

Study of Activation Energy for Viscous Flow of Mixtures as a Measure of Dilution Efficiency for Heavy Oil-Diluent Systems

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Abstract

As the demand for crude oil continues to increase in response to the continued global needs for it, the development of unconventional crude oil reserves is the only way to sustain global supply. However, the excessively higher viscosity of heavy crude oil makes it less attractive for conventional pipeline transportation. Therefore, reducing the viscosity of heavy crude oil to meet crude oil transporting pipeline regulations is a necessity. This paper has assessed the dilution efficiency of well-known diluents in the petroleum industry, using different dilution ratios based on a thermodynamic approach involving activation energy and heat of vaporization determination. Based on selected dilution ratios, kinematic viscosities of binary and ternary systems of toluene and natural gas condensate as diluents, and Saudi Heavy crude oil as the base oil were measured, using anticipated field based temperatures reported in the literature, which facilitated the experimental approach. The study shows that although the ternary systems have the lowest activation energy for viscous flow and heat of vaporization in accordance with the thermal activation theory of viscous flow, natural gas condensate binary systems have the lowest cost of transportation per barrel of total fluid in the transporting pipeline. The study further shows that the binary systems for toluene and Saudi Heavy crude oil have higher activation energy for viscous flow compared to the toluene systems.

Keywords: Kinematic viscosity, activation energy, vegetable oil, Cannon-Fenske viscometer, Heat of vaporization

1. Introduction

In the context of hydrocarbon fluid resources economics, the value of a given accumulation is judged by several factors. For instance, when energy analysts deliberate on the price of crude oil, they generally refer to one of a small group of specific types of crude oils that are actively bought and sold on the market, such that the use of benchmark crudes facilitates buying and selling worldwide (IEA, 2014). In this regard, the most widely used benchmarks are associated with a crude oil that has four common qualities, namely stable and ample production, a transparent and free-flowing market located in a geopolitically and financially stable region that facilitates interactions, and adequate storage to encourage market development, among other factors. However, other types of crude oils can be compared to these benchmarks based on agreed differential, which takes into account two important factors, such as API gravity (density) or sulfur content (Zyher et al., 2022; Demirbas et al., 2015; IEA, 2017; Aikaterini & Wolfgang, 2021). The implication is that the continuous increase in world energy demand driven by the economic development and the dramatic population growth recorded in recent decades have resulted in eminent decline of the availability of crude oil resources characterized by more efficient production and refining activities (Santos et al., 2014) (Santos, Lo, Bannwart, & Trevisan, 2014). These resources consist mainly of conventional crude oil reserves and giant discoveries which peaked in the late 1960s (Fisher, 2008). Meanwhile, forecast predicts that the continuous expansion in world energy consumption has the potential to at least last until 2035 (Santos et al., 2014). Therefore, supplementing world crude oil exponential demand trend (Newswires, 2022) requires the exploitation of nonconventional heavy crude oil resources (Zou, 2017). However, efficient development and exploitation of these resources are limited by their exceptionally high viscosity, which impacts both subsurface and pipeline line efficient flow (Gokcal et al., 2008), causing regulatory bodies to impose maximum viscosity for pipeline transportation in the downstream sector of the petroleum industry (Muñoz et al., 2016; Saniere et al., 2004). Therefore, meeting the pipeline transportation challenge requires viscosity reduction, using appropriate means (Li et al., 2022; Hao et al., 2022). To efficiently reduce the viscosity of heavy oil to meet pipeline regulations, a thorough understanding of its origin

at molecular level is important (Cho & Urquidi, 1999).

Several methods exist for heavy oil viscosity reduction depending on environmental conditions. For instance, for viscosity reduction under subsurface conditions, thermal energy input (Alomair, et al., 2012; Yu et al., 2022) has proven technically feasible as have dilution methods (Hosseini et al., 2016; Mohammadi et al., 2019; Gateau et al., 2004; Miadonye and Amadu, 2022) in the case of pipeline transportation beyond wellhead. Intermolecular forces control several physicochemical properties of chemical substances (Raman et al., 1923; Kamil Raczyński, 2021; Viswanath et al., 2007), and the scientific knowledge behind the interactions have a bearing on the theory of absolute reaction rates and its application to viscosity (Kincaid et al., 1941). Thus, the molecular level theory gives an expression for the viscosity of a dense fluid that integrates molecular shape, where the molecules of the fluid are approximated by chains of equal-size, tangentially joined, and rigid spheres. The key to this model are two molecular parameters; the molecular diameter of the spherical segment and the chain (Ewell & Eyring, 1937; Wijn et al., 2008). Besides the kinetic theory, the thermal activation theory of viscosity is well-known (Macías-Salinas et al., 2003; Kistemaker et al., 2016), which emphasizes the need for the attainment of a minimum energy barrier to overcome the resistance of flow units in the fluid (Avramov, 2007), considering the absolute rate theory (Bosse & Bart, 2005).

While the absolute rate theory forms the fundamental basis for the thermal activation theory of viscosity, the effect of other factors, on this theory, such as stress, has been demonstrated (Spikes, 2018; Ewen et al., 2021). Besides, the thermodynamic activation parameters for viscous flow include density, viscosity, enthalpy, entropy and free energy of activation (Saleh et al., 2007). Generally, higher the intermolecular forces, higher the activation energy, which translates to higher viscosity. Consequently, any process that alters any of these thermodynamic parameters will equally alter intermolecular forces and viscosity. Thus, dilution of heavy crude oil using solvents produce an effect analogous to the stress augmented thermal activation energy barrier, where the rate of atomic and molecular processes is reduced, leading to exponential rate trend consistent with the absolute rate theory (Eyring & Urry, 2010; Geszti, 1967), considering the impact of dilution on molecular structure and intermolecular forces (Ewell & Eyring, 1937).

In the literature, the empirical relationship between viscosity and temperature contains the activation energy for viscous flow (Messaâdi, et al., 2015) as a molecular specific thermodynamic parameter that is experimentally accessible, and the sensitivity of this model to the polarity of liquids has been demonstrated (Kacema et al., 2017). Therefore, knowledge of efficient dilution of high viscosity crude oil for pipeline transport using diluents with varying polarity can be obtained by quantifying the extent of intermolecular interaction which has a direct bearing on the viscous flow activation energy. In this regard, some researchers have determined the activation energy for viscous flow, using viscosity versus temperature data set (Messaâdi, et al., 2015; Ike & Ezike, 2018; Budtova & Navard, 2015), concentrating on non-mixtures except in the metallurgical literature, where the temperature dependence of the kinematic viscosity for multicomponent melts of nanocrystalline soft magnetic alloys has been investigated (Starodubtsev et al., 2021). Moreover, while the technical feasibility of dilution based on petroleum derived fuels has been exploited for decades (Argillier et al., 2005; Martínez-Narro et al., 2020; Jing et al., 2020), the viscosity temperature data of such systems have not been specifically exploited in the context of the activation theory of viscous flow (Kotas & Valešová, 1986); with a published work in this regard being only related to diffusion in fluid mixtures (Abbasi et al., 2011). Herein, we integrate Arrhenius equation with the activated rate theory of Eyring to derive an equation for the activation energy change for viscous flow per unit volume of diluent, assuming that the thermodynamic activation volume and entropy of the flow unit consisting of heavy oil and diluent will change with the extent of dilution. We chose to use change in activation energy over the absolute value of this parameter as an efficient means of assessing the efficiency of a diluent because our experimental program uses equal volumes of diluents and heavy oil samples for all diluents used, and the change in activation energy per unit volume of each diluent offers a technically meaning approach to quantifying the extent of viscosity reduction at a given temperature. Based on our experimental data sets, we calculated the activation energy change using our model and discussed the effect of diluent polarity on activation energy change. This research work underscores the importance of assessing the efficiency of a diluent based on activation energy change rather than on viscosity change, and the novelty stems from the fact that the activation energy of a rate process, such as viscous flow measures the minimum energy barrier, and its value will carry information on the energetics and the extent to which intermolecular interactions have been altered, given the direct relationship between these two parameters in viscous flow.

2. Background

2.1 Viscosity as a Thermally Activated Process

Viscosity is one of the thermophysical properties of a broad spectrum of fluids meant for optimization and design of industrial processes associated with transport phenomena (Miller et al., 1994; Haj-Kacem et al., 2014; Fasina & Colley, 2008). Activation energies are significant for many timescales other than chemical reaction rate constants and transport properties, such as diffusion coefficients, are always shown to obey the rate theory (Geszti et al., 1967). Moreover,

reorientation times, viscosity, and dielectric relaxation are typical examples of timescales that can be described by the activation energy related Arrhenius equation (Piskulich et al., 2022). One significant finding of the absolute rate theory of flow is the acknowledgment that the viscosity of a liquid is governed by a very small concentration of molecules in relatively shallow potential energy barriers from which the activated molecules are preferentially mobilized (Bondi, 1946). Consequently, some models of shear viscosity assume that it is a thermally activated process, and to move, the molecules have to overcome activation energy barriers (Glasstone et al., 1941) created by the resistance of the surrounding building units where a jump frequency is related to the vibration frequency (Dey et al., 2016). Such a model has been applied to mixtures of liquids to facilitate determination of activation energies characteristic of desired compositions that are of industrial importance (Sumudu et al., 2020; Abbasi et al., 2011; Mariano, et al., 2000). Considering the petroleum industry's role in meeting pipeline transport restrictions for heavy crude oil, dilution of these extraviscous fluids using readily available petroleum derived diluents or natural gas condensate fluids is more cost-effective. Therefore, the effects of such dilution ratios on intermolecular forces and viscosity can be understood based on experimental determination of the activation energy for viscous flow of mixtures. This is the focus of our work and the following section will be devoted to the processes of activation energy change of pure heavy crude oils by dilution.

2.2 Activation Energy Change of Heavy Crude Oil by Dilution

In Eyring theory of viscosity, ΔS is the entropy of the unit of flow in the activated state over and above that in the normal state and ΔH is the heat of activation of the flow unit (Eyring, 1936). Fundamental to the thermally activated theory of viscous flow is the probability of finding an adjacent hole of sufficient dimensions to permit movement (Abbott, 2004), with the energy of hole formation being related to the heat of vaporization ΔH_{vap} which in turn is related to the heat of activation (Kauzmann & Eyring, 1940). Moreover, the relationship between the cohesive forces, the Arrhenius energy of activation and enthalpy of viscous flow is well established in the thermodynamic literature (Dhouibi et al., 2015), as is the effect of mixing on intermolecular forces existing in pure liquids. For instance, in suspensions, the activation energy for viscous flow will control the temperature dependence of viscosity. However, the presence of the solids in suspension will control activation, leading to a clear difference between the activation energy for the pure and the suspension system (Timmons et al., 2018).

One of the most fundamental thermodynamic properties of a liquid is its cohesive energy density (CED), measured as the energy per unit volume of the liquid required to move a molecule from the liquid state to a vapor state, which has a strong bearing on the interactions between the molecules (Dee & Sauer, 2017). Consequently, the mathematical definition of the CED, viz the ratio of the molar energy of vaporization divided by the molar liquid volume leads to a strong link with the thermal activation theory for viscous flow in light of the heat of vaporization specification. Moreover, in light of solution thermodynamics, the molar volume of a pure component is different from that of the mixture by virtue of the concept of partial thermodynamic properties (Kwon & Lee, 2005; Bamzad et al., 2022), and the individual contribution to the CED considering intermolecular forces, namely hydrogen bonding, van der Waals interaction and electrostatic interaction (Shimiz et al., 2010). Consequently, the heat of vaporization related to hole formation in the thermally activated viscous flow theory as well as the activation energy for viscous low will change upon heavy crude oil dilution for pipeline transport. In this regard, a more efficient approach to quantifying the effect of different diluents will be the determination of intermolecular forces change following activation energy change, and the following section will be devoted to the underlying theoretical basis.

2.3 Theory Development

Following Arrhenius, the temperature dependence of kinematic viscosity is given as (Frenkel, 1975):

$$\nu = \nu_0 e^{\left(\frac{E_A}{RT}\right)} \quad (1)$$

In this equation, ν is the kinematic viscosity [m^2s^{-1}], ν_0 is the pre-exponential factor [m^2s^{-1}], E_A is the activation energy [Jmol^{-1}], R is the universal gas constant [$\text{JK}^{-1} \text{mol}^{-1}$] and T is the absolute temperature.

To derive an equation for the activation energy change due to dilution of heavy crude oil using a suitable diluent, E_A in Eq. (1) will be regarded as the activation energy for viscous flow (Ojovan, 2015). In this regard, the viscous flow activation energy for the original viscous heavy oil will be different from that of the mixture consisting containing a known fraction of diluent due to change in molar volume following the dilution. Therefore, Eq. (1) can be written for the case of pure heavy oil and mixture as:

$$\nu_P = \nu_{0P} e^{\left(\frac{E_P}{RT}\right)} \quad (2)$$

$$v_M = v_{0M} e^{\left(\frac{E_M}{RT}\right)} \quad (3)$$

In which, v_P is the kinematic viscosity of the pure heavy oil [m^2s^{-1}], v_{0P} is the pre-exponential factor for the heavy oil [m^2s^{-1}], v_{0M} is the pre-exponential factor for the mixture, E_P is the activation energy for the pure heavy oil [$Jmol^{-1}$], and E_M is the activation energy for the mixture [$Jmol^{-1}$].

Following the mathematical linearity between the natural logarithm of Eq. (1) through (Eq. (3) and the reciprocal of temperature, the activation energy for viscous flow can be obtained from the gradient of the plot of viscosity versus the reciprocal of temperature as:

$$E_A = R \left[\frac{d \ln(v)}{d\left(\frac{1}{T}\right)} \right] \quad (4)$$

Therefore, Eq. (4) can be written for Eq. (2) and Eq. (3) as:

$$E_P = R \left[\frac{d \ln(v_P)}{d\left(\frac{1}{T}\right)} \right] \quad (5)$$

$$E_M = R \left[\frac{d \ln(v_M)}{d\left(\frac{1}{T}\right)} \right] \quad (6)$$

Dilution of heavy oil with the diluent will lead to changes in intermolecular interaction which will affect the heat of vaporization related to hole formation as established in the thermally activated theory for viscous flow. The change in heat of vaporization leads to change in the activation energy for viscous flow, which can be calculated based on values for pure and mixture systems as follows:

$$\Delta E_{dil} = E_M - E_P = R \left[\frac{d \ln(v_M)}{d\left(\frac{1}{T}\right)} - \frac{d \ln(v_P)}{d\left(\frac{1}{T}\right)} \right] \quad (7)$$

The extent to which a diluent can reduce viscosity can best be measured based on the activation energy change per unit volume of dilution, which also measures the extent of intermolecular interaction change per unit volume of dilution. This parameter can be deduced based on Eq. (7) as:

Equation (7) as:

$$\frac{\Delta E_A}{V_{dil}} = \frac{R}{V_{dil}} \left[\frac{d \ln(v_M)}{d\left(\frac{1}{T}\right)} - \frac{d \ln(v_P)}{d\left(\frac{1}{T}\right)} \right] \quad (8)$$

In which V_{dil} is the volume of diluent used in the mixture for viscosity reduction.

Equation (8) provides both mathematical and experimental approaches to studying the effect of diluent on activation energy change, while the activation energy change per unit volume of dilution provides the basis for comparing the effectiveness of diluent where equal volumes of dilution are used.

Consistent with the thermally activated viscous flow theory, holes must be available comparable to the size of the molecule in the activated state, and the work necessary to form a hole of molecular size in the liquid state is the enthalpy of vaporization. For a large number of liquids the ratio of the enthalpy of vaporization to the viscous flow activation energy is a constant, equal to 3 ± 0.5 (Zeggeren, 1956). From Eq. (7), the heat of vaporization can be obtained as:

$$\Delta H_{vap} = 3R \left[\frac{d \ln(v_M)}{d\left(\frac{1}{T}\right)} - \frac{d \ln(v_P)}{d\left(\frac{1}{T}\right)} \right] \quad (9)$$

The viscosity of a fluid is temperature dependent. Unlike the approach somewhere (Chandler, 2014) that separates the effect of temperature on the viscosity of the components in the mixture, we consider temperature effect on the mixture as whole; the activation energy is a lumped one. Therefore, data on kinematic viscosity versus temperature are critical to achieving this objective and the following section will be devoted to that.

3. Material and Methods

3.1 Material

Reagent grade toluene (99%) was purchased from Sigma Aldrich. Natural gas condensate was sample was received from Suncor, while Saudi Heavy crude oil was received from Saudi Aramco. All samples were used as provided without further purification.

4. Methods

To provide enough samples for experiments, 50 ml solutions were prepared by mixing Saudi Arabia heavy crude oil with toluene and natural gas condensate at concentrations 5%, 10%, 15%, 20%, 25% and 30% respectively in conical flasks. Solutions were then homogenised by shaking for about 30 minutes the New Brunswick scientific Gyrotory shaker at 150 rpm. To prepare the natural gas condensate and Saudi Heavy binary systems, the same procedure was followed. To prepare ternary systems, a 100 ml volume consisting 30 mL toluene and 70 mL natural gas condensate mixture was prepared and well homogenised. Samples of the mixture (5%, 10%, 15%, 20%, 25% and 30%) were combined with Saudi Heavy crude oil followed by homogenization. Kinematic viscosity at experimental temperature was measured, using the ASTM D445 abased on the Cannon-Fenske viscometer (ACE-GLASS, 2022). In heavy oil transportation using pipelines, the inlet and outlet temperatures are important for wellhead gathering and transpiration systems (Zhu, Liu, Xu, Liu, & Wang, 2021), and for long distance bulk transportation (Dong et al., 2019; Xie et al., 2022). The experimental temperatures of Zhu et al., (2021) and Dong et al. (2019) cover practical field based conditions, and we chose to measure kinematic viscosity of all systems studied within temperature ranges of the cited literatures.

5. Results and Discussion

5.1 Thermodynamic Activation Parameters of Binary and Ternary System

Under a constant shear rate, the plot of the natural logarithm of kinematic viscosity versus the reciprocal of absolute temperature is theoretically linear, suggesting that the dependence of the kinematic viscosity on temperature can be well described by the Arrhenius equation (Eq. (1)) like the case of absolute viscosity (Toth et al., 2018). In this regard, Figure 1 shows such a plot while Figs. 2 through 4 indicate those for the binary systems Toluene and Saudi Heavy oil, Natural Gas Condensate and Saudi Heavy oil and ternary systems Toluene: Natural Gas Condensate: Saudi Heavy oil respectively. In all cases, the regression coefficient of the plot is 0.999, which is indicative of constant activation energy fore viscous flow for all systems studied (Haj-Kacem et al., 2015). Figure 5 shows the combined plots for systems.

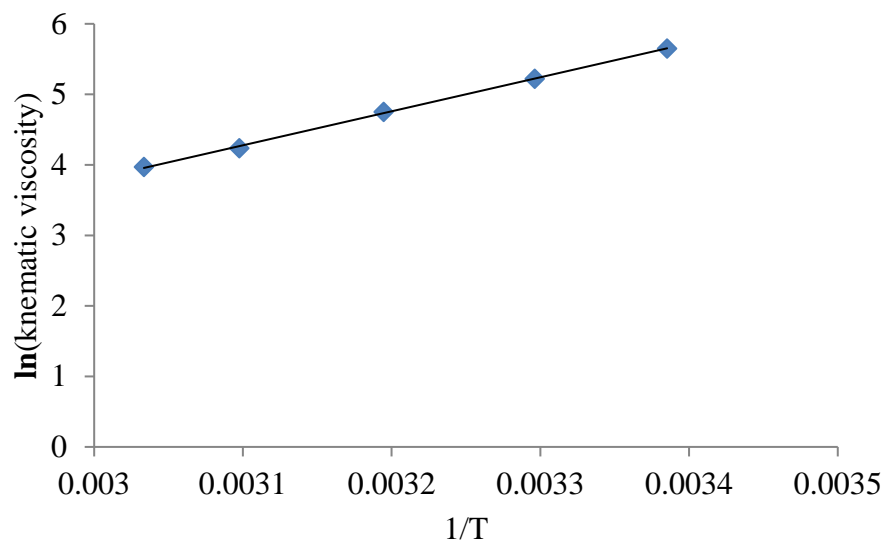


Figure 1. Semi-log plot of Kinematic viscosity versus the reciprocal of absolute temperature for Saudi Heavy oil.

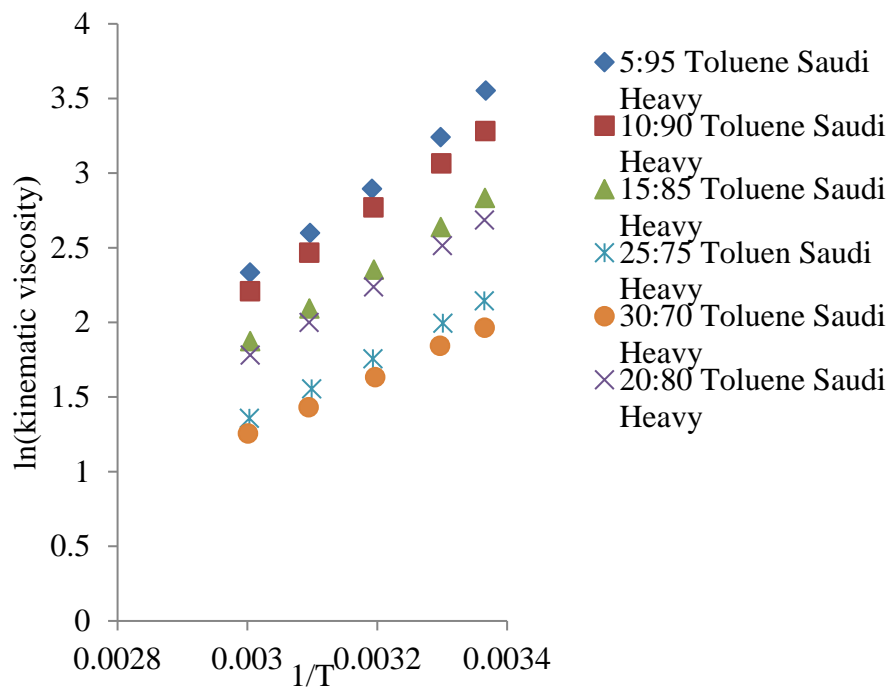


Figure 2. Semi-log plot of kinematic viscosity versus the reciprocal of absolute temperature for a binary system of toluene and Saudi Heavy oil

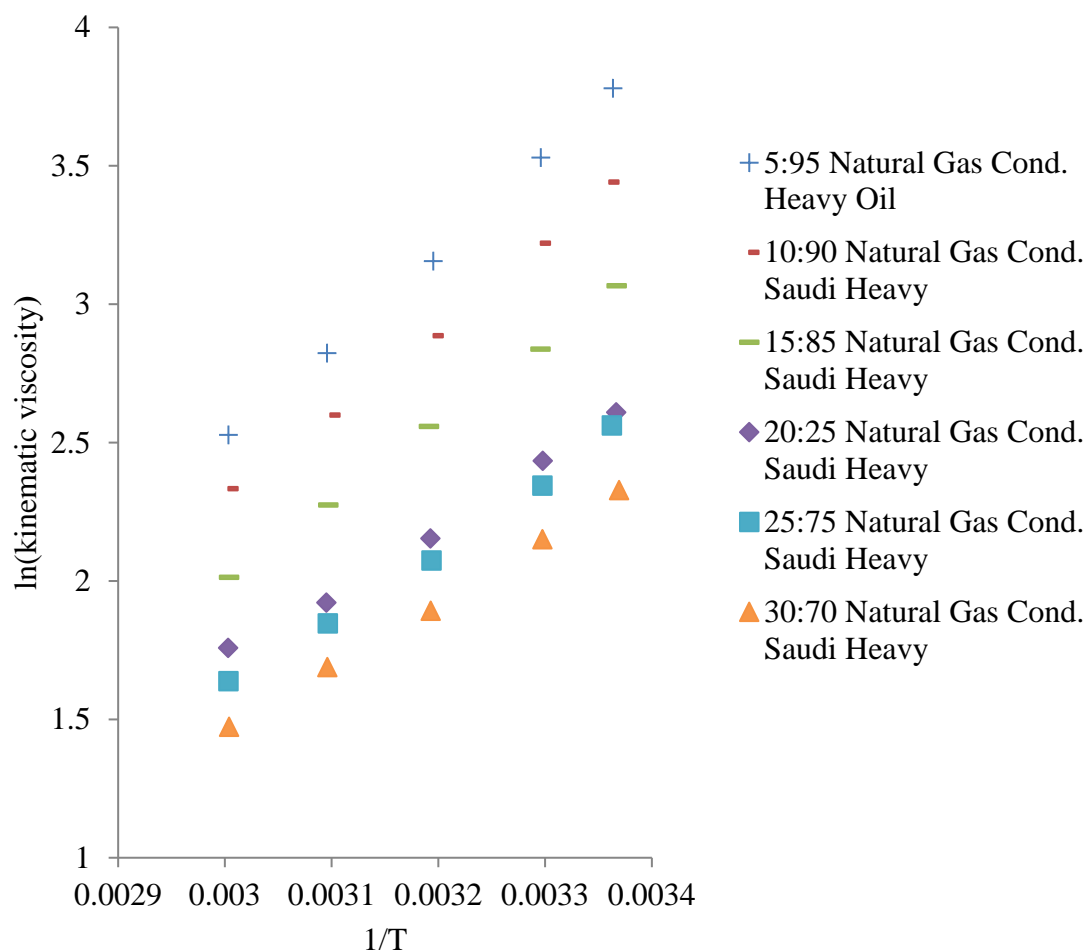


Figure 3. Semi-log plot of kinematic viscosity versus the reciprocal of absolute temperature for a binary system of natural gas condensate and Saudi Heavy oil

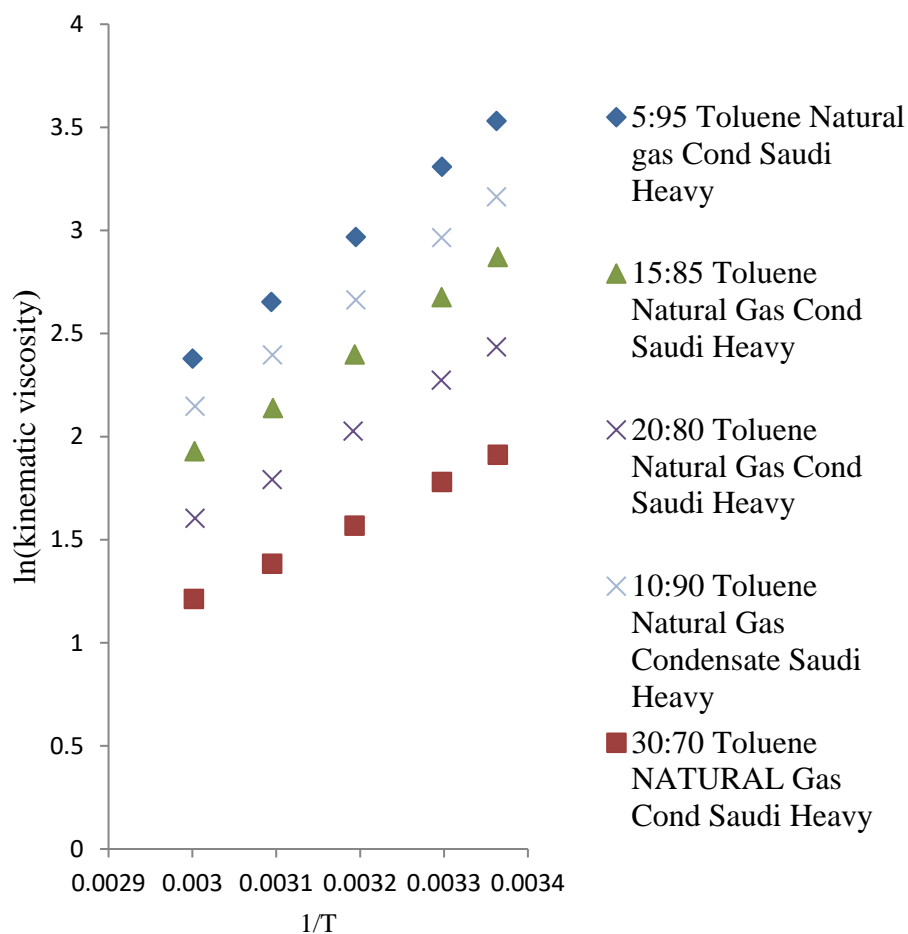


Figure 4. Semi-log plot of kinematic viscosity versus the reciprocal of absolute temperature for ternary systems consisting of different volumes of an add mixture of 30 mL toluene and 70 mL natural gas condensate and different volumes of Saudi Heavy oil

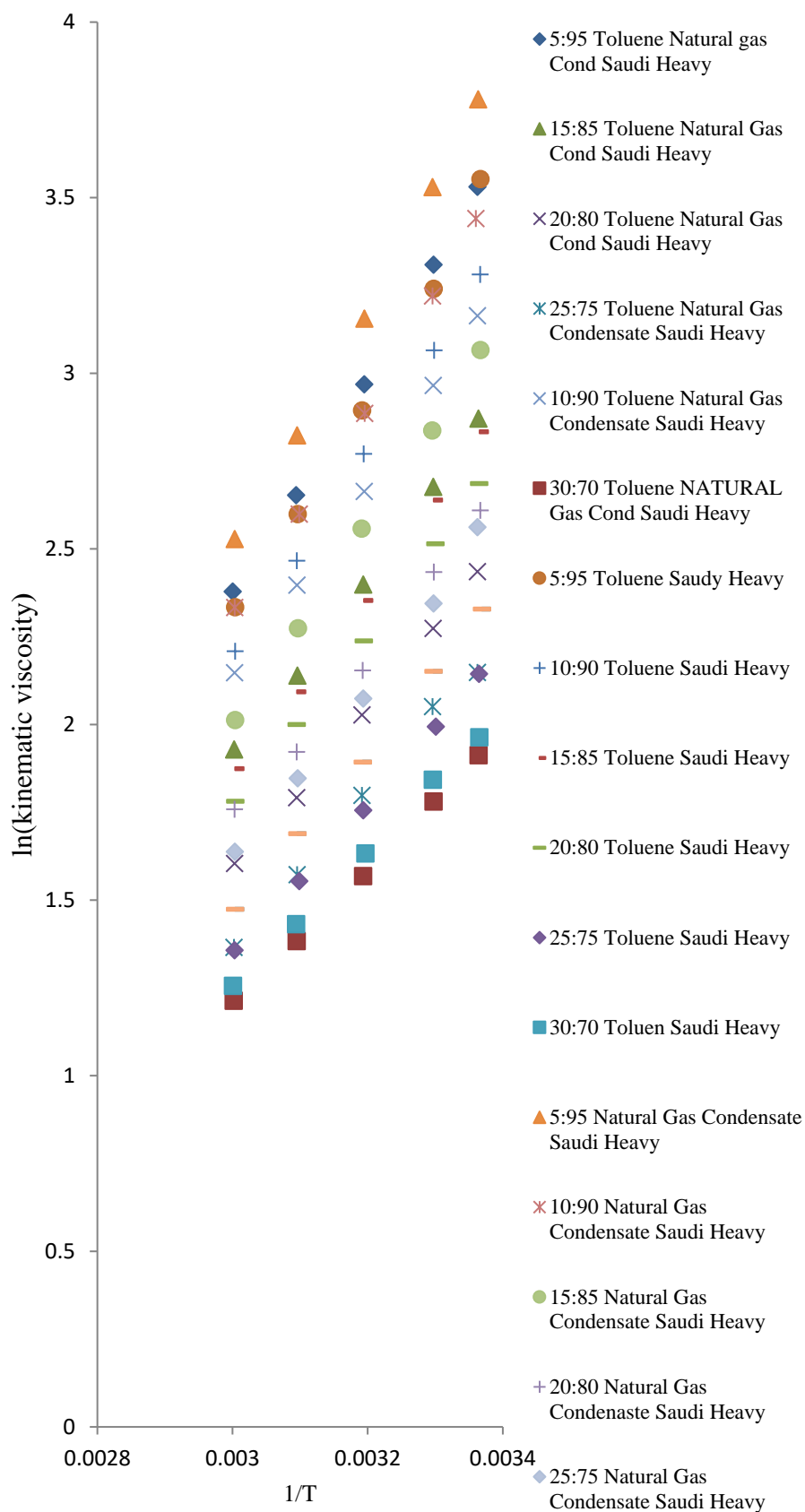


Fig 5. Combined plots for binary and ternary systems

Tables 1A and B show the activation energies for viscous flow determined using Eq. (5) for the neat Saudi Heavy oil data and Eq. (6) for mixture data consisting of binary and ternary systems. At a given temperature, the activation energy for viscous flow characterizes the energy needed by the molecules to be set in motion against the frictional forces of the neighboring molecules. This requires exceeding the internal flow resistance of a material-specific energy barrier called the potential barrier (Meichsner et al., 2003).

Table 1A. Activation energy and Heat of vaporization for binary and ternary systems consisting of Toluene (T), Saudi crude oil (S) and Natural gas condensate (G)

Dilution ratio	Binary system		Tertiary system	
	E_{avis} Jmol ⁻¹	H_{vap} Jmol ⁻¹	E_{avis} Jmol ⁻¹	H_{vap} Jmol ⁻¹
5:95 T:S	27523	82568	26508	79525
10:90 T:S	24562	73688	23456	70395
15:85 T:S	22118	66354	21760	65281
20:80 T:S	20821	62462	19357	58072
25:75 T:S	18077	54230	18526	55577
30:70 T:S	16322	48967	16098	48294

Table 1B. Activation energy and Heat of vaporization for the binary system consisting of natural gas condensate (G) and Saudi crude oil(S)

Dilution ratio	Binary system	
	E_{avis} Jmol ⁻¹	H_{vap} Jmol ⁻¹
5:95 G:S	28961	86883
10:90 G:S	25843	77529
15:85 G:S	23980	71941
20:80 G:S	19781	59344
25:75 G:S	21137	63410
30:70 G:S	19357	58072

The activation energy for viscous flow of the neat Saudi Heavy crude oil obtained from the plots of Figure (1) is 40095 Jmol⁻¹ while the heat of vaporization is 582012 Jmol⁻¹. Given that the kinematic viscosity of the diluents, toluene and natural gas condensate are lower than that of Saudi Heavy oil, a given level of dilution will lead to viscosity decrease of the mixture. Therefore, increasing the volume fraction of the diluent must lead to a decrease in the activation energy for viscous flow, which is seen in Table 1, where the activation energy follows the expected trend. From the table, the ternary system for toluene: natural gas condensate: Saudi Heavy crude oil mixture has the lowest activation energy for every dilution ratio followed by the binary system for toluene: Saudi Heavy. To compare the differences in activation for the binary systems, knowledge of the physicochemistry and molecular level interactions of the system is required. Saudi Heavy crude oil like all heavy oils has a measurable amount of heteroatomic asphaltenes, which are soluble in aromatic solvents but precipitate in lower molecular weight paraffins (Moghanloo et al., 2018). Gas condensates consist predominantly of pentane (C₅H₁₂) with varying amounts of higher-boiling hydrocarbon derivatives (up to C₈H₁₈) but relatively little methane or ethane, propane (C₃H₈) and butane (C₄H₁₀) may be present in condensate by dissolution in the liquids (Speight, 2018). Asphaltenes can be regarded as colloidal in nature (Storm, 1994), and the heaviest molecular weight fractions in crude oil and, therefore, nanomaterial in crude oils (Farooq et al. 2021; Montoya et al., 2021)). Consequently, a mixture of natural gas condensate with Saudi Heavy crude oil will cause precipitation of asphaltenes. To investigate the effect of nanoparticles on the viscosity of a fluid, Rudyak & Krasnolutski, (2014) have carried out a simulation work, using molecular dynamics approach. Their approach modelled the interaction between the molecules of

the carrier fluid, using the Lennard–Jones potential (Simulation, 199; Norman & Stegailov, 2013). The interaction between carrier–fluid molecules and a nanoparticle was described by the Rudyak–Krasnolutskii (RK) potential (Rudyak & Krasnolutskii, 1999). For the nanoparticle interaction potential, they used a specially constructed potential (Rudyak et al., 2012). They demonstrated that the effective viscosity of nanofluids depends not only on the concentration of nanoparticles, but also on their size where the increase in the viscosity is due mainly to nanoparticle–molecule interactions, and the correlations between molecule–molecule and molecule–nanoparticle interactions. Moreover, Qi et al. (2018) have demonstrated that during solvent injection, hydrocarbon solvents containing n-alkanes (e.g., pentane or heptane) dilute the bitumen, which results in precipitation of asphaltenes. Therefore, on the basis of Rudyak & Krasnolutskii, (2014) and Qi et al., (2018), we expect natural gas condensate and Saudi Heavy crude oil systems to have higher kinematic viscosity compared to those of toluene and the oil, and that is what Table 1 reveals. In this regard, as dilution of oil increases with natural gas condensate, asphaltene precipitation is expected to increase but at the same time, the increase in volume of lower viscosity solvent also reduces viscosity consistently, causing viscosity increase by asphaltene precipitation to be reduced consistently. The net effect, therefore, is a decrease in activation for viscous flow with increase in dilution as seen in the table. Accordingly, lower values of activation energy for viscous flow encountered with ternary systems (toluene : natural gas condensate:Saudi Heavy oil) is due to the possible dissolution of asphaltene in the mixture, causing the disappearance of asphaltenes, and making it possible to regard the system as a non nanofluid compared to the binary systems of natural gas condensate and Saudi Heavy oil.

Table 1 also shows calculated heat of vaporization using Eq. (9). Accordingly, the heat of vaporization follows the same observable trends as those of activation energies. The implication is that, a given level of dilution reduces the heat of vaporization required for hole formation in the thermal activation theory for viscous flow (Tong, et al., 2017).

Table 2 shows the activation energy change of neat Saudi Heavy crude oil for viscous flow per unit volume of dilution calculated using Eq. (8). In this regard, the ternary systems with averagely the lowest activation energy for dilution ratios have the highest values followed by toluene systems and then natural gas condensate systems.

Table 2. Activation energy change for viscous flow per unit volume of dilution for binary and ternary systems.

Dilution Ratio	Binary System T:S	Binary System G:S	Ternary System
	E_{avis}/vol	E_{avis}/vol	E_{avis}/vol
5:95	31.35	27.77	33.89
10:90	38.74	35.55	41.48
15:85	44.84	40.19	45.73
20:80	48.07	50.66	51.72
25:75	54.92	47.28	53.80
30:70	59.29	51.72	59.85

Figure 5 shows plots of the activation energy change per unit volume of dilution versus diluent volume. The figure shows that at dilution volumes of 20, 25 and 30 mL, the ternary and binary systems consisting of toluene and Saudi Heavy crude oil have the same activation energy change per unit volume of dilution. Generally, the price of toluene which is refined crude fraction is higher than that of natural gas condensate. Therefore, the observation provides the opportunity to use a mixture 30 mL toluene and 70 mL natural gas condensate as an efficient diluent to mitigate the excessive cost involved in using only toluene to obtain lower activation energy for viscous flow in pipeline transportation. Moreover, dissolution of asphaltenes in the heavy crude oil in the presence of natural gas condensate will be guaranteed, using this mixture.

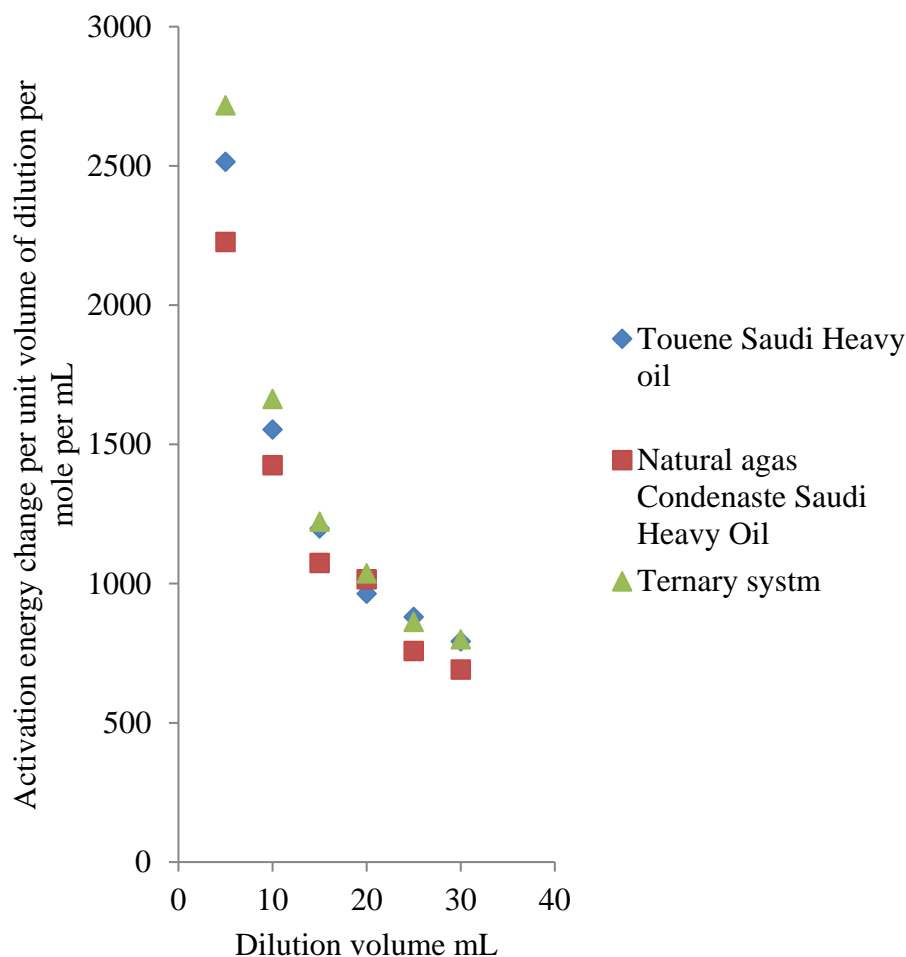


Figure 6. Activation energy change per unit volume of dilution for binary and ternary systems

Figure 7 shows plots of relative change in activation energy for viscous flow obtained by subtracting the activation energy for viscous flow at a given dilution from that of the neat Saudi Heavy crude oil and dividing the result by the latter and calculated as a percentage. We consider this parameters to be a more representative measure of the efficiency of dilution because it measures the extent to which the activation energy for neat oil changes relative to the base value after a given volume of diluent dilution. The figure shows that apart from 20 mL dilution, dilution at 15 mL, 25 mL and 30 mL provide the same effect for toluene binary and the ternary systems, which again testifies to the efficiency of the ternary system. The trend is also seen in Figure 8, which shows activation energy change for dilution volumes.

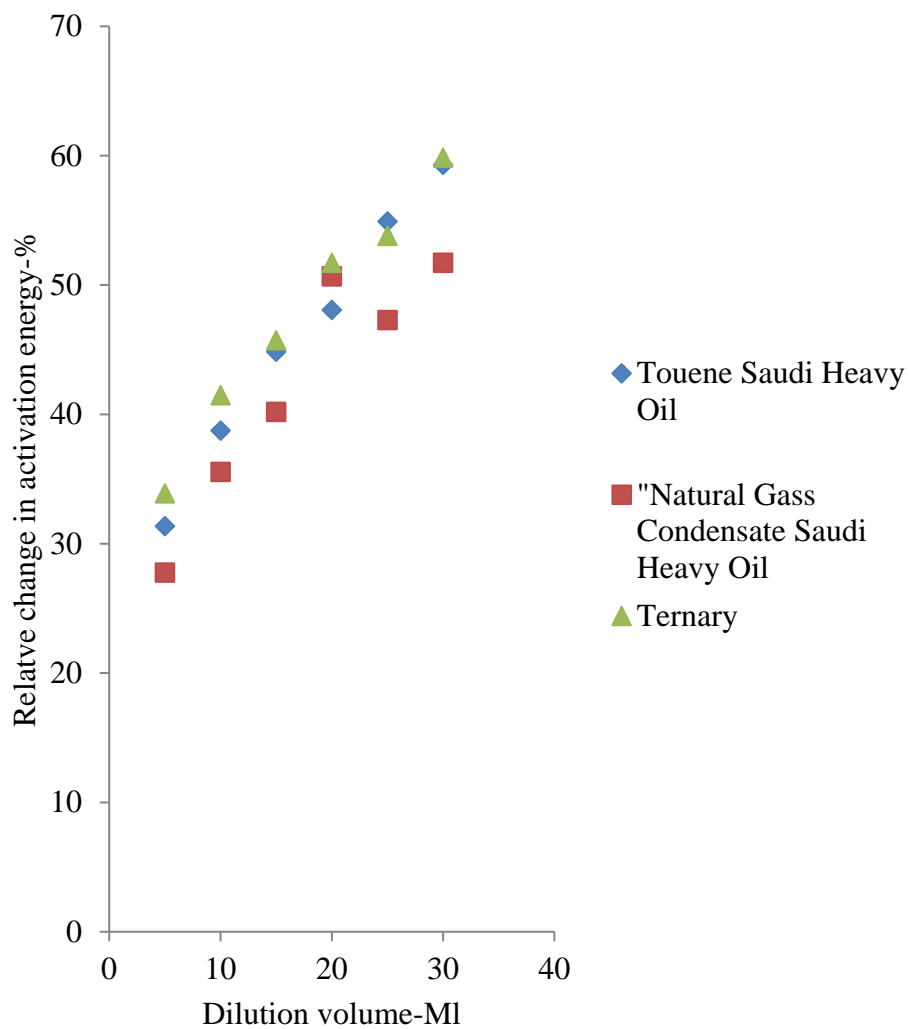


Figure 7. Relative change in activation energy for different systems

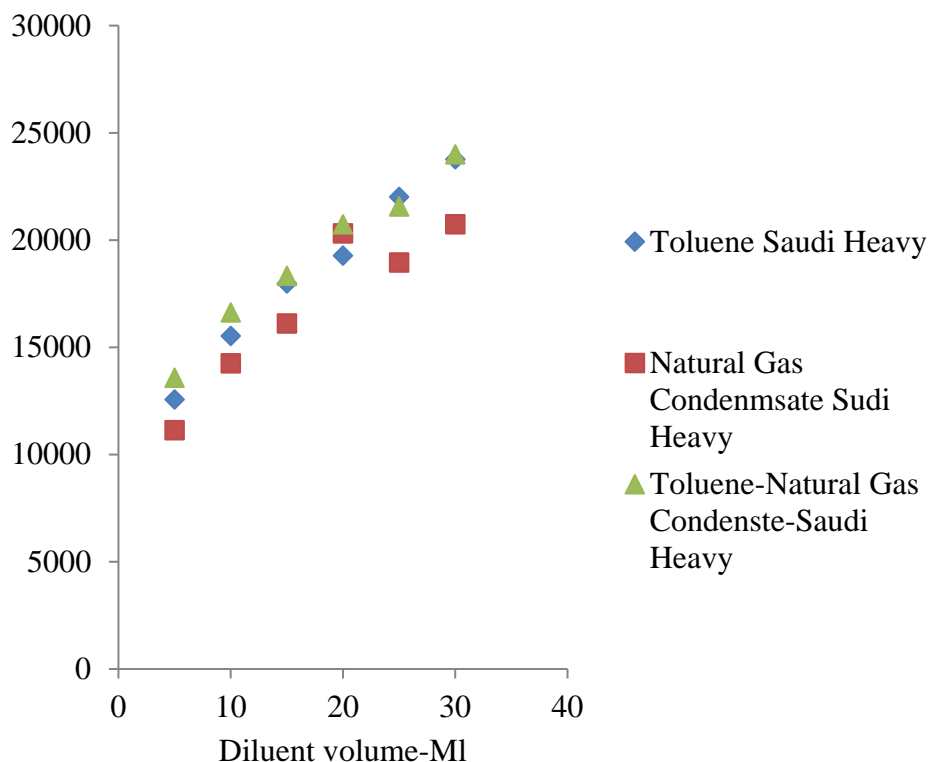


Figure 8. A plot of activation energy change versus dilution volume for all systems

Generally, higher the activation energy for viscous flow, higher the sensitivity of viscosity to temperature changes (Sin & Tueen, 2019). Therefore, a reduction of the flow activation energy corresponds to a reduced influence of the temperature on the viscosity, for example by a pronounced interaction of solvent molecules with crude oil similar to the case of the ceramic particles interactions with polymer chains (Menz et al., 2006). From Table 1, therefore, the ternary systems have the lowest sensitivity to temperature change, followed by the toluene binary systems and the natural gas condensate binary systems.

5.2 Implications of Activation Energy for Viscous Flow on Crude Oil Pipeline Transportation Cost

The cost of crude oil transportation from produced fields to refineries form a substantial portion of capital investments of the energy sector and knowledge of it is critical to determining net profit. For instance, in 2004, Transport Canada initiated a major project called the Full Cost Investigation (FCI) with the objective of computing estimates of the financial and social costs associated with transportation infrastructures and services (Karangwa, 2014). This effort was complemented by the generation of estimates of the financial costs associated with the pipeline transportation sector. These costs include capital costs and operating costs. The estimation of the financial costs for the pipeline transport industry is based on the whole pipeline network, which includes gathering, transmission and distribution networks. Therefore, given the significant role played by viscous friction pressure drop along crude oil transporting pipelines and the associated energy loss and cost, knowledge of the activation energies for viscous flow provide a reasonable platform for cost analysis based on the following theoretical foundations:

Considering the binary systems for toluene and Saudi Heavy crude oil mixture, the total cost per barrel of transportation is obtained as follows, considering a mixture volume of 100 mL:

$$C_{TSH} = \frac{158990}{1000} \left(\frac{V_T C_T}{100} \right) \quad (10)$$

For the binary systems of natural gas condensate and Saudi Heavy crude oil, the following holds:

$$C_{GSH} = 158990 \left(\frac{V_G}{100} \frac{C_G}{158990} \right) \quad (11)$$

For the ternary systems the following applies:

$$C_{TER} = \frac{158990}{1000} \left(\frac{V_T C_T}{100} \right) + \left(\frac{V_G C_G}{100} \right) \quad (12)$$

In which C_T is the cost of toluene [dollar per mL], V_T is the dilution volume of toluene [mL], V_G is the volume of natural gas condensate diluent [mL], C_G is the cost of natural gas condensate [dollars per mL], C_{TER} the total cost ternary a ternary system, C_{TSH} is the total cost of a toluene binary system [dollars] and C_{GSH} is the total cost of gas condensate binary system [dollars]. One barrel of total fluid is 158990 mL.

Based on Eq. (10) through Eq. (12), and 78 \$ per barrel of natural gas condensate (Morgan, 2017), 22 \$ per liter of toluene (Sydney-Solvents, 2022), the following table shows the total cost of dilution for all systems based on one barrel of total fluid consisting of diluents and crude oil for all dilution ratios. Based on Table 3, the binary systems for natural gas condensate has the lowest transportation cost followed by the ternary systems, with a substantial cost difference for every dilution ratio.

Table 3. Cost analysis for different diluent systems

Dilution Ratio	Toluene: Saudi Heavy-Dollars	Gas cond. Saudi Heavy-Dollars	Ternary System Dollars
5	175	4	55
10	350	8	110
15	525	11	165
20	700	16	220
25	874	20	276
30	1049	23	331

For transportation of crude oil, the pumping power requirement varies as the crude oil viscosity changes. The reduction of viscosity results in higher Reynolds number, lower friction factor and in effect, lower pumping power requirements. However, the activation energy for viscous flow is indicative of the flow resistance at a given dilution ratio. In this regard, comparison of the activation energies for the natural gas condensate binary systems to those of the ternary systems as seen in Table 4 shows that apart from using a diluent volume of 20 mL, the difference in activation energy is significant, which corresponds to higher viscous pressure drops for the binary systems on the average, compared to the ternary systems. Table 4 shows comparison of activation energies for natural gas condensate binary and ternary systems for different dilution ratios

Table 4. Activation energy differences for natural gas condensate binary and ternary systems

Dilution Ratio	Natural Gas Cond Saudi Heavy: E_{avis} $Jmol^{-1}$	Ternary Systems E_{avis} $Jmol^{-1}$	Difference in Activation Energy- E_{avis} $Jmol^{-1}$
5	28961	26508	2453
10	25843	23456	2387
15	23980	21760	2220
20	19781	19357	424
25	21137	18526	2611
30	19357	16098	3259

Therefore, based on the cost information of Table 3, the justification for using the ternary systems is the use of Drag-

reducing agents, which are additives in pipelines that reduce turbulence and increase the pipeline capacity by allowing more efficient flow of oil (Drag_reducing_agent, 2015), otherwise the binary systems of natural gas condensate are the most cost-effective. Moreover, natural gas condensate has become the preferred blending agent, and the most common ratio of bitumen to condensate is about 28% diluent to 72% bitumen or on a per barrel of bitumen production about 0.39 barrels of condensate are required (Rawlusyk, Hwang, & Birn, 2021).

5.3 Relation of Activation Energy Trend to Noncovalent Intermolecular Interaction

Noncovalent interactions have been found to play significant roles in molecular structure and properties (Deng et al., 2020; Ma, et al., 2021; Wheeler, 2013). In this regard, molecules may involve one or more π -interactions such as C-H \cdots π , O-H \cdots π , N-H \cdots π or π - π interactions (Mizuguchi et al., 1995; Janiak, 2000; (Rubes & Bludsky, 2008), and each of them has its directional requirement. For instance, the delocalized π electrons impart a quadrupolar moment to benzene, toluene, and other aromatic molecules, giving rise to favorable electrostatic interactions when molecules are either in a parallel or perpendicular. These additional electrostatic interactions compete with the attractive dispersion forces, which favor maximum molecular contact (Tsuzuki et al., 2002). Such noncovalent intermolecular interaction can affect viscosity and, therefore, the activation energy for viscous flow. Considering the systems studied in this paper, pi-pi intermolecular interaction can occur between toluene and Saudi Heavy oil due to the presence of the fused aromatic rings of asphaltene (Singh et al., 1999; Ralston et al., 1996). Therefore, in the binary systems Toluene and Saudi Heavy crude oil, these intermolecular interactions occur in addition to van der Waals dispersion forces. Also, for the ternary system Toluene-Natural Gas condensate-Saudi heavy crude oil, these interactions are present. However, for the binary systems natural gas condensate-Saudi Heavy crude oil, we have only dispersion interactions between components. Generally, intermolecular forces are much weaker than the intramolecular forces of attraction, but are important because they determine the physical properties of molecules like their boiling point, melting point, density, and enthalpies of fusion and vaporization.

Noncovalent pi-pi intermolecular interactions will compete with the attractive dispersion forces, reducing maximum molecular/intermolecular contact, which translates to a net effect of reduced intermolecular forces. The net effect is a reduction in heat of vaporization and activation energy for viscous flow. Therefore, from Table 1 it is expected that in the binary systems for Toluene-Saudi Heavy, increasing the volume of toluene will increase pi-pi interaction with a resulting decrease in the activation energy for viscous flow, which is the observed trend. Regarding the ternary system of Toluene-Natural Gas condensate-Saudi Heavy, there is an additional C-H \cdots π interaction, which has an added weakening effect on dispersion forces causing a greater reduction in the overall intermolecular forces compared to the binary system Toluene-Saudi Heavy crude oil, and this explains the lower values of activation energy for viscous flow. For the natural gas condensate binary systems, the predominant dispersion force is expected to result in higher activation energy as seen in the table. The implication is that based on Noncovalent intermolecular interaction effect, we expect the activation energy to be higher in the natural gas binary systems compared to toluene systems and the ternary systems to have the lowest and that is the trend in Table 1.

5.4 Industrial Relevance

In the scientific literature dealing with viscosity, research on activation energy has centered mostly on its determination for the bulk fluid system (Brewer et al., 2021; Toth et al., 2018; Schott, 1962; Hanemann et al., 2006). For instance, Brewer et al. (2021), have shown that the experimentally determined activation energy of viscous flow for seawater is approximately equal to that required to break two hydrogen bonds. The prominent outcome of our research is seen in the calculation of change of activation parameters per unit volume of diluent rather than as a bulk parameter. Since the principal objective in pipeline transportation design is to reduce viscosity of heavy crude oil using diluent, the approach used in this paper is beneficial not only to the petroleum industry, but to also to industries that rely on viscosity reduction to reduce energy consumption associated with pipeline transportation. In this regard, knowing the activation parameter change per unit of dilution gives an idea about the volume of diluent required to achieve the desired viscosity related to the anticipated mixture.

6. Conclusions

As the demand for crude oil continues to increase in response to the continued global needs for it, the development of unconventional crude oil reserves is the only way to sustain continued global supply. Therefore, reducing the viscosity of heavy crude oil to meet crude oil transporting pipeline regulations is a necessity. In this paper, we have assessed the dilution efficiency of well-known diluents in the petroleum industry based on different dilution ratios using a thermodynamic approach involving activation energy and heat of vaporization determination. Based on selected dilution ratios, we measured kinematic viscosity of crude oil and diluent mixtures, using anticipated field based temperatures reported in the literature, which facilitated our thermodynamic approach. The following sum up the conclusion of our study:

1. The ternary systems have the lowest activation energy for viscous flow followed by the binary systems of toluene while natural gas condensate has the highest activation energy,
2. Accordingly, the ternary systems have the lowest heat of vaporization and will provide the greatest ease for hole formation in accordance with the thermal activation theory for viscous flow,
3. Based on cost analysis, the binary systems of natural gas condensate is the most cost-effective for heavy oil transportation,
4. The cost analysis justifies the current emphasis on the use of natural gas condensate as the most preferred diluent in the petroleum industry,
5. Based on the activation energy for viscous flow for different systems, the ternary systems will have the lowest sensitivity to temperature change and this is an advantage in environments where heat losses causes significant changes of the inlet temperature of a crude oil transporting pipeline, which translates to viscosity increase and increase pressure drop leading to increase pumping cost,
6. The study shows that using additives in the ternary systems to further reduce flow resistance is the only way to prefer the ternary systems to the binary systems based on natural gas condensate,
7. Observed trends of activation energy for viscous flow for the systems studied are those expected, considering the effect of noncovalent intermolecular interactions.

Future work

While the ternary systems studied in this paper have the lowest activation energies for viscous flow, the cost per barrel of transportation is substantially higher compared to the natural gas condensate binary systems. Therefore, determination of the activation energy for viscous flow for the ternary systems in the presence of additives that will further reduce drag is necessary to compare its dilution efficiency to the natural gas condensate binary systems and this is our future research goal.

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Authors contributions

Professor Adango Miadonye and Dr. Mumuni Amadu were responsible for study design and revising. Professor Adango Miadonye and Dr Mumuni Amadu drafted the manuscript. Dr Mumuni Amadu wrote the manuscript. The experiments were conducted by the research interns (Iysha Kumari and Isha Jain). Professor Adango Miadonye edited the manuscript. All authors read and approved the final manuscript. All authors contributed substantially and meaningfully in the research work.

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Data sharing statement

No additional data are available.

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