FLUIDITY CHANGE BY HYDROXYL-CARBOXYL GROUP INTERACTION WITH ASPHALTENES IN HEAVY CRUDE OIL

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ABSTRACT

Asphaltene or paraffin are the main compounds that produce high viscosity in extra-heavy crude oil that could precipitate during transport or interaction with some compounds like viscosity reducers or flow enhancers. Additives interact with these fractions allowing heavy-phase dispersion and viscosity reduction. We analyzed interaction among heavy molecules presented in crude and carboxyl part, by energy calculation as the multiple minimum hypersurfaces, and developing of a stochastic model, finding the behavior of heavy phase aggregation and viscosity change according to a carboxyl-enhancer concentration. We found that molecular geometry and molecule with carboxyl and hydroxyl groups, as active compounds, considering a biodiesel molecule, affect the additive efficiency, allowing aggregation reduction with the presence of the functional group. We also conducted laboratory experiments comparing theoretical and experimental results.

KEYWORDS: asphaltene-wax interaction, heavy fraction dispersion, MMH in asphaltenes.

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1. INTRODUCTION

Asphaltenes are complex, high molecular weight compounds that constitute the most massive fraction of crude oil. These molecules tend to form molecular aggregates in such a way that they generate a dispersed phase that increases the viscosity of the oil¹. Additionally, these aggregates can reach a critical size and precipitate, depositing in the walls of the tube and decreasing the operational efficiency of the crude transportation².

The viscosity of the extra-heavy crude can be reduced by the injection of chemicals, known as viscosity reducers or flow enhancers, where the molecular mechanism through which viscosity decreases is not clear^{3,4,5}. The use of flow enhancer decreases the asphaltene deposition in pipelines^{4,6}, it has been established that the enhancer interacts with the asphaltenes reducing the fraction of these that are as a dispersed phase, manifesting in an appreciable reduction of the viscosity even at relatively low concentrations of the enhancer, which is one of the properties that this type of products must manifest^{1,7}.

The objective of the research was to analyze if there is theoretical evidence to support this hypothesis. To this end, the molecular interaction energies associated with different conglomerates formed by the molecules of asphaltenes, waxes, and hydroxyl-carboxyl calculating, qualitatively predict the transition probabilities associated

with the formation and dissociation processes of the same. Later, we developed a stochastic model based on the master equation to qualitatively predict the average behavior of the asphaltene aggregates concentration for the ester concentration. Ester is the hydroxyl-carboxyl compound considered in this work. The viscosity depends on the concentration of the dispersed phase, then the qualitative behavior of this property concerning the enhancer concentration is predicted, and we obtain a theoretical result contrasted with the experimental observations.

This paper has structured as follows: In section two are presented the theoretical results related to the calculation of the energy of molecular interactions paraffin-ester-asphaltenes obtained applying the multiple minimum hypersurfaces (MMH) approximation methodology. In section 3, we show a stochastic model to predict the average behavior of the concentration of molecular aggregates taking as a criterion that the probability of transition per unit of time associated with the processes of aggregate formation is proportional to the energy of molecular interaction between the molecules that compose them. In section 4, the experimental results of the viscosity for the enhancer concentration are shown, which contrasted with the predicted results about the fraction of the dispersed phase given by the stochastic model and, finally, conclusions.

2. STUDY OF MOLECULAR PARAFFIN-ASPHALTENE-ESTER INTERACTIONS USING THE MMH METHODOLOGY

The multiple minimum hypersurfaces (MMH) approach allows us to study the collective effects of the molecular environment by combining the quantum-mechanical procedures for the calculation of the molecular aggregate energies with the statistical thermodynamics, for the determination of the thermodynamic properties of association of polyatomic systems⁸. This methodology based on exploring the potential energy surface to find those molecular arrangements that, with their respective geometries and energies, can form the group of the most significant states for the calculation of the thermodynamic properties of the complete system⁹.

For MMH procedure, a set of random ordering of the different molecules under study is generated and rearranged until the minimum value of the internal energy obtention. These minima may be considered as a canonical set representative of the macroscopic state (closed system at constant temperature and pressure) according to a typical Boltzmann distribution. Through this methodology, a random conformational search is performed, from which essential conformations that can be established between the molecules forming the aggregate under study are analyzed. The subsequent optimization of the cells is performed by mechano-quantum calculation methods, using a semi-empirical Hamiltonian.

The reference state for the calculations is assumed to be a set of the same number of non-interacting molecules, which implies a process of the isothermal association from the molecular point of view, i.e., all other degrees of freedom (translational, vibrational and rotational) are considered identical in the individual molecules and the molecular aggregates, so that the sum of their total energies is taken as the reference value in the scale of the energies. Consequently, the energy of the cell for the new reference scale $\Delta\epsilon_i$, is:

$$\Delta\epsilon_i = \epsilon_i - \epsilon_{ref} \quad (1)$$

where:

$$\mathcal{E}_{ref} = \sum_i \mathcal{E}_i \quad (2)$$

The analyzed cases in this study correspond to the following molecular associations:

- Paraffin-asphaltene interaction
 - Paraffin-asphaltene-ester interaction
 - Paraffin-paraffin interaction
 - Paraffin-paraffin-ester interaction
 - Asphaltene-asphaltene interaction
 - Asphaltene-asphaltene -ester interaction
 - Asphaltene-ester interaction

We used these combinations because of hydroxyl carboxyl groups may be the principal compound in some viscosity reducers biodiesel-based case. For each of the molecular associations considered the most favorable conformations were obtained through the application of the following steps:

- Initial optimization of the molecules under study using the GAUSSIAN09 program with the B3LYP method, base 6-31g.
- Using the Granada program, we generated 300 random conformations of the molecules for interaction.
- A Single Point calculation was performed for each of the conformations obtained using the MOPAC2016 program.
- Using the Energy program, the energies corresponding to each conformation were determined.
- A statistical analysis of the results obtained in step 4 through the Q3 program was performed to determine the most favorable structures (minimum energy).
- The most favorable conformations were optimized using the program MOPAC2016 with the keywords pm7 ef precise geo-ok xyz.

The obtained results are shown in Table 1 and the images of some of the more stable structures are shown in Figure 1.

Table 1: Values of the Molecular Interaction Energies Determined using the MMH Methodology

Type of Interaction	Energy (eV)
Asphaltene - Asphaltene -2Ester	-30406.77196
Asphaltene - Asphaltene -1Ester	-27594.04812
Asphaltene - Asphaltene	-24781.64700
Paraffin - Asphaltene -2Ester	-22542.37275
Paraffin - Asphaltene -1Ester	-19729.39962
Paraffin - Asphaltene	-16916.68999
Paraffin - Paraffin -2Ester	-14677.31834
Paraffin - Paraffin -1Ester	-11864.47893
Paraffin -Paraffin	-9051.78487
Asphaltene -1Ester	-1520.35110

Figure 1. Initial structures considered; wax or paraffin (a), hydroxy-carboxyl or ester (b) and asphaltene (c).

As can be seen, the ester interacts with both asphaltenes and their aggregates, forming the lower energy conglomerates, and therefore those that are expected to form more likely in this system.

3. OBTAINING THE STOCHASTIC MODEL TO PREDICT THE FORMATION OF WAXES, ASPHALTENES, AND ESTER AGGREGATES

To obtain a stochastic model that describes the formation of molecular aggregates, we established the following considerations:

The microscopic variable that describes the system under study is the vector:

$$\mathbf{N} = \begin{bmatrix} N_A \\ N_P \\ N_E \\ N_{AA} \\ N_{AP} \\ N_{AE} \end{bmatrix} \quad (3)$$

N_A is the number of asphaltenes molecules, N_P is the paraffin molecules number, N_E the number of molecules of ester, N_{AA} is the number of aggregates formed by two asphaltenes molecules, N_{AP} is the number of a molecule of asphaltene and a paraffin aggregates, and N_{AE} is the number of aggregates formed by an asphaltene molecule and a molecule with the ester functional group.

The macroscopic variable is the number of moles of each chemical species (visualizing aggregates as a chemical species), given by the vector:

$$\mathbf{n} = \frac{1}{\Omega} \begin{bmatrix} N_A \\ N_P \\ N_E \\ N_{AA} \\ N_{AP} \\ N_{AE} \end{bmatrix} = \begin{bmatrix} A \\ P \\ E \\ x \\ y \\ z \end{bmatrix} \frac{mol}{m^3} \quad (4)$$

where the scale of observation or size of the system is:

$$\Omega = N_0 V \quad (5)$$

where N_0 is the Avogadro number, and V is the total system volume.

- It assumed that the following processes take place on a microscopic scale:

1) Formation and rupture of asphaltene-asphaltene aggregates:

where the probability of transition per unit of time of each of these processes, established a priori, are:

$$W_{11} = \frac{k_{11}}{\Omega} N_A^2 \quad (7)$$

$$W_{12} = k_{12} N_{AA} \quad (8)$$

where k_{11} and k_{12} are the velocity constants.

2) Formation and disruption of asphaltene-paraffin aggregates:

$$W_{21} = \frac{k_{21}}{\Omega} N_A N_P \quad (10)$$

$$W_{22} = k_{22} N_{AP} \quad (11)$$

3) Formation and disruption of asphaltene-ester aggregates

$$W_{31} = \frac{k_{31}}{\Omega} N_A N_E \quad (13)$$

$$W_{32} = k_{32} N_{AE} \quad (14)$$

- We considered that the system is closed, applying the mass conservation law it is obtained the following relations between the moles of the species:

$$\begin{aligned} A_0 &= A + 2x + y + z \\ P_0 &= P + y \\ E_0 &= E + z \end{aligned} \quad (15)$$

where subindex 0 indicates the initial number of moles of the corresponding chemical species.

From the established considerations, it is obtained the master equation^{10,11} describing the behavior of the probability that the vector associated with the microscopic variables takes a specific value for a given time:

$$\begin{aligned} \frac{\partial \psi(N;t)}{\partial t} = & (\mathbf{E}_{N_A}^{+2} \mathbf{E}_{N_{AA}}^{-1} - 1) \frac{k_{11}}{\Omega} N_A^2 \psi(N;t) \\ & + (\mathbf{E}_{N_A}^{-2} \mathbf{E}_{N_{AA}}^{+1} - 1) k_{12} N_{AA} \psi(N;t) \\ & + (\mathbf{E}_{N_A}^{+1} \mathbf{E}_{N_P}^{+1} \mathbf{E}_{N_{AP}}^{-1} - 1) \frac{k_{21}}{\Omega} N_P N_A \psi(N;t) \\ & + (\mathbf{E}_{N_A}^{-1} \mathbf{E}_{N_P}^{-1} \mathbf{E}_{N_{AP}}^{+1} - 1) k_{22} N_{AP} \psi(N;t) \\ & + (\mathbf{E}_{N_A}^{+1} \mathbf{E}_{N_E}^{+1} \mathbf{E}_{N_{AE}}^{-1} - 1) \frac{k_{31}}{\Omega} N_A N_E \psi(N;t) \\ & + (\mathbf{E}_{N_A}^{-1} \mathbf{E}_{N_E}^{-1} \mathbf{E}_{N_{AE}}^{+1} - 1) k_{32} N_{AE} \psi(N;t) \end{aligned} \quad (16)$$

which is a partial differential equation in differences subject to the initial condition:

$$\psi([N]_0; 0) = 1 \quad (17)$$

From the master equation, we obtain the vector corresponding to the first moment associated to the probabilities of transition per unit of time:

$$\alpha_0 = \begin{bmatrix} 2xk_{12} + yk_{22} + zk_{32} - 2A^2k_{11} - APk_{21} - AEk_{31} \\ yk_{22} - APk_{21} \\ zk_{32} - AEk_{31} \\ A^2k_{11} - xk_{12} \\ APk_{21} - yk_{22} \\ AEk_{31} - zk_{32} \end{bmatrix} \quad (18)$$

And the matrix associated with the second moment:

$$\beta = \frac{1}{\Omega} \begin{bmatrix} \left(\begin{array}{c} 4xk_{12} + yk_{22} + zk_{32} \\ + 4A^2k_{11} + APk_{21} + AEk_{31} \end{array} \right) & yk_{22} + APk_{21} & zk_{32} + AEk_{31} & -2k_{11}A^2 - 2xk_{12} & -yk_{22} - APk_{21} & -zk_{32} - AEk_{31} \\ yk_{22} + APk_{21} & yk_{22} + APk_{21} & 0 & 0 & -yk_{22} - APk_{21} & 0 \\ zk_{32} + AEk_{31} & 0 & zk_{32} + AEk_{31} & 0 & 0 & -zk_{32} - AEk_{31} \\ -2k_{11}A^2 - 2xk_{12} & 0 & 0 & k_{11}A^2 + xk_{12} & 0 & 0 \\ -yk_{22} - APk_{21} & -yk_{22} - APk_{21} & 0 & 0 & yk_{22} + APk_{21} & 0 \\ -zk_{32} - AEk_{31} & 0 & -zk_{32} - AEk_{31} & 0 & 0 & zk_{32} + AEk_{31} \end{bmatrix} \quad (19)$$

The nonlinear system of differential equations gives the temporal behavior of the first moment or expected value of the molar concentration of the present chemical species:

$$\frac{d\mathbf{n}}{dt} = \alpha_0 \quad (20)$$

subject to the initial condition:

$$n(0) = n_0 \quad (21)$$

while the behavior of the covariance matrix, expressed as a function of the expected values, is given by:

$$\frac{d\Phi}{dt} = \alpha_{0,1}\Phi + \Phi^T\alpha_{0,1} + \beta \quad (22)$$

where:

$$\alpha_{0,1} = \frac{d}{dn}\alpha_0 \quad (23)$$

The systems of differential equations associated with expected value behavior and covariance constitute the stochastic model that allows a partial description of the system behavior. Because the scale of observation is much larger than the size of microscopic entities (molecules and aggregates) the fluctuations associated with microscopic processes, which escalate with this relation, can be considered negligible so that for practical purposes behavior of the expected values is enough to analyze the behavior of the system.

In steady-state, the temporal derivatives are equal to zero, so that for the expected values the system of nonlinear algebraic equations is obtained:

$$\begin{aligned} 0 &= 2xk_{12} + yk_{22} + zk_{32} - 2A^2k_{11} - APk_{21} - AEk_{31} \\ 0 &= yk_{22} - APk_{21} \\ 0 &= zk_{32} - AEk_{31} \\ 0 &= A^2k_{11} - xk_{12} \\ 0 &= APk_{21} - yk_{22} \\ 0 &= AEk_{31} - zk_{32} \end{aligned} \quad (24)$$

This nonlinear closed system obeys conservation laws. For this reason, we replaced three equations by the three conservation mass ones so that the steady-state is:

$$\begin{aligned} 2xk_{12} + yk_{22} + zk_{32} - 2A^2k_{11} - APk_{21} - AEk_{31} &= 0 \\ yk_{22} - APk_{21} &= 0 \\ zk_{32} - AEk_{31} &= 0 \\ A_0 - y - z - 2x - A &= 0 \\ P_0 - y - P &= 0 \\ E_0 - z - E &= 0 \end{aligned} \quad (25)$$

4. COMPARISON BETWEEN EXPERIMENTAL AND PREDICTED RESULTS

The obtaining of the behavior of the formation of molecular aggregates, as a function of the ester concentration in the system, is from the solution of equation (25), which is necessary to specify the total concentration of asphaltene, paraffin, and ester (A_0 , P_0 , E_0). The initial concentration values of each of the chemical species considered were established based on the composition of two crude oils, shown in Table 2.

Table 2: Composition of Crude Oil Taken as Reference for Simulation

Crude	asphaltene A	paraffin P	A/P
A	20.7%	18.1%	1. 143 6

B	25.8%	10.9%	2.367 0
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In the case of the velocity constants associated with aggregate formation, considering that, for a qualitative estimation, which is the aim, what matters is the relative value of the bond energy value, so that the conglomerates in which the bond energy is small we see a higher velocity constant. For this purpose, we considered the bond energies presented in Table 3. The model assumed that the velocity constants associated with the dissolution of the aggregates have a value equal to 1:

$$k_{12} = k_{22} = k_{32} = 1$$

Furthermore, that the velocity constants associated with the formation of the aggregates are calculated by dividing the corresponding binding energy by the energy value associated with the formation of the asphaltene-asphaltene aggregates and multiplying the obtained value by 10, therefore, it is assumed:

$$k_{11} = 10, k_{21} = 6.8262, k_{31} = 6.1337$$

Table 3: Link Energies Considered for the Simulation of the System

Aggregate	Link Energy
A-A	-24781
P-A	-16916
A-E	-1520

Figure 2 shows the fraction behavior of each molecular aggregates calculated by reference to the concentration of total asphaltenes concerning the ester concentration, determined from the solution by numerical methods of the equation (25) and the assumed values of the velocity constants and initial concentrations for each of the crude considered.

Figure 2: The behavior of the asphaltene-ester (AE / A₀), asphaltene-asphaltene (AA / A₀), and asphaltene-paraffin (AP / AA) aggregates fraction for the initial ester concentration (E₀) for each of the crudes considered.

For this case, we predicted that, for both crude oils, the dispersed fraction of asphaltene-asphaltene aggregates decreases linearly with the ester concentration. This fraction is higher in crude B, in which the asphaltene/paraffin ratio is almost double as compared to crude A. On the other hand, the asphaltene-paraffin fraction also decreases with the ester concentration, while the asphaltene-ester fraction increases.

The fraction of asphaltene-asphaltene aggregates, which appears to form a dispersed phase in the crude. The obtained model predicts that this concentration decreases linearly concerning the enhancer concentration:

$$AA = \beta_0 - \beta_1 E_0 \quad (26)$$

Constants β_0 , β_1 depends on the oil total composition, the temperature, and the pressure of the system, as well as the molecular interaction energies. Unfortunately, the value of these constants cannot be determined directly from the experimental observations because it is nearly impossible, with available technology, to determine precisely which fraction of the total asphaltenes present in crude oil is forming the dispersed phase. The dispersed phase manifests in the viscosity μ , establishing:

$$\mu = \mu_0 + \eta \phi \quad (27)$$

μ_0 is the viscosity of the dispersion media, ϕ the volume fraction of the dispersed phase and η a parameter which depends on the complex form on the size and shape of the dispersed particles. Considering that the volume fraction of the dispersed phase is proportional to the concentration of asphaltenes forming the aggregates and by appropriately combining equations (26) and (27), obtaining that the behavior of the reduction of viscosity concerning the concentration of enhancer will be given by:

$$R_u = 1 - \frac{\mu(E)}{\mu(0)} = 1 - \frac{\lambda_0 - \lambda_1(E)}{\lambda_0} = mE \quad (28)$$

where the parameter m depends on the molecular interaction energies between the asphaltene and the ester, the crude composition, the temperature and the pressure of the system. According to this equation, the model predicts that the viscosity reduction is linearly increased with the enhancer concentration.

Figure 3 shows the experimental behavior observed in relation to the viscosity reduction as a function of the enhancer concentration for the crude oils considered and at two different temperature values.

Figure 3. I: experimental behavior of the viscosity reduction for ester percent at 60 Celsius. II: experimental behavior of the reduction of viscosity concerning the ester percentage at 80 Celsius.

These experimental results indicate that the reduction of viscosity due to the presence of ester is greater in crude oil with a lower asphaltene/paraffin ratio (crude A), which is precisely the case where it was obtained that the fraction of asphaltenes which forms asphaltene-asphaltene aggregates is lower. Therefore, this difference indicates that, at least in the analyzed cases, the effectiveness of the action of a flow enhancer depends on its composition. On the other hand, note that at the temperature of 60 C, although the reduction is increased as predicted qualitatively in the model, the behavior is not strictly linear. This difference in the qualitative behavior can be attributed to the existence of molecular interactions that have not been considered in the model, such as the interaction of the ester with the asphaltene aggregates, and it has been assumed that the dispersed phase is formed by aggregates constituted by two asphaltene molecules, when in principle the aggregates may be formed by several molecules.

CONCLUSIONS

An application study of the MMH methodology was carried out to calculate the molecular interaction energies associated with the different molecular aggregates that are formed in a paraffin-asphaltene-ester system, with the objective of investigating the mechanism of action of a flux enhancer on the physical properties of crude oil. In this case, it was found that the associations of lower energy are those involving ester with asphaltenes and their aggregates, so it is expected that the active component of the analyzed enhancer, which in this case has an ester functional group, interacts fundamentally with the fraction of crude composed by asphaltenes.

To predict the effect of the ester concentration on the formation of aggregates, a stochastic model was developed, where the model constants were estimated from the calculated interaction energies and the composition of two crude oils. Results show that the fraction of asphaltene-asphaltene and asphaltene-paraffin aggregates decrease with the ester concentration, while the fraction of asphaltene-ester aggregates increases. An equation is obtained to predict the reduction of viscosity as a function of the enhancer concentration, obtaining a positive linear dependence between both variables. This theoretical result was contrasted with the experimental behavior, observing in a general way a qualitative correspondence between both. However, at a lower temperature, the observed experimental correlation shows a slightly nonlinear behavior, which is attributed to the existence of other interactions that may occur that have not been considered in this research.

Despite these limitations, the obtained results do not contradict the initially established hypothesis concerning the action of the enhancer on the dispersed phase that is present in the heavy crudes.

REFERENCES

1. Padula, L., Balestrin, L. B. D. S., Rocha, N. D. O., de Carvalho, C. H. M., Westfahl Jr, H., Cardoso, M. B., et al. Role of Asphaltenes and Additives on the Viscosity and Microscopic Structure of Heavy Crude Oils. *Energy & Fuels*, 2016, 30(5), 3644-3651.
2. Moreno-Arciniegas, L., & Babadagli, T. Optimal application conditions of solvent injection into oil sands to minimize the effect of asphaltene deposition: an experimental investigation. *SPE Reservoir Evaluation & Engineering*, 2014, 17(04), 530-546.
3. Taborda, E. A., Franco, C. A., Ruiz, M. A., Alvarado, V., & Cortés, F. B. Experimental and theoretical study of viscosity reduction in heavy crude oils by addition of nanoparticles. *Energy & Fuels*, 2017, 31(2), 1329-1338.
4. Subramanian, D., & Firoozabadi, A. Effect of Surfactants and Water on Inhibition of Asphaltene Precipitation and Deposition. In Abu Dhabi International Petroleum Exhibition and Conference. Society of Petroleum Engineers, November 2015.
5. Marcano, F., Moura, L. G., Cardoso, F. M., & Rosa, P. T. Evaluation of the Chemical Additive Effect on Asphaltene Aggregation in Dead Oils: A Comparative Study between Ultraviolet-Visible and Near-Infrared-Laser Light Scattering Techniques. *Energy & Fuels*, 2015, 29(5), 2813-2822.
6. Moreno-Arciniegas, L., & Babadagli, T. Optimal application conditions of solvent injection into oil sands to minimize the effect of asphaltene deposition: an experimental investigation. *SPE Reservoir Evaluation & Engineering*, 2014, 17(04), 530-546.
7. Hashemi, R., Nassar, N. N., & Almas, P. P. Nanoparticle technology for heavy oil in-situ upgrading and recovery enhancement: Opportunities and challenges. *Applied Energy*, 2014, 133, 374-387.
8. Montero, L. A.; Molina, J.; & Fabian, J. Multiple minima hypersurfaces of water clusters for calculations of association energy. *International Journal of Quantum Chemistry*, 2000, 79, 8-16.
9. Ardévol, A. Métodos de simulación QM/MM y de mecánica estadística: una aproximación teórica a la biología molecular. *Anales de Química*, 2013, 109(4), 268-275.
10. Gardiner, C. W., *Handbook of stochastic methods*, Springer-Verlag, Berlin, 2004.
11. Van Kampen, N.G., *Stochastic processes in physics and chemistry*, Elsevier, The Netherlands, 1992.
12. Kumar, M., Reddy, B. V., & Reddy, P. V. (2018). Experimental Comparison of Solar Paraboloid Collector with and without Mirror in Aluminum Foil as Reflectors. *International Journal of Mechanical and Production Engineering Research and Development (IJMPERD)*, 8(2), 1117-1124.
13. Dabbagh, B. M. A., Shimary, H. J. A., & Salih, R. M. Separation Of Oil/Water System By Polymeric The Super Hydrophobicmaterial For Civil Application.
14. Reddy, M. C., & Gupta, B. Soil Organic Carbon Stocks Under Different Forest Types Of Himalayan Moist Temperate Forests In Shimla District, Himachal Pradesh, India. *Forest*, 12, C2c.
15. Kumar, C. V., & Satyanarayana, P. Influence Of Index Properties On Prediction Of Compaction Characteristics Of Red Soils.