-heptane of the model oil, first without the addition of inhibitors, and then with the addition of DES1, DES2, and DES3, respectively. As can be seen from the figures, in the presence of DES, the size of asphaltene particles in oil decreases, this shows the interaction of hydrogen bonds in deep eutectic solvents with asphaltene particles in oil. Fig. 6a shows a visual image of large asphaltene particles in the model oil (asphaltene + toluene), as the amount of n-heptane increases, the polarity of the entire sample decreases, and asphaltene particles tend to agglomerate, this leads to the attraction of asphaltene particles to each other and causes precipitation. Similar findings can be found from the authors when they studied the sizes of asphaltenes after adding polymeric additives to the model oil.[16] From these models, it can be seen that in comparison with DES 1 (b) and DES 2 (c) as a precipitation inhibitor, DES 3 (d) shows an optimal dissolution trend.

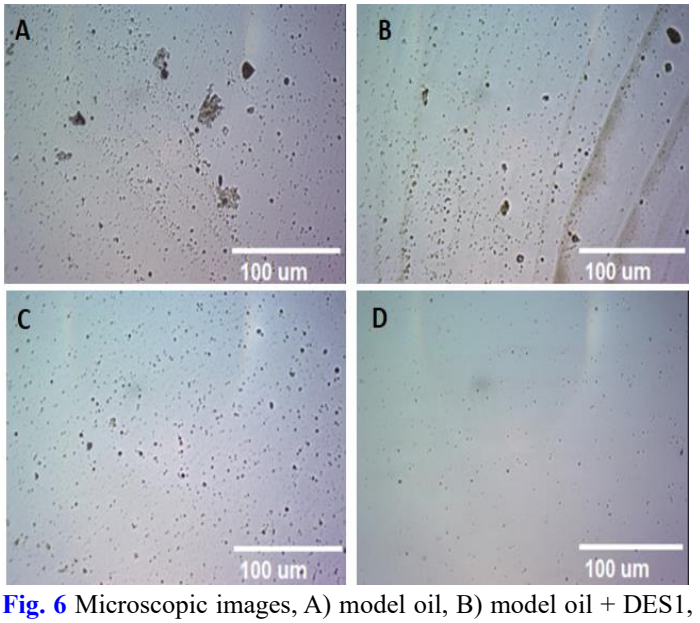


Fig. 6 Microscopic images, A) model oil, B) model oil + DES1, C) model oil + DES2, D) model oil + DES3.

4. Conclusion

During the research, various types of deep eutectic solvents (DESs) were synthesized and tested as inhibitors of asphaltene deposition in West Kazakhstan oil. The effectiveness of DESs in preventing asphaltene deposition was assessed using UV spectroscopy, and the microscopic method was employed to observe asphaltene deposition behavior and validate the UV spectroscopy results.

The experimental study involved titrating model samples (asphaltene + toluene) with different ratios of n-heptane, both with and without an inhibitor. The results indicated that asphaltene deposition occurred in samples without inhibitors, according to the specified n-heptane/model oil ratio.

DES3 effectively delayed the onset of asphaltene deposition by approximately 60% by weight of n-heptane compared to other samples with DES additives. Strong hydrogen bonds and hydrophobic interactions between asphaltenes and inhibitors led to the partial disintegration of asphaltenes.

Based on the study results, DESs show promise as inhibitors of asphaltene deposition due to their ease of synthesis, affordability, and biodegradability compared to traditional inhibitors.

Acknowledgments

The research is funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan (Grant No: IRN AP19676664)

Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

References

[1] N. Tileuberdi, M. Mashrapova, Zh. Toktarbay, A Review on Nitrogen Flooding for Enhanced Oil Recovery, *ES Materials & Manufacturing*, 2023, **22**, 968, doi: 10.30919/esmm968.

[2] C. Zheng, M. Brunner, H. Li, D. Zhang, R. Atkin, Dissolution and suspension of asphaltenes with ionic liquids, *Fuel*, 2019, **238**, 129-138, doi: 10.1016/j.fuel.2018.10.070.

[3] S. Ozdoyev, V. Popov, N. Tileuberdi, M. Huadong, Paleographic conditions and oil-gas prospects in the alakol depression (east kazakhstan), International Multidisciplinary Scientific GeoConference: SGEM, 2020, **20**, 727-732, doi: 10.5593/sgem2020/1.2/s06.092.

[4] A. Sanati, MR. Malayeri, Hydrophobic Deep Eutectic Solvent and Glycolipid Biosurfactant as Green Asphaltene Inhibitors:Experimental and Theoretical Studies, *Energy Fuels*, 2021, **35**, 4791-4802, doi: 10.1021/acs.energyfuels.0c03922.
[5] J. G. Speight, Petroleum Asphaltenes - Part 1: Asphaltenes, resins and the structure of petroleum, *Oil and Gas Science and Technology*, 2004, **59**, 467-477, doi:10.2516/ogst:2004032.
[6] S. I. Ali, Z. Awan, S.M. Lalji, Laboratory evaluation experimental techniques of asphaltene precipitation and deposition controlling chemical additives, *Fuel*, 2022, **310**, 122194, doi: 10.1016/j.fuel.2021.122194.
[7] H. Groenzin, O.C. Mullins, Asphaltene Molecular Size and Structure, *Journal of Physical Chemistry*, 1999, **103**, 11237-11245, doi: 10.1021/jp992609w.
[8] F. R. Sultanov, Ye. Tileuberdi, Ye. Ongarbayev, Z.A. Mansurov, K.A. Khaseinov, B.K. Tuleutaev, F. Behrendt, Study of Asphaltene Structure Precipitated from Oil Sands, *Eurasian Chemico-Technological Journal*, 2012, **15**, 77, doi: 10.18321/ectj143.
[9] S. I. Andersen, Flocculation onset titration of petroleum asphaltenes, *Energy Fuels*, 1999, **13**, 315-322, doi:10.1021/ef980211d.
[10] T. A. Al-Sahhaf, M. A. Fahim, A. S. Elkilani, Retardation of asphaltene precipitation by addition of toluene, resins, deasphalted oil and surfactants, *Fluid Phase Equilibria*, 2002, **194**, 1045-1057, doi:10.1016/S0378-3812(01)00702-6.
[11] E. Y. Sheu, Petroleum asphaltene properties, characterization, and issues, *Energy Fuels*, 2002, **16**, 74-82, doi:10.1021/ef010160b.
[12] A. Sanati, M. R. Malayeri, O. Busse, J. J. Weigand, Inhibition of asphaltene precipitation using hydrophobic deep eutectic solvents and ionic liquid, *Journal of Molecular Liquids*, 2021, **334**, 116100, doi: 10.1016/j.molliq.2021.116100.
[13] L. K. Kundarapu, S. Choudhury, S. Acharya, Combined experimental and molecular dynamics investigation of 1D rod-like asphaltene aggregation in toluene-hexane mixture, *Journal of Molecular Liquids*, 2021, **339**, 116812, doi: 10.1016/j.molliq.2021.116812.
[14] X. Li, S. Lu, M. Niu, R. Cheng, Y. Gong, J. Xu, Asphaltene inhibition and flow improvement of crude oil with a high content of asphaltene and wax by polymers bearing ultra-long side chain, *Energies*, 2021, **14**, 8243, doi: 10.3390/en14248243.
[15] S. Jahangiri, A. Shahrabadi, A. Heydari, S. Javadian, A. H. Nazemi, S. M. Jahangiri, Choline chloride/monoethylene glycol deep eutectic solvent as a new asphaltene precipitation inhibitor, *Petroleum Science and Technology*, 2017, **35**, 1896-1902, doi: 10.1080/10916466.2017.1369116.
[16] Ye. S. Panova, Ye. A. Issabayev, M.T. Baigaziyeva, G. I. Boiko, N. P. Lyubchenko, R.G. Sarmurzina, Analysis of oil sludge and selection of solvents for the extraction method of petroleum products recovery, *Bulletin of the Karaganda University Chemistry Series*, 2018, **92**, 75-80, doi: 10.31489/2018ch4/75-80.
[17] S. S. Kozhabekov, A. A. Zhubanov, Z. Toktarbay, Study the rheological properties of waxy oil with modified pour point depressants for the South Turgai oil field in Kazakhstan, *Oil & Gas Science and Technology – Revue D'IFP Energies Nouvelles*, 2019, **74**, 28, doi: 10.2516/ogst/2019004.
[18] A. P. Abbott, D. Boothby, G. Capper, D. L. Davies, R. K. Rasheed, Deep eutectic solvents formed between choline chloride and carboxylic acids: versatile alternatives to ionic liquids, *Journal of the American Chemical Society*, 2004, **126**, 9142-9147, doi: 10.1021/ja048266j.
[19] A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed, V. Tambyrajah, Novel solvent properties of choline chloride/urea mixtures, *Chemical Communications*, 2003, **23,** 70-71, doi: 10.1039/b210714g.
[20] B. Y. Zhao, P. Xu, F. X. Yang, H. Wu, M. H. Zong, W. Y. Lou, Biocompatible deep eutectic solvents based on choline chloride: characterization and application to the extraction of rutin from Sophora japonica, *ACS Sustainable Chemistry & Engineering*, 2015, **3**, 2746-2755, doi: 10.1021/acssuschemeng.5b00619.
[21] W. Tang, G. Li, B. Chen, T. Zhu, K. H. Row, Evaluating ternary deep eutectic solvents as novel media for extraction of flavonoids from Ginkgo biloba, *Separation Science and Technology*, 2017, **52**, 91-99, doi: 10.1080/01496395.2016.1247864.
[22] W. Rahmalia, A. Shofiyani, Y. Sutiknyawati, S. Septiani, Simple green routes for metal-bixin complexes synthesis using glycerol-based deep eutectic solvent, *Indonesian Journal of Chemistry*, 2022, **22**, 1759, doi: 10.22146/ijc.76759.
[23] E. L. Smith, A. P. Abbott, K. S. Ryder, Deep eutectic solvents (DESs) and their applications, *Chemical Reviews*, 2014, **114**, 11060-11082, doi: 10.1021/cr300162p.
[24] Y. Dai, J. van Spronsen, G. J. Witkamp, R. Verpoorte, Y. H. Choi, Natural deep eutectic solvents as new potential media for green technology, *Analytica Chimica Acta*, 2013, **766**, 61-68, doi: 10.1016/j.aca.2012.12.019.
[25] H. Qin, X. Hu, J. Wang, H. Cheng, L. Chen, Z. Qi, Overview of acidic deep eutectic solvents on synthesis, properties and applications, *Green Energy & Environment*, 2020, **5**, 8-21, doi: 10.1016/j.gee.2019.03.002.
[26] Y. Liu, J. B. Friesen, J. B. McAlpine, D. C. Lankin, S.-N. Chen, G. F. Pauli, Natural deep eutectic solvents: properties, applications, and perspectives, *Journal of Natural Products*, 2018, **81**, 679-690, doi: 10.1021/acs.jnatprod.7b00945.
[27] A. Dwamena, Recent advances in hydrophobic deep eutectic solvents for extraction, *Separations*, 2019, **6**, 9, doi: 10.3390/separations6010009.

