



A new empirical K -value equation for reservoir fluids

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ABSTRACT

This article proposes a new physically sound empirical equation for computing the K -values in reservoir fluids applications in a wide range of pressure and temperature. In order to examine the accuracy of the presented equation, its results for bubble pressure calculations were compared with the experimental data of 122 reservoir mixtures collected from literature. In addition, bubble pressure predictions of the new equation were compared with those of the state equations of Peng–Robinson (PR) and Soave–Redlich–Kwong (SRK) and three empirical equations, i.e. Whitson, Standing and Wilson. Compared to the experimental data, the average relative deviations of bubble pressure calculations for the proposed equation, PR, SRK, Whitson, Standing and Wilson were obtained 11%, 14%, 29%, 66%, 30% and 38% respectively.

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1. Introduction

In equilibrium calculations of reservoir fluids, the prediction of properties such as the bubble and dew pressures and temperatures and gas and liquid compositions are of great importance, especially for oil and gas industries. The bubble pressure is a key factor in many industrial aspects such as oil production rate and the solubility of material like asphaltene, wax and light gases in reservoir oils. The methods applied to calculate bubble point pressure fall into four categories: (i) empirical correlations which predict bubble pressures directly as a function of thermo-physical properties, (ii) neural network and fuzzy logic algorithm approaches, (iii) using the K -values predicted based on an empirical relation (iv) using the K -values predicted based on equation of states. While performing bubble pressure calculations for an applied purpose, it is important to make a balance between accuracy and computation time. Accordingly, using the K -values predicted based on an empirical relation, which has been recognized as a favorite method for short-cut calculations, can be considered as an appropriate method. The study performed by Souders et al. can be recognized as a pioneering work in defining equilibrium ratio or K -value. According to this study, K -value is described as the ratio of vapor-phase (y_i) to liquid phase (x_i) mole fractions of a constituent at given temperature and pressure [1]:

$$k_i = \frac{y_i}{x_i} \quad (1)$$

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Katz and Hachmuth (1937) investigated the effect of temperature and pressure on K -value through studying 23 mixtures of natural gas and crude oil samples. They observed that all equilibrium constants approached to a so-called critical pressure as pressure rose. This pressure later was named as converge pressure [2]. In 1953, investigating a number of gas-condensate experimental data sets Hoffman et al. [3] found out the fact that $\log(k_iP)$ was a linear function of $\left(\frac{1}{T_{bi}} - \frac{1}{T}\right)$, and proposed the following relation:

$$\log(k_iP) = b_i \left(\frac{1}{T_{bi}} - \frac{1}{T} \right) \quad (2)$$

where P is reservoir pressure in psia and b_i is defined as follows:

$$b_i = \log \left(\frac{P_{ci}}{14.7} \right) / \left(\frac{1}{T_{bi}} - \frac{1}{T_{ci}} \right) \quad (3)$$

where P_{ci} , T_{ci} , and T_{bi} are critical pressure (psia), critical temperature (R) and normal boiling point of component (R), respectively. Brinkman and Sicking modified Hoffmann equation by employing the convergence pressure and proposed the following equation for the equilibrium ratio [4]:

$$K_i = \frac{P_k}{P} \exp[s_i(F_i - F_k)] \quad (4)$$

where F_i is a component characterization factor and is defined as following:

$$F_i = b_i \left(\frac{I}{T_{bi}} - \frac{1}{T} \right) \quad (5)$$

Here I is the intercept of $\ln(k_iP)$ versus F_i curve. P_k , P and s_i are the convergence pressure, reservoir pressure, and slope of $\ln(k_iP)$ versus

Nomenclature

AAD	absolute average deviation	x_i	liquid mole fraction of component i
b_i	slope of log of vapor pressure curve versus inverse temperature of component i in Eq. (3)	y_i	vapor mole fraction of component i
k_i	K -value of component i	<i>Greek symbols</i>	
k_w	watson K factor	ω_i	acentric factor for component i
M_{C7+}	molecular weight of heptane plus fraction	γ_{C7+}	gravity of heptane plus fraction
T_{bi}	normal boiling point for component i ,	<i>Subscripts and superscript</i>	
T	temperature	B	boiling
T_{Ci}	critical temperature for component i	C	critical
T_{Ri}	reduced temperature of component i	C_{7+}	heptane plus fraction
T_{Rmix}	reduced temperature of mixture T/T_{Cmix}		
P	pressure		
P_{Ci}	critical pressure for component i		
P_k	convergence pressure of mixture		

F_i respectively. F_i is called as F_k when P approaches P_k . Wilson introduced a new generation of equations which was a function of more common properties such as critical pressure, temperature, and acentric factor as follows [5]:

$$K_i = \frac{P_{Ci}}{P} \exp[5.37(1 + \omega_i)(1 - T_{Ri}^{-1})] \quad (6)$$

where P_{Ci} is the critical pressure of component i (Psia), T_{Ri} is the reduced temperature of component i and P is the system pressure (psia). Standing modified Hoffmann's equation (Eq. (2)) by adding two pressure-dependent parameters and found their values by fitting the equation to the experimental equilibrium ratio data of Katz and Hachmuth for the pressures below 1000 Pisa [6]. This equation can be written as follows:

$$\log(k_i P) = a + c \left[b_i \left(\frac{1}{T_{bi}} - \frac{1}{T} \right) \right] \quad (7)$$

where a and c are functions of pressure. Almehaidib et al. proposed two correlations for a and c in Eq. (7) by fitting this equation to PVT data of 22 crude oil samples taken from different reservoirs in UAE [7]. McWilliams offered the following equation for K -value by correlating Depriester equilibrium ratio charts [8]:

$$\log(k_i) = c_1 \ln(P) + \frac{c_2}{P} + \frac{c_3}{P^2} + c_4 + \frac{c_5}{T} + \frac{c_6}{T^2} \quad (8)$$

where c_1 to c_6 are the constants. Finally, Whitson and Torp [9] proposed a new equation by incorporating the convergence pressure (P_k):

$$K_i = \left(\frac{P_{Ci}}{P_k} \right)^{\alpha-1} \frac{P_{Ci}}{P} \exp[5.37\alpha(1 + \omega_i)(1 - T_{Ri}^{-1})] \quad (9)$$

where α is a function of pressure as follows:

$$\alpha = 1 - \left(\frac{P}{P_k} \right)^{0.7} \quad (10)$$

Table 1

Some well-known equations for K -value according to the general patterns $\{\ln K_i = f(P) + g(T), \ln K_i = f(P) + h(T, P)\}$.

Equation	$f(P)$	$g(T)$	$h(T, P)$
Haffmann (1953)	$\ln \left(\frac{P}{P_k} \right)$	$b_i \left(\frac{1}{T_{bi}} - \frac{1}{T} \right)$	-
Wilson (1968)	$\ln \left(\frac{P}{P_{Ci}} \right)$	$5.37(1 + \omega_i)(1 - T_{Ri}^{-1})$	-
McWilliams (1973)	$c_1 \ln(P) + \frac{c_2}{P} + \frac{c_3}{P^2}$	$c_4 + \frac{c_5}{T} + \frac{c_6}{T^2}$	-
Standing (1979)	$c_1 \log(P) + c_2 P + c_3 P^2$	-	$b_i \left(\frac{1}{T_{bi}} - \frac{1}{T} \right) (c_4 + c_5 P + c_6 P^2)$
Whitson (1983)	$(\alpha - 1) \ln \left(\frac{P_{Ci}}{P_k} \right) + \ln \left(\frac{P_{Ci}}{P} \right)$	-	$5.37\alpha(1 + \omega_i)(1 - T_{Ri}^{-1})$

Note: $b_i = \log \left(\frac{P_{Ci}}{P_k} \right) / \left(\frac{1}{T_{bi}} - \frac{1}{T} \right)$, $\alpha = 1 - \left(\frac{P}{P_k} \right)^{0.7}$.

It should be pointed out that Eq. (9) is reduced to Eq. (6) (Wilson equation) for relatively low pressures (where α approaches to unity).

In this work, a new equation is developed for K -value for hydrocarbon systems. This equation can be used for accurate calculations of bubble pressure in reservoir conditions.

2. The proposed K -values equation

The following two general types of equation are the basis for many well-known empirical or semi-empirical correlations for K -value of hydrocarbon systems:

$$\ln K_i = f(P) + g(T) \quad (11)$$

$$\ln K_i = f(P) + h(T, P) \quad (12)$$

Table 1 introduces a number of equations for K -value found in literature following the above general patterns. Some of the correlations have been developed based on the pattern appeared in Eq. (11) while the others have been applied the type shown in Eq. (12).

There are several experimental studies confirming the fact that K -values of all components in a reservoir fluid converge to a common value of unity as the pressure isothermally approaches a particular pressure. This pressure is known as convergence pressure of the mixture and is strongly dependent on the mixture composition. At a constant temperature, the behavior of variation of K -value versus pressure follows the following rules [10]:

- (1) In a log–log scale, the curve exhibits a linear behavior at low pressure.
- (2) At higher pressure, the curve passes through a minimum and then increases to the about unity at convergence pressure depending on temperature.
- (3) All isotherms terminate to the convergence pressure.
- (4) The minimum point for K -value is a function of temperature.

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