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Modelling Viscosity based on a Molecular Description

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Abstract- In this paper, we illustrate that the modern trends for viscosity prediction are moving away from empirically based methods to those that make use of a sound theoretical framework and are validated against primary experimental data. The Vesovic-Wakeham (VW) method is in the forefront of these developments. It is founded on the kinetic theory of hard-sphere fluids that is appropriately modified to take into account the behaviour of real fluids. It makes use of mixing rules that are thermodynamically consistent and more importantly have no adjustable parameters. In this work the VW model has been used to predict the viscosity of reservoir fluids that are of interest to the oil and gas industry. In particular, we examined the predictive capabilities of VW model by comparing against accurate experimental data on natural gas and liquid alkane mixtures that form the main constitutes of oil. The natural gas data were reproduced with uncertainty of better than 1%, while the viscosities of liquid alkane mixtures were reproduced with the uncertainty of 4%.

Keywords**:** Viscosity, VW model, kinetic theory, prediction, modelling, mixtures, oil.

1. Introduction

Industrial process design creates a considerable demand for reliable values of the viscosity of a wide variety of fluid mixtures over extensive ranges of pressure/density and temperature. The economic case for improving the accuracy with which viscosity is determined is strong; however, the wide range of possible fluid mixtures and of conditions of interest precludes obtaining the relevant data by experimental means alone. There is, therefore, a clear need for predictive methods that are accurate, reliable and internally consistent. They range from purely empirical and correlative where the experimental data used governs the accuracy of the prediction to more sophisticated models that take a more fundamental approach (Assael et al., 2014). The most successful models are based on the best available theory, simplified just sufficiently to allow ready application and validated against a critical set of experimental data of proven accuracy. The modern trends are thus moving away from simple empirical correlations that have historically placed the emphasis on the simplicity to the detriment of both accuracy and wide applicability.

The accuracy and the sophistication of the predictive models are to a great extent determined by availability a solid theoretical framework used in developing the model. In a dilute gas region the underlying kinetic theory provides us with a good understanding of how the molecular interactions and a shape of the molecule govern the viscosity. It is thus possible to predict the viscosity, of at least simple gases, with the accuracy commensurate with the best experimental measurements over wide range of temperatures (Assael et al., 2014). Near the critical point the current models are also capable of predicting the viscosity critical enhancement with good accuracy (Assael et al., 2014). However, in a dense fluid region the lack of solid theoretical framework has hampered the development of a single accurate and reliable prediction method. Instead, people have followed a number of distinct routes taking advantage of different, primarily semi-theoretical formulations. Thus, predictive models based on kinetic theory, corresponding-states principle and those that exploit the link with thermodynamics are available (Assael et al., 2014). One of the difficulties that all the models face is that viscosity exhibits a strong nearly exponential dependence on temperature and/or density near the solidification line. Hence, precise knowledge of temperature and/or density is required to predict the value of viscosity. This high sensitivity makes accurate estimation essentially impossible, in this region, irrespective of the complexity and sophistication of a given model.

In this paper we focus on Vesovic-Wakeham (VW) model (Vesovic and Wakeham, 1989; Royal et al., 2003; de Wijn et al., 2012) and discuss how this state-of-the-art modelling approach, based on molecular description, provides us with an accurate, reliable and internally consistent method to predict the viscosity of fluid mixtures over wide ranges of density and temperature.

2. VW Model

The VW method is founded on the kinetic theory of the hard-sphere fluid. In its simplest form it takes Enskog formulation (Chapman and Cowling, 1970) as its starting point and consequently represents the viscosity of a hard-sphere fluid as,

$$\eta = \eta^{(0)}\left[\frac{1}{\chi} + \alpha\rho + 1.205\alpha^2\rho^2\chi^2\right] \tag{1}$$

where ρ is the molar density and $\eta^{(0)}$ is the viscosity in the limit of zero density. The quantity χ is the radial distribution function at contact, while α is a parameter proportional to the excluded volume per molecule. In order to render the Enskog formulation viable for the description of the real fluids, the traditional approach is to treat the hard sphere diameter as an effective diameter, weakly dependent on temperature. Hence, a proper choice of the effective diameter is paramount for success in representing the viscosity of the real fluid. For fluid mixtures, the problem of choosing the appropriate effective diameters is compounded by the presence of more than one species. The innovation of the VW method is to treat the radial distribution function as adjustable and obtain its value from the viscosity of pure species constituting the mixture of interest. By constraining the radial distribution function to be a continuous, monotonically increasing function of density, it is possible to obtain a unique and internally consistent value of parameter α

$$\alpha = \frac{0.313\eta^*}{\rho^*\eta^{(0)}} \tag{2}$$

where an asterisk (*) indicates that the physical quantity is evaluated at a switch-over density. In order to predict the viscosity of a mixture one also requires the knowledge of the radial distribution function and the parameter α for unlike interactions. These parameters are obtained from mixing rules that are thermodynamically consistent and based on the expressions for the hard sphere fluid (Royal et al., 2003; de Wijn et al., 2012). Hence, in line with all the other methods for predicting the viscosity of fluid mixtures, the VW method requires mixing rules. However, unlike other methods (Assael et al., 2014) no empiricism is introduced and the mixing rules used in the VW method have no adjustable parameters. In essence, the VW method interpolates amongst the viscosities of pure component species based on the best available kinetic theory. It has no adjustable parameters, and requires no dense mixture viscosity data.

We have recently extended the kinetic theory of hard-sphere fluid to deal with fluid consisting of long chain-like molecules, where the molecules of the fluid are modelled as chains of equally sized, tangentially joined hard spheres (de Wijn et al., 2008; de Wijn et al., 2012). Thus, allowing the application of the VW method to mixtures of interest to petroleum industry, where the presence of long chain hydrocarbons cannot be adequately represented by a simple hard sphere fluid.

3. Results

To illustrate the predictive power of the VW method we investigate two types of fluid mixtures of interest to petroleum industry. Figure 1 illustrates the comparison of the VW prediction with the experimental data of Schley and co-workers (2004) for natural gas. The natural gas in question consisted of 84% methane by volume, with minor components N_2 (9.7%), C_2H_6 (3.4%) and CO_2 (1.4%), the rest being trace components (C_3-C_{8+}, H_2 and He). The experimental data were obtained in a proven vibrating-wire viscometer and have claimed accuracy of 0.5%, thus representing a stringent test for any viscosity prediction method. The mixture was modelled as 8-component mixture. The VW method predicts the data with an AAD deviation of 0.2%, bias of 0.1% and maximum deviation of 0.8%. This is an excellent agreement, with hardly any systematic trend observed.

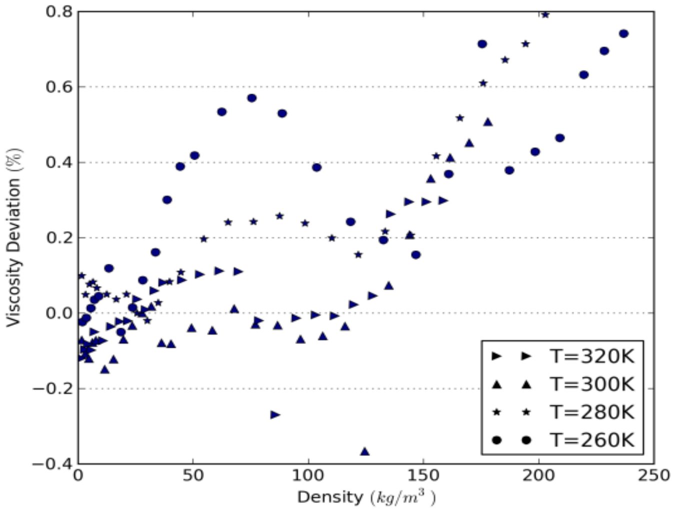

Fig. 1. Percentage deviation of the predicted values of the viscosity of natural gas from the experimental values (Schley et al., 2004) as a function of pressure for different isotherms.

Figure 2 illustrates the comparison of the VW-chain prediction with the experimental data of Wu and co-workers (1998; 1999) for binary and multicomponent alkane mixtures.

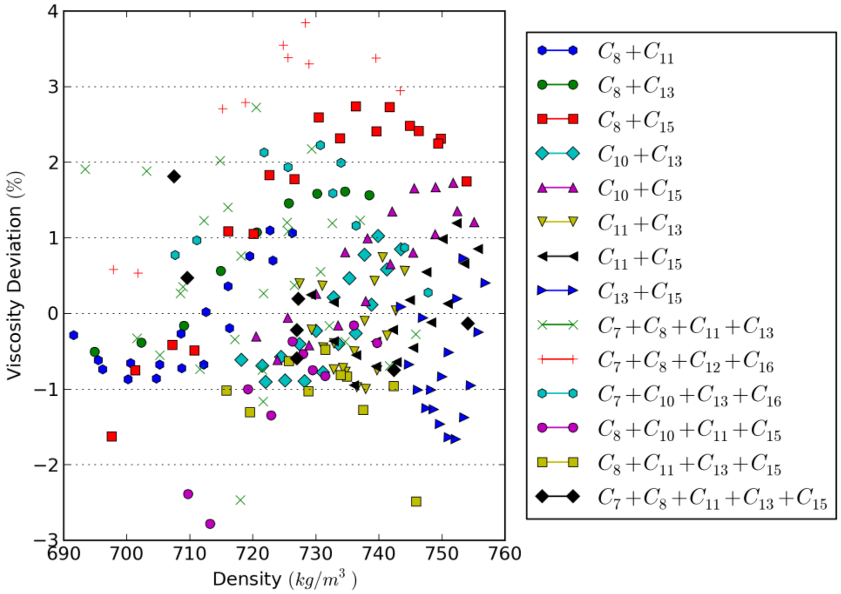

Fig. 2. Percentage deviation of the predicted values of the viscosity of alkane mixtures from the experimental values (Wu et al., 1998 & Wu et al., 1999) as a function of density.

The experimental data were obtained in a capillary viscometer. Notwithstanding that all the measurements were performed at atmospheric pressure and in temperature range 293-313 K the agreement is very good. All the examined data were reproduced within 4%. Overall, the deviation plots confirm that the VW method is capable of predicting the viscosity of mixtures encountered in oil and gas industry accurately. This further extends the range of application of the VW model that previously also included refrigerant mixtures (Royal et al., 2005) and supercritical fluid mixtures (Royal et al. 2003; Vesovic and Wakeham, 1989). It is worth pointing out that the accuracy of the VW model depends to a great extent on the accuracy with which the viscosity of pure species is known. Thus, the improvements in correlating pure species viscosity where the data are more plentiful will also lead to improvements in predicting the viscosity of mixtures.

4. Conclusion

The VW method, which is founded on the kinetic theory and on a set of thermodynamically consistent mixing rules with no adjustable parameters, has been used to predict the viscosity of natural gas and liquid alkane mixtures that form the main constitutes of oil. The natural gas data were reproduced with uncertainty of better than 1%, while the liquid alkane viscosities were reproduced with the uncertainty of 4%. Thus, indicating that the newly developed VW–chain model (de Wijn et al., 2012) is capable of accurately representing the viscosity of mixtures of interest to the oil industry. This further supports the modern trends in viscosity prediction of replacing the empirical methods with models that have a solid theoretical pedigree.

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References

Assael M.J., Goodwin A.R.H. Vesovic V., Wakeham W.A. (edts.). (2014). “Experimental Thermodynamics Volume IX: Advances in Transport Properties of Fluids”. The Royal Society of Chemistry.

Chapman S., Cowling T. (1970). “The Mathematical Theory of Non-uniform Gases”. Cambridge University Press.

de Wijn A.S., Vesovic V., Jackson G., Trusler J.P.M. (2008). A Kinetic Theory Description of the Viscosity of Dense Fluids consisting of Chain Molecules. J. Chem. Phys., 128, 204901.

de Wijn A.S., Riesco N., Vesovic V., Jackson G., Trusler J.P.M. (2012). Viscosity of liquid mixtures: The Vesovic-Wakeham method for chain molecules. J. Chem. Phys., 136, 074514.

Royal D.D., Vesovic V., Trusler J.P.M., Wakeham W.A. (2003). Prediction of the Viscosity of Dense Fluid Mixtures. Mol. Phys., 101, 339-352.

Royal D.D., Vesovic V., Trusler J.P.M., Wakeham W.A. (2005). Predicting the Viscosity of Liquid Refrigerant Blends: Comparison with Experimental Data. Int. J. Refrig., 28, 311-319.

Schley P., Jaeschke M., Kuchenmeister C., Vogel, E. (2004). Viscosity Measurements and Predictions for Natural Gas, Int. J. Thermophys., 25, 1623-1652.

Vesovic V., Wakeham W.A. (1989). Prediction of the viscosity of fluid mixtures over wide ranges of temperature and pressure Chem. Eng. Sci., 44, 2181-2189.

Wu J., Shan Z., Asfour A.A. (1998). Viscometric properties of multicomponent liquid n-alkane systems. Fluid Phase Equil., 143, 263-274.

Wu J., Nhaesi A.H., Asfour A.A. (1999). Viscosities of eight binary liquid n-alkane systems at 293.15 K and 298.15 K. Fluid Phase Equil., 164, 285-293.