

Supporting Information for:

Investigating the performance of carboxylate-alumoxane nanoparticles as a novel chemically functionalized inhibitor on the asphaltene precipitation

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Section S1. Asphaltene extraction

For extracting asphaltenes from crude oil, the ASTM (D6560) – IP143 technique was employed. Figure S1 exhibits the schematic of this process. For this reason, in a ratio of 40:1 (vol.%), *n*-heptane was mixed with crude oil. The stirring of the mixture continued for 24 hours, and then, the mixture left in ambient conditions for 24 hours. This process was repeated for another 48 hours to obtain the maximum amounts of asphaltene. For separation of deposited asphaltene, the Whatman filter paper with 42 µm pore size was utilized. In order to purify the asphaltenes separated from crude oil, hot *n*-heptane was applied for washing the asphaltene deposits by the utilization of the soxhlet apparatus. This step is of high necessity due to removing the maltenes which are precipitated along with asphaltene in the asphaltene extraction process. This process continued until clear *n*-heptane was obtained. Then, toluene was substituted with *n*-heptane,

followed by the reflux process until the clear toluene obtained. For having the purified asphaltene, the toluene containing asphaltene was transferred to a glass beaker, which was located under a fume hood for the evaporation of toluene.

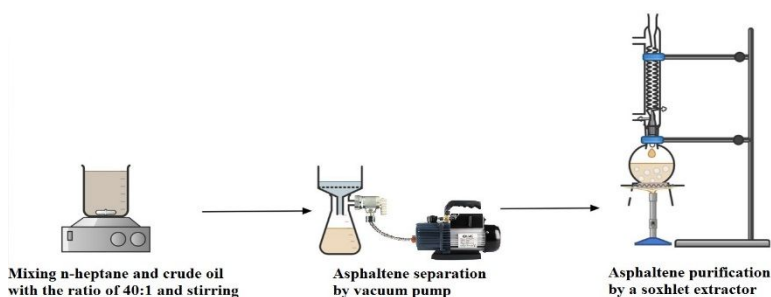


Figure S1. The schematic of the asphaltene extraction process

Section S2. Identifying the λ_{\max} of asphaltene molecules and calibration curve for adsorption experiments

In this research, adsorption capacity experiments were carried out to evaluate carboxylate-alumoxane nanoparticles potentiality for asphaltene adsorption. For performing these experiments via the UV-vis technique, the λ_{\max} of asphaltene molecules was required to obtain the maximum absorbance values for different samples. A standard asphaltene solution was prepared in order to identify the exact λ_{\max} for asphaltene molecules. Wavelength scan was conducted for this solution by applying a Dynamica DB20-Spectrophotometer on the quartz cuvette, and toluene was used as the blank. The result is illustrated in Figure S2. As it can be seen, the λ_{\max} for the asphaltene used in this study was around 300 nm, which was employed for adsorption capacity experiments.

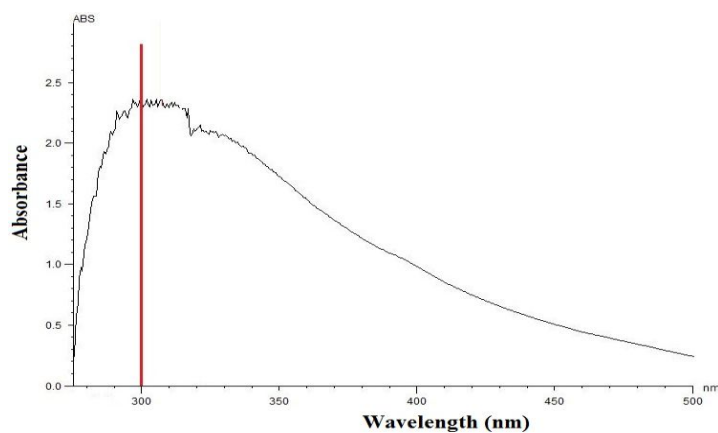


Figure S2. Wavelength scan for a standard asphaltene solution

Additionally, for measuring the asphaltene concentration of different samples after adsorption capacity experiments, a calibration curve confirming Beer-Lambert law was utilized. For plotting this calibration curve, ten standard solutions, which consist of 5-50 ppm asphaltene concentration, were prepared. The absorbance values of these solutions were measured by the Uv-vis instrument, which was set at a wavelength of 300 nm. Figure S3 shows the calibration curve applied for the adsorption capacity experiments. As it is observed, the coefficient of determination, R^2 , can indicate the Beer-Lambert law. After centrifuging different samples, the samples were diluted by toluene to reach the concentration (50 ppm) compatible with the standard curve. For instance, since the synthetic oil used in the adsorption capacity experiments had 500 ppm asphaltene concentration, 1 CC of supernatant was diluted by 9 CC toluene to be adjusted the standard curve.

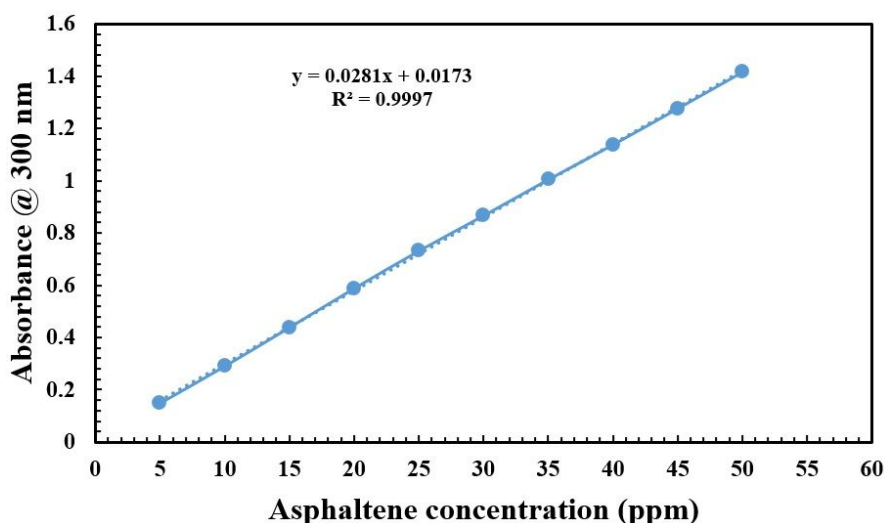


Figure S3. Calibration curve for the adsorption capacity experiments

Section S3. Identifying a suitable wavelength for performing the experiments related to determining the “onset” point of asphaltene precipitation

In this study, in order to find the “onset” point of asphaltene precipitation for various synthetic oils, an indirect method which used the Uv-vis technique was applied. Since there were different materials, including asphaltene, toluene, and *n*-heptane, in this experiment, the effect of toluene and *n*-heptane must be removed. For this reason, the absorbance values of toluene and *n*-heptane should be subtracted from the absorbance values obtained from the indirect technique in order to find the absorbance values of remaining soluble asphaltene in different supernatants. Because the

absorbance values of toluene and *n*-heptane may differ in different wavelengths, for performing these experiments, a wavelength should be selected in which the difference of their absorbance value is insignificant. Thus, the wavelength scans of toluene and *n*-heptane were plotted and were compared. Figure S4 exhibits the wavelength scans related to toluene and *n*-heptane when air is as the blank. The wavelength scans were plotted for these solvents in the range of 300 to 1100 nm. As it can be seen, the wavelength scans of toluene and *n*-heptane overlap in the ranges of 553 to 703 nm and 775 to 803 nm. However, the wavelength scans diverge in the wavelengths which are less than 553 nm and more than 703 nm, as well as less than 775 nm and more than 803 nm. Consequently, selecting the wavelength outside of the mentioned ranges may cause significant errors in the results of the indirect technique. Since the experiments related to the “onset” point of asphaltene precipitation have a relationship with the precipitated asphaltene amount, choosing a wavelength should be based on these experiments. That is because for calculating the precipitated asphaltene amount, the concentration of soluble asphaltene should be calculated after the centrifugation process. In order to calculate these concentrations, a calibration curve which is consistent with the Beer-lambert law should be plotted in the ranges in which the wavelength scan curves of toluene and *n*-heptane overlap. For this reason, 15 standard solutions with the asphaltene concentration of 50-1000 ppm were prepared. Afterward, the absorbance values of these solutions were detected via a Dynamica DB20-Spectrophotometer on the quartz cuvette, which toluene was as the blank. Also, in order to understand the behavior of the plots in different wavelengths, these curves were plotted in 12 wavelengths which were 350-1000 nm (Figure S5). By investigation of the curves exhibited in this figure, it is observed that in shorter wavelengths and higher asphaltene concentration, the standard curves are not consistent with the Beer-lambert law. This phenomenon is attributed to the self-association of asphaltene molecules by increasing the asphaltene concentration. On the other hand, in longer wavelengths, the calibration curves tend to conduct a linear behavior with asphaltene concentration augmentation. Consequently, for the synthetic oil with high concentration, using longer wavelengths is proposed for reducing the volume of solvents used for the dilution of supernatants. According to previous results related to the wavelength scan curves of toluene and *n*-heptane (Figure S4), the standard curves attributed to the wavelengths of 600, 650, 700, and 800 nm can be assumed as acceptable wavelengths for conducting indirect method. However, among these calibration curves, the best curve is the curve which has a maximum slope (related to maximum absorbance values which contribute to calculating the more

precise concentration of supernatants), as well as maximum coefficient of determination, R^2 . Therefore, the wavelength of 600 nm was applied for performing indirect technique due to overlapping the toluene and *n*-heptane curves in this wavelength due to having a maximum slope and maximum coefficient of determination, R^2 (Figure S6).

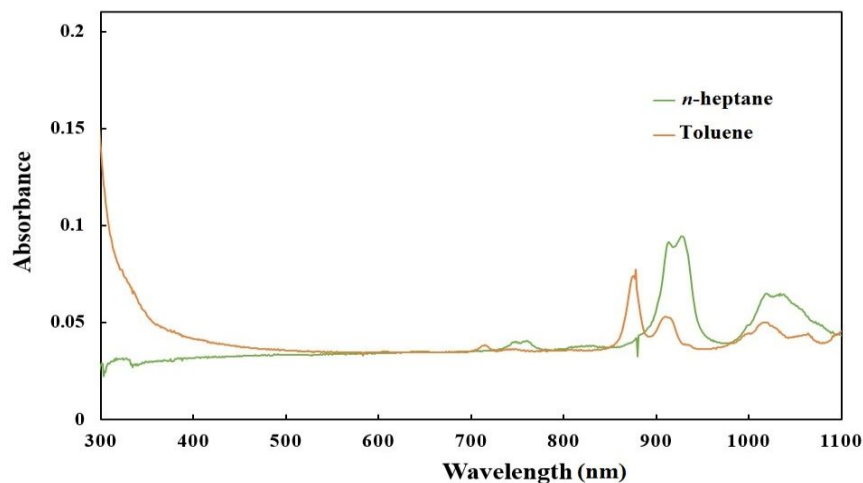


Figure S4. Wavelength scans for *n*-heptane and toluene

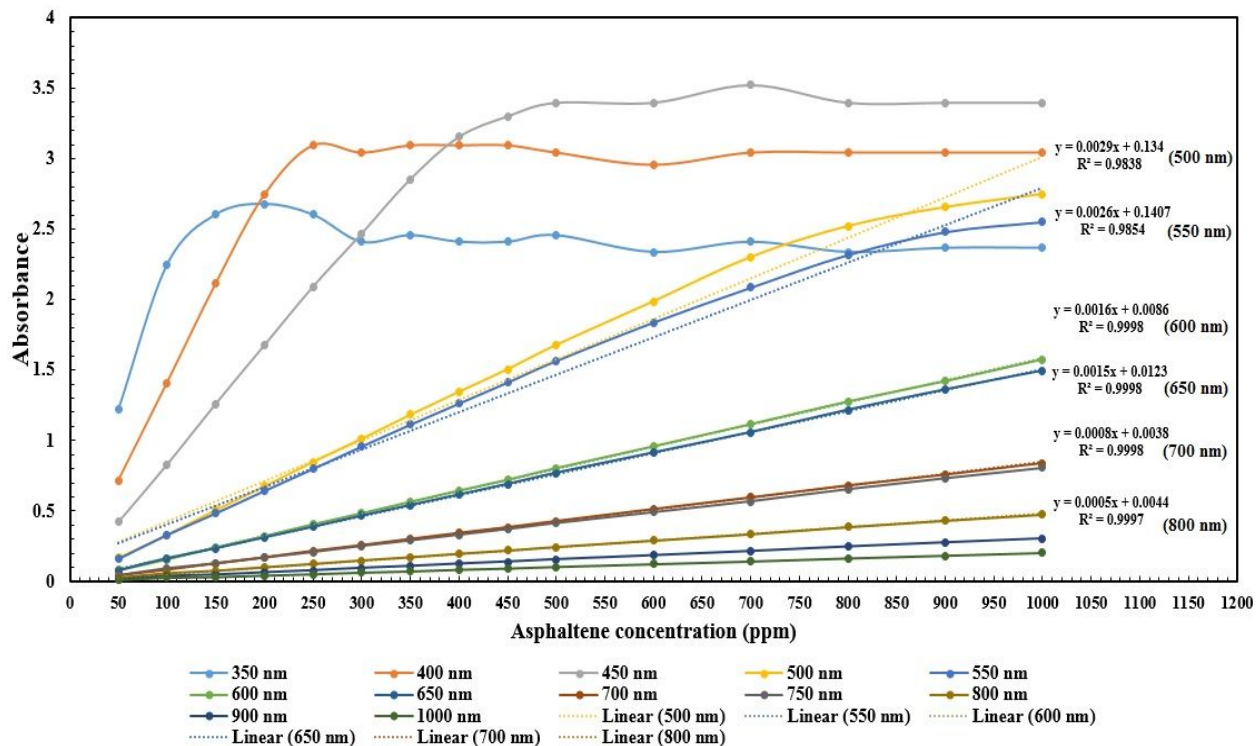


Figure S5. the plots ascribed to the absorbance values in different concentrations of asphaltene and various wavelengths

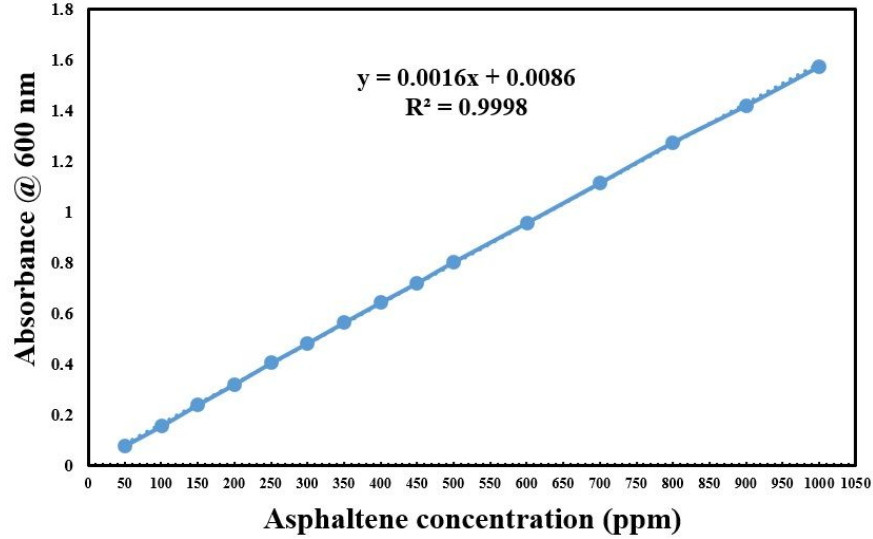


Figure S6. Calibration curve for calculating the precipitated asphaltene amount in the indirect method

Section S4. Dilution impact correction

For determining the “onset” point of asphaltene precipitation, the dilution effects should be corrected. For this reason, at first, the exact volume of *n*-heptane and toluene should be calculated according to their density. The absorbance values obtained from the indirect method should be subtracted from the overlapped absorbance value of *n*-heptane and toluene (Eq. S(1)).

$$ABS_2 = ABS_1 - \text{overlapped absorbance value of } n\text{-heptane and toluene in } 600 \text{ nm} \quad \text{Eq. S(1)}$$

For correcting the dilution impact, the dilution ratio related to adding the *n*-heptane and toluene to the different supernatants should be calculated (Eq. S(2) and S(3)).

$$\text{Dilution impact of } n\text{-heptane} = \frac{\text{Supernatant volume (CC)} + n\text{-heptane volume (CC)}}{\text{Supernatant volume (CC)}} \quad \text{Eq. S(2)}$$

$$\text{Dilution impact of toluene} = \frac{\text{Supernatant volume (CC)} + \text{Toluene volume (CC)}}{\text{Supernatant volume (CC)}} \quad \text{Eq. S(3)}$$

The corrected absorbance values are calculated by Eq S(4) and Eq S(5).

$$ABS_3 = ABS_2 \times \text{overall ratio of dilution impact} \quad \text{Eq. S(4)}$$

$$\text{The overall ratio of dilution impact} = \text{Dilution impact of } n\text{-heptane} \times \text{Dilution impact of toluene} \quad \text{Eq. S(5)}$$

For calculating the amount of precipitated asphaltene, the correction of dilution impact for different concentrations obtained from the calibration curve should be done. Eq S(6) calculates the corrected concentrations for different samples.

$$\text{Corrected concentrations} = \text{concentration from the calibration curve} \times \text{The overall ratio of dilution impact} \quad \text{Eq. S(6)}$$

The correction method is based on Tavakoli et al.¹.

References

(1) Tavakkoli, M.; Grimes, M. R.; Liu, X.; Garcia, C. K.; Correa, S. C.; Cox, Q. J.; Vargas, F. M. Indirect method: a novel technique for experimental determination of asphaltene precipitation. *Energy Fuels* **2015**, *29*, 2890-2900.

