Theoretical Background for Predicting the Properties of Petroleum Fluids via Group Contribution Methods

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Abstract

The major problem encountered in the petroleum industry lies in the proper thermodynamic representation of rather complex fluids. In this work, the UNIFAC group contribution method for predicting the properties of such fluids has been exploited as a basis for their description in terms of model compounds. Standard thermodynamic procedures are used to estimate the critical properties, acentric factors, and molecular weights for the model compounds. In such a way, the already available generalized methods can be used for calculations of the phase equilibrium in complex petroleum mixtures.

Keywords: petroleum fluids; physico-chemical properties; prediction; group contribution method

1. Introduction

Recently, an important and specific research has been carried out dealing with the synthesis and evaluation of polymeric additives for improving the flow properties of crude oil and gas condensates [1 – 4]. The phase equilibria in the systems of additives in different solvents were measured [5, 6] in order to understand better the mechanism of the additive influence on the transport properties of crude oil and middle distillates. Methods for modelling the important properties of solid or liquid polymers and of polymer solutions have also been well elaborated and published lately [7]. However, many problems still remain unresolved in this field.

Crude oil, gas condensate and their derivatives are ill-defined highly complex natural mixtures in the sense that they contain too many components to be identified and analyzed. At best, we are aware of their complexity. Nevertheless, such petroleum fluids can be characterized after splitting them into fractions (e.g. by fractional distillation, extraction, or crystallization) and after subsequent experimental determination of properties of each fraction (e.g., molecular weight, boiling point, density, viscosity, etc.). The phase equilibria in such mixtures are usually computed by standard thermodynamic procedures wherein each fraction is considered as a certain equivalent of a pure component. Such an approach called the pseudo-component method [8, 9] will be exploited in this work. The existing methods which were developed during the "golden age" of classic thermodynamics [10] will be used for the estimation of different physico-chemical properties. These methods are still approximate and have to be perfected. In any case, the need for advancement makes thermodynamics a living discipline which requires a good combination of experimentation and progress in modelling.

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2. Procedure

As stated above, petroleum fluids are complex mixtures consisting of paraffinic, naphthenic, and aromatic compounds. The sheer number of components and the poorly defined structure of some types of these components requires simplifications, which are more or less justifiable for fractions of a molecular weight higher than 100. The main difficulty during the phase equilibrium calculation of such a fraction is overcome after its representation as a mixture of well-defined model components enabling an evaluation of the averaged characteristic parameters. Based on our previous work [7, 11, 12], a simplified method of the characterization of heavy petroleum fractions is described in this paper. The semi-empirical approach will be used as it is frequently utilized in this field, because fundamental thermodynamic theories are still not sufficiently applicable in practice. Our pragmatic approach is based on the UNIFAC group-contribution model for predicting vapour–liquid equilibria [7, 13].

The method requires the following input data: a complete TBP-analysis (true boiling point vs. liquid volume boil-off), a PNA (paraffin–naphthene–aromate) analysis and density data, preferably for each subfraction. If some of these values are not available, various procedures for transforming incomplete information on the C_{6+} fraction into satisfactory TBP analyses are used as described in references [9, 14].
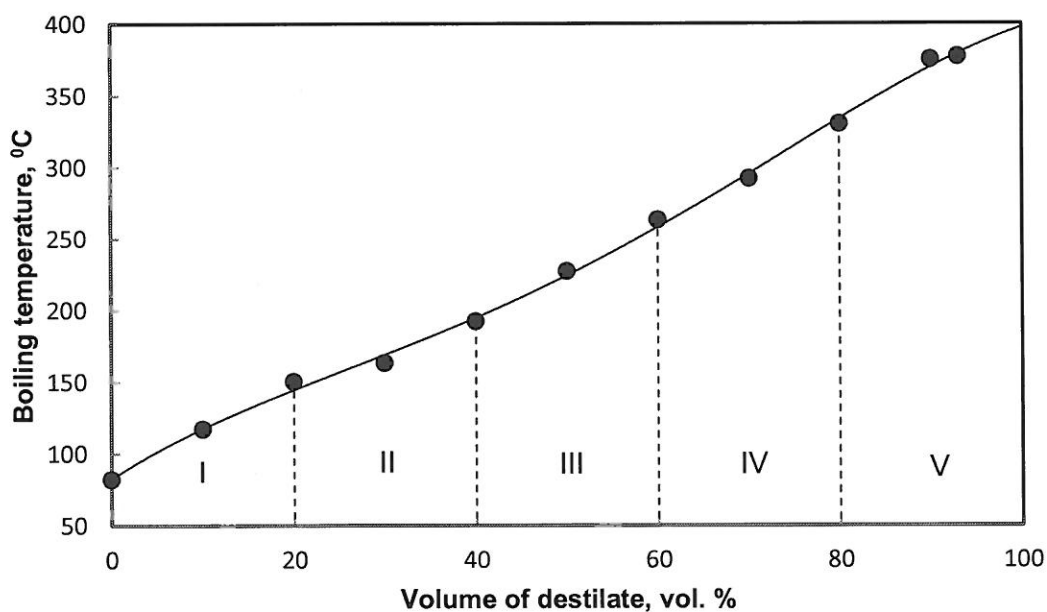

Figure 1. The true boiling point curve for a crude oil from the north Croatian oil field Obod divided in five subfractions

The procedure is as follows: the TBP curve is divided in several subfractions (the number of subfractions should be as low as possible: five to ten is recommended), as shown in Figure 1 for a crude oil from the Croatian oil field Obod. It is assumed that each subfraction contains three model compounds: paraffinic (P), naphthenic (N), and aromatic (A). The structure of the model compounds of the subfractions is defined in terms of the UNIFAC model. An example of the model compounds is shown in Figure 2, but the final adjustment of the number of groups must be estimated in order to match the mid-volume boiling point for each

subfraction. The result of this procedure provides a set of well-defined model compounds which represent the complex petroleum mixture.
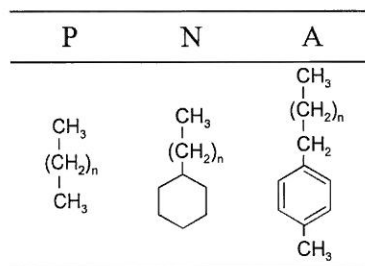

Figure 2. An example of the model compounds

The physical characteristics of the crude oil sample from the north Croatian oil field Obod together with the TBP and PNA analyses are listed in Table 1. The PNA analysis yields 28 % P, 55 % N and 17 % A.

Table 1. The physical characteristics of the crude oil sample from the north Croatian oil field Obod

Property	Method	Value
Density, d_4^{15}, kg/m^3	ASTM D 5002	846.3
API degree	DMA 4500	35.69
Pour point, $^{\circ}$C	ASTM D 97	23
Dynamic viscosity, 30 $^{\circ}$C, mm^2/s	ASTM D 445	8.58
Paraffins, wt.%	ASTM D6733	28
Naphthenes, wt.%		55
Aromates, wt.%		17
Water, wt%	ASTM D 86/93	Traces
Sulphur, wt%	Leco S 132	0.24
TBP distillation	ASTM D-2892	

V, vol.%	T, $^{\circ}$C
0	82
10	117
20	150
30	163
40	192
50	227
60	263
70	292
80	330
90	375

The composition of the petroleum fractions in terms of the pseudo-components is calculated by fitting the bubble point of the model subfraction to the mid-volume boiling

point of the actual subfraction. The bubble point is computed assuming

$$P = \sum_i x_i \gamma_i P_i^0 \,, \tag{1}$$

where P is the pressure, P_i^0 the pure component vapour pressures, x_i is the liquid mole fraction and γ_i the activity coefficient of component i. For the activity coefficient calculation, the UNIFAC group contribution method with linear temperature-dependent parameters by Hansen is used [15]. The pure component vapour pressures P_i^0 are calculated using the following equation as proposed by Jensen et al. [13]

$$RT \ln P_i^0 = \sum_k \upsilon_k^{(i)} \Delta g_k + RT \sum_k \upsilon_k^{(i)} \ln \Gamma_k^{(i)} \,, \tag{2}$$

where $\upsilon_k^{(i)}$ is the number of groups, Δg_k is the group Gibbs energy function and $\ln \Gamma_k^{(i)}$ is the residual activity coefficient of type k in molecule i. The group Gibbs energy functions, Δg_k, depends on the detailed structure of the molecules. The first term in the equation 2 can be written as

$$\sum_k \upsilon_k^{(i)} \Delta g_k = \sum_k \upsilon_k^{(i)} \Delta g_k' + \Delta G_i'' \,, \tag{3}$$

where $\Delta g_k'$ is the structure-independent contribution, with temperature dependence given by the following equation

$$\Delta g_k' = A_{k,1}/T + A_{k,2} + A_{k,3}T + A_{k,4} \ln T \,, \tag{4}$$

where $A_{k,1}$ are Jensen's parameters. The $\Delta G_i''$ term which takes into account effects arising from molecular structure

$$\Delta G_i'' = \sum_k \sum_j \upsilon_{kj}^{(i)} \Delta g_{kj}'' \tag{5}$$

depends only slightly on temperature, as shown in reference [13].

3. Results and conclusion

The calculation is illustrated for subfraction II in Figure 1. The observed mid-volume boiling point is 160 °C at 0.101 MPa. The standard procedures [16] are used for the estimation of the critical properties, acentric factor, and molecular masses of the model compounds.

The input set of the groups of the model compounds is listed in Table 2. The number n is established with the bubble point of the mixture of model compounds adjusted to the observed mid-volume boiling point (T = 160 °C), using the equation 4 and

$$0.28\gamma_P P_P^0 + 0.55\gamma_N P_N^0 + 0.17\gamma_A P_A^0 = 0.101 \tag{6}$$

Table 2. The input set of model compound

Groups	Model compounds		
	P	N	A
CH_3	2	1	1
CH_2	6n	2n	3n
cy-CH_2	0	5	0
cy-CH	0	1	0
ACH	0	0	4
$ACCH_2$	0	0	1
$ACCH_3$	0	0	1

The input set of the groups of the model compounds is listed in Table 2. The number n is established with the bubble point of the mixture of model compounds adjusted to the observed mid-volume boiling point (T = 160 °C), using the equation 4 and

$$0.28\gamma_P P_P^0 + 0.55\gamma_N P_N^0 + 0.17\gamma_A P_A^0 = 0.101 \tag{6}$$

Good agreement with the experimental mid-volume boiling point was obtained after five iterations, and as a result, $n = 0.45$ was obtained for $T = 160$ °C, which corresponds to $M_r = 304$ (observed value 298), $P_P^0 = 0.110$, $P_N^0 = 0.09$ and $P_A^0 = 0.107$ MPa.

The procedure shown in the above example is repeated for each of five subfraction, and the boiling point temperatures were calculated using the Soave equation of state and an algorithm as described in reference [17].

Table 3. Prediction of boiling temperatures for crude oil from field Obod

V, vol.%	T^{exp}, °C	T^{cal}, °C	ΔT
10	117	114	3
30	163	152	11
50	227	216	11
70	292	282	10
90	375	356	19

The differences between experimental and calculated boiling points shown in Table 3 are quite satisfactory in comparison with other more complex methods.

The calculated thermodynamic properties are compared with the corresponding experimental values and good agreement was achieved for the light to medium crude oil fractions. More experimental data are needed in order to obtain reliable results for fractions with a true boiling point above 300 °C.

Literature

[1] Vuković R, Erceg A, Bogdanić G. Process of preparation the polymeric additives as flow improvers of a gas condensate. Patent No. HR P980606, 30 June 2002.

[2] Erceg Kuzmić A, Radošević M, Bogdanić G, Vuković R. Process for the preparation of polymeric additives for improving the flowing of a crude oil. Patent No. HR P20070164 A2, 30 November 2008.

[3] Erceg Kuzmić A, Radošević M, Bogdanić G, Vuković R. Flow improver additives for gas condensate. *Fuel* 2007;**86**:1409–1416.

[4] Erceg Kuzmić A, Radošević M, Bogdanić G, Srića V, Vuković R. Studies on the influence of long chain acrylic esters polymers with polar monomers as crude oil flow improver additives. *Fuel* 2008;**87**:2943–2950.

[5] Pavlíček J, Bogdanić G, Wichterle I. Circulation micro-ebulliometer for determination of pressure above mixtures containing solvent and non-volatile component. *Fluid Phase Equilib* 2010;**297**:142–148.

[6] Bogdanić G, Wichterle I. Vapor–liquid equilibrium in diluted polymer + solvent systems. *J Chem Eng Data* 2011;**56**:1080–1083.

[7] Bogdanić G. Additive group contribution methods for predicting the properties of polymer systems. In: Nastasijević A, editor. *Polymeric materials*, Trivandrum, India: Transworld Research Signpost; 2009, p. 155–197.

[8] Cotterman RL, Prausnitz JM. Flash calculations for continuous or semicontinuous mixtures using an equation of state. *Ind Eng Chem Process Des Dev* 1985;**24**:434–443.

[9] Pedersen KS, Fredenslund A, Thomassen P. *Properties of oils and natural gases*. Houston: Gulf Publishing Company, Book Division; 1985.

[10] Vidal J. *Thermodynamics. Application in chemical engineering and the petroleum industry*, Paris: Editions Technip; 2003.

[11] Vidal J, Bogdanić G. Equation of state, mixing rules and phase equilibrium calculations. Part 1. Equations of state derived from the Van der Waals theory. Pure components. *Chem Biochem Eng Q* 1999;**13**:89–100.

[12] Vidal J, Bogdanić G. Equation of state, mixing rules and phase equilibrium calculations. Part 2. Mixing rules and vapor-liquid equilibrium calculations. *Chem Biochem Eng Q* 1999;**13**:101–125.

[13] Jensen T, Fredenslund A, Rasmussen P. Pure-component vapor pressures using UNIFAC group contribution. *Ind Eng Chem Fundam* 1981;**20**:239–246.

[14] Erbar JH. *Research report 13*, Tulsa OK: Gas Process Association; 1977.

[15] Hansen H, Coto B, Kuhlmann B. UNIFAC with linearly temperature-dependent group interaction parameter. *Technical report No. 9211*. Lyngby: IVC–SEP Research Engineering Center, Technical University of Denmark; 1992.

[16] Poling BE, Prausnitz JM, O'Connell JP. *The properties of gases and liquids*. 5th ed. New York: McGraw-Hill; 2000.

[17] Asselineau L, Bogdanić G, Vidal J. A versatile algorithm for calculation of vapor-liquid equilibria. *Fluid Phase Equilib* 1979;**3**:273–290.