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The Scott-Magat Polymer Theory for Determining Onset of Precipitation of Dissolved Asphaltene in the Solvent + Precipitant Solution

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Abstract: The Scott-Magat polymer theory, which assumes that polymers have heterogeneous structure and takes into account the polydispersity in the molecular weight of polymers, is a method to model asphaltene precipitation conditions. The traditional Scott-Magat polymer theory based models assume that the precipitated phase consists of asphaltene only. In the present work, we introduce a model based on the Scott-Magat polymer theory assuming that the precipitated phase consists of asphaltene and non-asphaltene components and the oil phase is free of asphaltene (Due to low concentration of asphaltene in the oil phase). It is shown that the latter model is similar to a previously reported thermodynamic model in the literature based on the Flory-Huggins polymer theory (R. Cimino, S. Correra, P.A. Sacomani, C. Carniani, "Thermodynamic Modelling for Prediction of Asphaltene Deposition in Live Oils", *SPE 28993, Presented at the SPE International Symposium on Oilfield Chemistry held in San Antonio*, TX, USA, 14-17 February 1995), in which it is assumed that asphaltene has a homogeneous structure and the precipitated phase consists of asphaltene and non-asphaltene components and the oil phase is free of asphaltene.

Keywords: Asphaltene, maltene, Scott-Magat theory, Flory-Huggins theory, modeling, precipitation, predictive model.

INTRODUCTION

Asphaltene precipitation in oil industry can cause serious operational, safety and economical problems because it causes fouling in the reservoir, in the well, in the pipeline and in the production and processing facilities. Asphaltene phase behavior has therefore been the subject of numerous theoretical studies [1-34]. One of the fundamental difficulties encountered in describing the phase behavior of asphaltene-containing systems is the lack of suitable characterization parameters [1, 7]. In fact, asphaltenes are not well-identified components/ mixtures. They consist of several polar components of aromatic nature with high molecular weights [1, 7]. In the majority of cases, the complexity of the asphaltene fraction leads to the assumption that the asphaltenes can be regarded as one single pseudo-component (monodisperse) [1, 7]. The main drawback of the monodisperse models is that they may not take into account the aggregation phenomena of asphaltenes [1, 7]. In fact, the aggregation process produces a molecular weight distribution of aggregates, which also causes a polydispersity in asphaltene properties [1, 7]. A few models use a polydisperse concept in terms of asphaltene properties, especially molecular weight and size [21-23].

The traditional models reported in the literature normally use polymer solutions theories (Scatchard-Hildebrand [7], Flory-Huggins [7, 35], and Scott-Magat [36]) to model the phase behavior of asphaltene-containing fluids [1, 2, 5, 7, 8, 14, 20-23]. In addition to these models, there are also a few models, which are based on cubic equations of state [17, 24]. New thermodynamic models have recently been developed, which can take into account the aggregation natures of asphaltene [5, 13, 16, 26-31]. On the other hand, most of the models reported in the literature assume that the precipitated phase consists of asphaltene only and the presence of non-asphaltene components in the precipitated phase is normally ignored. Cimino *et al*. [2, 14] employed the Flory-Huggins polymer theory [35] and assumed that the precipitated phase contains not only asphaltene but also a fraction of non-asphaltene components. They showed that their proposed model [2, 14] can better predict phase behavior of dissolved asphaltene in mixtures of solvents and precipitants and none of the literature models is capable of predicting this behavior satisfactorily. Cimino *et al*. [2, 14] also reported a need to modify other polymer theory based asphaltene models in order to take into account the presence of non-asphaltene components in the precipitated phase.

In this work, we use a more comprehensive polymer theory than the Flory-Huggins model [35], namely the Scott-Magat polymer theory [36] for modeling asphaltene phase behavior. Different from the Flory-Huggins polymer theory [35] based asphaltene models (which assume that asphaltenes have homogeneous structure and properties), the Scott-Magat polymer theory [36] based asphaltene models assume that asphaltenes have heterogeneous structure and the polydispersity can be taken into account in the molecular weight of asphaltene. Kawanaka *et al*. [21, 22] and Park [23] used this theory for modeling asphaltene phase behavior. However, they assumed that the precipitated phase consists of asphaltene only. Using this theory [36], and assuming that the precipitated phase consists of both asphaltene and non-asphaltene components, we propose a thermodynamic model. It is shown that the new model is similar to a previously reported model based on the Flory-Huggins polymer theory [35], namely Cimino *et al*. [2, 14] model, in which the precipitated phase consist of asphaltene and non-asphaltene components.

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THERMODYNAMIC MODEL BASED ON FLORY-HUGGINS POLYMER THEORY

Following the Flory-Huggins polymer theory [20], the chemical potential change of the maltene (asphaltene free oil) relative to a reference value, $\Delta\mu_m$, and the chemical potential change of the aspahltene relative to a reference value, $\Delta\mu_a$, are given, respectively by [8]:

$$\Delta\mu_m = RT[\ln\Phi_m + (1-\Phi_m)(1-\frac{V_m}{V_a}) + \chi(1-\Phi_m)^2] \quad (1)$$

$$\Delta\mu_a = RT[\ln(\Phi_a)+(1-\Phi_a)(1-\frac{V_a}{V_m}) +(1-\Phi_a)^2\frac{V_a}{V_m}\chi] \quad (2)$$

where R, T, Φ_m ,V_m, Φ_a and V_a are universal gas constant, temperature, volume fraction of maltene, molar volume of maltene, volume fraction of asphaltene and molar volume of asphaltene, respectively. χ stands for interaction parameter between asphaltene and maltene and is given by the following equation [2, 8, 14]:

$$\chi = \frac{V_m[(\delta_m-\delta_a)^2]}{RT} \quad (3)$$

where δ_m and δ_a are solubility parameters (the square root of the internal energy of vaporization per molecular volume) for the maltene and the asphaltene, respectively. In the above equation [37, 38]:

$$\Phi_a = 1-\Phi_m = \frac{x_a V_a}{x_a V_a + x_m V_m} \quad (4)$$

or

$$\Phi_a = \frac{w_a/\rho_a}{w_a/\rho_a + w_m/\rho_m} \quad (5)$$

where x_a and x_m are the mole fractions of asphaltene and maltene, respectively. w_a and w_m are the weight fractions of asphaltene and maltene, respectively and ρ_a and ρ_m represent the mass densities of asphaltene and maltene, respectively.

Cimino *et al.* [2, 14] performed some tests to estimate onset of precipitation of dissolved asphaltene in different ratios of solvent and precipitant. The results showed that the precipitated asphaltene does dissolve in appropriate solvent and the ratio of "solvent mass per asphaltene mass" and "precipitant mass per asphaltene mass" is linear and independent of the asphaltene concentration at onset of asphaltene precipitation conditions [2, 14]. Their experiments showed poor capability of colloidal model [25] and traditional Flory-Huggins polymer theory [35] based models [21, 22] in reproducing the observed behavior, where the latter models assume pure asphaltene for the precipitated phase. Cimino *et al.* [2, 14] employed a more correct application of the Flory-Huggins polymer theory [35] to better represent asphaltene phase behavior. They assumed that not a pure asphaltene phase but a phase containing concentrated asphaltene and a fraction of solvent nucleates on phase separation.

Some simplifications are made by considering the physics of phase splitting. Considering the typically low volume fraction of asphaltene in the oil phase (Φ_a, which is about 10^{-2} to 10^{-3} when the asphaltene weight percent ranges from 1 to 10) the oil can safely be assumed to be pure maltene, that is $\Phi_a = 0$ [2, 14]. Such an assumption leads to the following final equation [2, 14]:

$$\ln[1-\Phi_a'] + \left(1-\frac{V_m}{V_a}\right)\Phi_a' + \chi\Phi_a'^2 = 0 \quad (6)$$

where the *prime* represents the asphaltene-rich phase, and Φ_a' is the volume fraction of asphaltene in asphaltene-rich phase.

According to this model [2, 14], δ_a is assumed to be independent of pressure, and Φ_a' is assumed to be constant. The parameters Φ_a' and δ_a are regressed from experimental data on onset of asphaltene precipitation. V_a is calculated from density and molecular weight of asphaltene. For given δ_a, Φ_a' and temperature, equation (6) only varies with V_m and δ_m. Cimino *et al.* [1, 2] successfully examined the capability of this model [2, 14] against their own experimental data.

THERMODYNAMIC MODEL BASED ON SCOTT-MAGAT POLYMER THEORY

A more comprehensive approach for predicting asphaltene precipitation conditions can be developed by using the Scott-Magat polymer theory [36], in which a distribution of asphaltene molecular weight is taken into account, as mentioned earlier. Based on the Scott-Magat polymer theory [36], the chemical potential change of the maltene relative to a reference value, and the chemical potential change of the *i*th asphaltene fraction relative to a reference value ($\Delta\mu_i$) are calculated using the following equations [36]:

$$\Delta\mu_m = RT[\ln\Phi_m + (1-\Phi_m)(1-\frac{1}{\overline{M}}) + \chi(1-\Phi_m)^2] \quad (7)$$

$$\Delta\mu_i = RT[\ln\Phi_i + (1-\Phi_m)(1-\frac{M_i}{\overline{M}}) - M_i\Phi_m + \chi M_i\Phi_m^2] \quad (8)$$

where Φ_i is volume fraction of the *i*th asphaltene fraction. $\overline{M}$ and M_i represent the average molecular weight of asphaltene and the molecular weight of the *i*th asphaltene fraction, respectively. χ is given by equation (3).

To determine the solubility/precipitation conditions based on the assumption made by Cimino *et al.* [2, 14], one must utilize the equilibrium conditions between the two-phases:

$$\Delta\mu_m = \Delta\mu_m' \quad (9)$$

where $\Delta\mu_m$ is the chemical potential change of the maltene relative to a reference value, as mentioned earlier. The *prime* represents the asphaltene-rich phase, as pointed out earlier. Therefore:

$$\ln\Phi_m+(1-\Phi_m)(1-\frac{1}{\overline{M}})+\chi(1-\Phi_m)^2=$$
$$\ln\Phi_m'+(1-\Phi_m')(1-\frac{1}{\overline{M}'})+\chi(1-\Phi_m')^2 \quad (10)$$

According to Scott-Magat polymer theory [36], for values of χ sufficiently high (>>0.5), one may take $\Phi_m = 1$ and $\overline{M} = \infty$, so that Φ_a' is a function of χ alone:

$$\ln[1-\Phi_a'] + \Phi_a' + \chi\Phi_a'^2 = 0 \quad (11)$$

Equation (11) is similar to equation (6) considering the ratio $\frac{V_m}{V_a}$ in equation (6) is negligibly small compared to unity. The result indicates that taking into account the polydispersity in asphaltene molecular weight is insignificant for the phase behavior modeling of dissolved asphaltene in solvent + precipitant solutions.

CONCLUSIONS

A phase equilibrium model (equation 11) was developed from the Scott-Magat polymer theory [36], which assumes that the precipitated phase consists of an asphaltene fraction and a non-asphaltene fraction, and the oil phase is free of asphaltene (due to low concentrations of asphaltene in the oil phase). It was shown that the new model is similar to a previously reported model (equation 6) based on the Flory-Huggins polymer theory [35], which assumes that the precipitated phase consists of asphaltene and non-asphaltene components. The study showed that taking into account the polidispersity in aspahtelene molecular weight does not have important effect on phase behavior modeling of dissolved asphaltene in different ratios of solvent and precipitant.

REFERENCES

[1] J.G. Speight, *The Chemistry and Technology of Petroleum*. New York: Marcel Dekker, Inc, 1991.

[2] R. Cimino, S. Correra, A. Del Bianco, and T.P. Lockhart, "Solubility and Phase Behavior of Asphaltenes in Hydrocarbon Media" Asphaltenes: Fundamentals and Applications, E.Y. Sheu and O.C. Mullins (eds.), New York: Plenum Press, 1995, 97-130.

[3] G. Porte, H. Zhou, and V. Lazzeri, "Reversible Description of Asphaltene Colloidal Association and Precipitation", *Langmuir*, Vol. 19, pp. 40-47, 2003.

[4] F.I. Nellensteyn, "The Colloidal Structure of Bitumens", *The Science of Petroleum*, Oxford University Press, London, Vol. 4, pp. 2760, 1938.

[5] A. Firoozabadi, *Thermodynamics of Hydrocarbon Reservoirs*. First ed. McGraw-Hill, 1999.

[6] IP 143/90 (Standard Number) Asphaltene (heptane insolubles) in Petroleum Products, Standards for Petroleum and its Products, Institute of Petroleum, London, UK, 143.1-143.7, 1985.

[7] S.I. Andersen, and J.G. Speight, "Thermodynamic models for asphaltene solubility and precipitation", *J. Pet. Sci. Eng*., Vol. 22, pp. 53-66, 1999.

[8] A. Hirschberg, L.N.J. DeJong, B.A. Schipper, and J.G. Meijer, "Influence of Temperature and Pressure on Asphaltene Flocculation", *SPE J*., Vol. 24, pp. 283-293, June 1984.

[9] H. Rassamdana, B. Dabir, M. Nematy, M. Farhani, and M. Sahimi, "Asphalt Flocculation and deposition: I. The onset of Precipitation", *AIChE J*., Vol. 42, pp. 10-22, 1996.

[10] H. Rassamdana, and M. Sahimi, "Asphalt Flocculation and deposition: II. Formation and Growth of Fractal Aggregates", *AIChE J*., Vol. 42, pp. 3318-3332, 1996.

[11] F. Chung, P. Sarathi, and R. Jones, "Modeling of Asphaltene and Wax Precipitation", DOE, Topical Report No. NIPER-498, January 1991.

[12] K.J. Leontaritis, "Asphaltene deposition: a comprehensive description of problems manifestations and modelling approaches", Presented at the SPE Production Operations Symposium, Oklahoma City, 13-14, March 1989.

[13] A.C.S. Ramos, C.C. Delgado, R.S. Mohamed, V.R. Almeida, and W. Loh, "Reversibility and Inhibition of Asphaltene Precipitation in Brazilian Crude Oils", *SPE 38967*, Presented at the Latin American and Caribbean Petroleum Engineering Conference, Rio de Janeiro, Brazil, 30 August - 3 September 1997.

[14] R. Cimino, S. Correra, P.A. Sacomani, and C. Carniani, "Thermodynamic Modelling for Prediction of Asphaltene Deposition in Live Oils", *SPE 28993*, Presented at the SPE International Symposium on Oilfield Chemistry held in San Antonio, TX, USA, 14-17 February 1995.

[15] H. Pan, and A. Firoozabadi, "Thermodynamic Micellization Model for Asphaltene Precipitation From Reservoir Crudes at High Pressures and Temperatures", *SPE Prod. Fac*., Vol. 15, pp. 58-65, February 2000.

[16] H. Pan, A. Firoozabadi, and P. Fotland, "Pressure and Composition Effect on Wax Precipitation: Experimental Data and Model Results", *SPE Prod. Fac*., Vol. 12, pp. 250-258, 1997.

[17] S.P. Godbole, K.J. Thele, and E.W. Reinbold, "EOS Modeling and Experimental Observations of Three-Hydrocarbon-Phase Equilibria", *SPE Reserv. Eng*., Vol. 10, pp. 101-108, 1995.

[18] S. Kokal, J. Najman, S. Sayegh, and A. George, "Measurement and correlation of asphaltene precipitation from heavy oils by gas injection", *J. Can. Pet. Tech*., Vol. 31, pp. 24-30, 1992.

[19] D.A. Storm, R.J. Barresi, and E.Y. Sheu, "Development of Solid Properties and Thermochemistry of Asphalt Binders in the 25-65 °C Temperature Range", *Energy Fuels*, Vol. 10, pp. 855 – 864, 1996.

[20] N.E. Burke, R.E. Hobbs, and S.F. Kashou, "Measurement and modeling of asphaltene precipitation", *J. Pet. Tech*., pp. 1440-1446, November 1990.

[21] S. Kawanaka, S.J. Park, and G.A. Mansoori, "The role of asphaltene deposition in EOR gas flooding: a predictive technique", SPE/DOE 17376, Presented at the SPE/DOE Enhanced Oil Recovery Symposium, Tulsa, Oklahoma, 17-20, April 1988.

[22] S. Kawanaka, S.J. Park, and G.A. Mansoori, "Organic Deposition from Reservoir Fluids: A Thermodynamic Predictive Technique", *SPE Reserv. Eng*., May 1991, 185-192.

[23] S.J. Park, A thermodynamic polydisperse polymer model: asphaltene flocculation, aggregation and deposition. Ph.D dissertation, University of Illinois, Chicago, USA, 1989.

[24] L.X. Nghiem, M.S. Hassam, R. Nutakki, and A.E.D. George, "Efficient Modelling of Asphaltene Precipitation", *SPE 26642*, Presented at the SPE Annual Technical Conference and Exhibition, Houston, Texas, 3-6 ,October 1993.

[25] K.J. Leontaritis, and G.A. Mansoori, "Asphaltene Flocculation During Oil Production and Processing: A Thermodynamic Colloidal Model", SPE 16258, Presented at the SPE International Symposium on Oil field Chemistry, San Antonio, TX, 4-6, February 1987.

[26] A.I. Victorov, and A. Firoozabadi, "Thermodynamic Micellization Model of Asphaltene Precipitation from Petroleum Fluids", *AIChE J*., Vol. 42, pp. 1753-1764, June 1996.

[27] H. Pan, and A. Firoozabadi, "Thermodynamic Micellization Model for Asphaltene Precipitation: Part I: Micellar Size and Growth", *SPE Prod. Fac*., Vol. 13, pp.118-127, 1998.

[28] H. Pan, and A. Firoozabadi, "Complex Multiphase Equilibrium Calculations by Direct Minimization of Gibbs Free Energy by Use of Simulated Annealing", *SPE Res. Eval. Eng*., Vol. 11, pp. 36-42, 1998.

[29] H. Pan, and A. Firoozabadi, "Thermodynamic Micellization Model for Asphaltene Precipitation Inhibition", *AIChE J*., Vol. 46, pp. 416-426, 2000.

[30] J.Z. Wu, J.M. Prausnitz, and A. Firoozabadi, "Molecular-Thermodynamic Framework for Asphaltene-Oil Equilibria", *AIChE J*., Vol. 44, pp. 1188-1199, 1998.

[31] J.Z. Wu, J.M. Prausnitz, and A. Firoozabadi, "Molecular Thermodynamics of Asphaltene Precipitation in Reservoir Fluids", *AIChE J*.. Vol. 46, pp. 197-209, 2000.

[32] A.K.M. Jamaluddin, J. Creek, C.S. Kabir, J.D. McFadden, D.D. Cruz, N. Joshi, and B. Ross, "A Comparison of Various Laboratory Techniques to Measure Thermodynamic Asphaltene Instability", SPE 72154, Presented at the SPE Asia Pacific Improved Oil Recovery Conference, Kuala Lumpur, Malaysia, 2001.

[33] S.I. Andersen, and K. Potsch, "Solid organic deposition from a gas condensate field", *AIChE National Spring Meeting*, 328-334, 14-18, March 1999.

[34] S. Thou, G. Ruthammer, and K. Potsch, "Detection of Asphaltenes Flocculation Onset in a Gas Condensate System", SPE 78321, Presented at the SPE 13th European Petroleum Conference, Aberdeen, Scotland, U.K 29-31, October 2002.

[35] P.J. Flory, *Principles of Polymer Chemistry*, New York: Cornell University Press, 1953.

[36] R.L. Scott, and M. Magat, "The Thermodynamics of High-Polymer Solutions: The Free Energy of Mixing of Solvents and Polymers of Heterogeneous Distribution", *J. Chem. Phys*., Vol. 13, pp. 172-177, 1945.

[37] S.I. Sandler, *Chemical and Engineering Thermodynamics*, Third Edition, Wiley, 1999.

[38] B.E. Poling, J.M. Prausnitz, and R. Reid, *Properties of Gases and Liquids*, Fifth Edition, McGraw-Hill, 2000.

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